PLASMA PRODUCTION OF ULTRAFINE POWDERS AND THEIR APPLICATION TO DISPERSION STRENGTHENED MATERIALS

by

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A thesis submitted for the Ph.D. degree under the Interdisciplinary
Higher Degrees Scheme, and the Department of Physics.
University of Aston in Birmingham.
September 1971

SUMMARY

This thesis is in three parts, preceded by an Introduction which describes the Interdisciplinary Higher Degrees scheme (under which this is the first Ph.D thesis submitted.) The Introduction defines the objectives of the thesis against the background of the sponsoring company, GKN.

The first part is concerned with powders in the size range 1 mμ to 1μ, and reviews methods of production. Production from the gas phase at high temperatures using a D.C. plasma torch is studied at length - the theory of nucleation and growth is related to observed phenomena, and a survey of the literature concerning both D.C. and R/F plasma torches presented. A method was developed for the production of silicon and titanium nitride samples in the size range 10 mμ to 50 mμ.

The second part describes the contribution of ultrafine particles to powder metallurgy materials, particularly dispersion strengthened (D.S.) metals. Powder metallurgy techniques, and production methods of D.S. materials, are discussed. The theory of the D.S. effect is presented, and related to observations. Compacts with iron as the matrix, and Al_2O_3, Si_3N_4 and TiN as dispersants, were made by selective reduction of oxides, isostatic pressing, then sintering or hot forging. Hot forging was more successful, giving pure iron compacts with ductilities over 25% and ultimate tensile strengths of 325 MN/m^2 and iron-alumina compacts with tensile strengths of 447 MN/m^2 but zero ductility.

The third part evaluates the applications of D.S. materials in the context of GKN's operations and concentrates on a computerised cost model for the production of a mixture of iron and silicon or titanium nitride powders. The model shows how the reaction thermodynamics and production rate determine the plasma equipment requirements and sensitivity analyses identify the range over which each parameter is cost controlling.

ACKNOWLEDGMENTS

None of this work would have been possible without industrial support, and my thanks are due to Mr. F.D. Bridge, as Head of the Research Unit of the GKN Group Technological Centre, for providing the facilities for the experimental work. The project was supervised by Mr. B.G. Carver, and lead by Mr. C.W. Tuck, who as Industrial Tutor under the I.H.D. scheme was responsible for the day to day progress of the work, and has made many valuable contributions in the metallurgical aspects of the work, and the final form of the thesis. I would also like to express my appreciation for the assistance I have received from the whole of the G.T.C. staff, and especially from Dr. S.C. McRobert for the design of the plasma torch, from Mr. N. Bird for the construction of apparatus and from Miss C.A. Jukes for typing the final version.

The main tutor was Dr. A.J. Cox, from the Department of Physics, who has acted throughout as co-ordinator between the University, the Associate Supervisors, and the G.T.C. He has also made many suggestions for improvements in the form and text of the final version of the thesis. The associate supervisors under the I.H.D. scheme were,

Mr. H. Williams - Visiting Reader, Department of Chemistry
Prof. F.M. Page - Department of Chemistry
Mr. A.J. Bennett - Department of Industrial Administration (Economics)

Help and advice was received from the staff of Department of Industrial Administration, especially from Prof. S.L. Cook (Operational Research) on the subject of Research Management. The I.H.D. interests were co-ordinated by Dr. S.S. Chang, as I.H.D. tutor.

For the first two years support was received from the SRC under the industrial studentship scheme and from GKN Group Technological Centre: for the final year the entire financial support was provided by GKN Group Technological Centre.

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INTRODUCTION

Interdisciplinary Higher Degrees

There are many differences between the approach to an I.H.D. and the approach to a traditional Ph.D. From the student's point of view these are mainly felt during the working of the project, that is in the way in which the work is supervised and carried out. These differences and the attendant problems have been discussed at length elsewhere, and are summed up in the Notes for Guidance (I.H.D. N.G.) approved by Senate in March, 1971.

The fundamental difference in approach, and the one which has a vital influence on the content of this thesis, is a result of the involvement with industry. It is significant that each studentis described as working on a 'project', which must be related to a specific problem or problem area for a particular firm. Traditionally, the onus for the conception of a Ph.D. thesis lay with an experienced academic, and the introduction contained a careful argument showing the relevance of the work to the history of the subject. The student relied entirely on his tutor at the initial stage, but was expected to be able to justify his work's relevance by the time he came to write his thesis. Under the I.H.D. scheme, the onus for the conception of the project lies with the firm, (taking account of the requirements of the scheme) which presumably has reasons for wanting the work done. The student is not thereby relieved of the traditional obligation of justification, but must be able to justify (or otherwise) the company's decision to proceed with the work.

It is usual with traditional Ph.D's, to word the thesis title carefully so as to define an area of study, whilst not specifying the points that are to be covered in the conclusions. Once again, the onus is on the tutor to produce a title which is at once sufficiently specific to be acceptable to the university authorities and broad enough to allow freedom for creative work and the accommodation of the unexpected. The work then follows a zig-zag path until one or more discoveries are made which fall within the area defined, and can be developed to give coherent, and preferably explicable, results.

In contrast, an I.H.D. project starts with a problem which must be solved, or questions which must be answered. Objectives are defined, and the degree to which they are reached is a major criterion on which the thesis may be judged. The work path is probably more direct, because of the specific objectives.

One result of constraining the work to a path which is relatively straight and narrow, is that interesting side alleys cannot be explored. Often, scientifically interesting points cannot be pursued, because precious effort would be diverted from the main objectives. An I.H.D. project, unlike a conventional Ph.D. produced wholly within a university, is subject to the usual industrial constraints, such as annual budgeting and changes in company policy. There is also the possibility that the initial results will show that continuation of the project to the end of the thesis period cannot be justified financially.

The GKN Group

The 1970 Annual Report describes the Group in the following way:

'GKN is one of the world's largest engineering groups. More than one-third of sales are of components - largely high precision - for the world's automotive industry; the other main markets are the engineering and allied industries and the building and construction industries. Although well placed to take advantage of developments in plastic and other materials, nearly all its products are at present manufactured or formed from steel. It is in fact the largest user of steel in the U.K. and has acquired over the years a unique knowledge of the skills and techniques necessary for the processing of metal in many different ways.'

The GKN Group is divided into twelve main Sub-Groups within the U.K. and seven overseas,(Figures 1 & 2). As the quotation above indicates, the activities of the Group cover a very wide range: although well known for its predominance in the screwed fastener market where high volume low cost production is carried out on repetition machinery, this now accounts for only 8% of the Group's turnover. 35% of the Group sales go to the automotive industry, including forgings, castings, pressings and precision machined transmission components having a comparatively high labour content; they are supplied largely, but by no means exclusively, from four Sub-Groups. Other large volume component markets of which GKN has a significant share, include concrete reinforcing bar, building supplies, nails, wire,

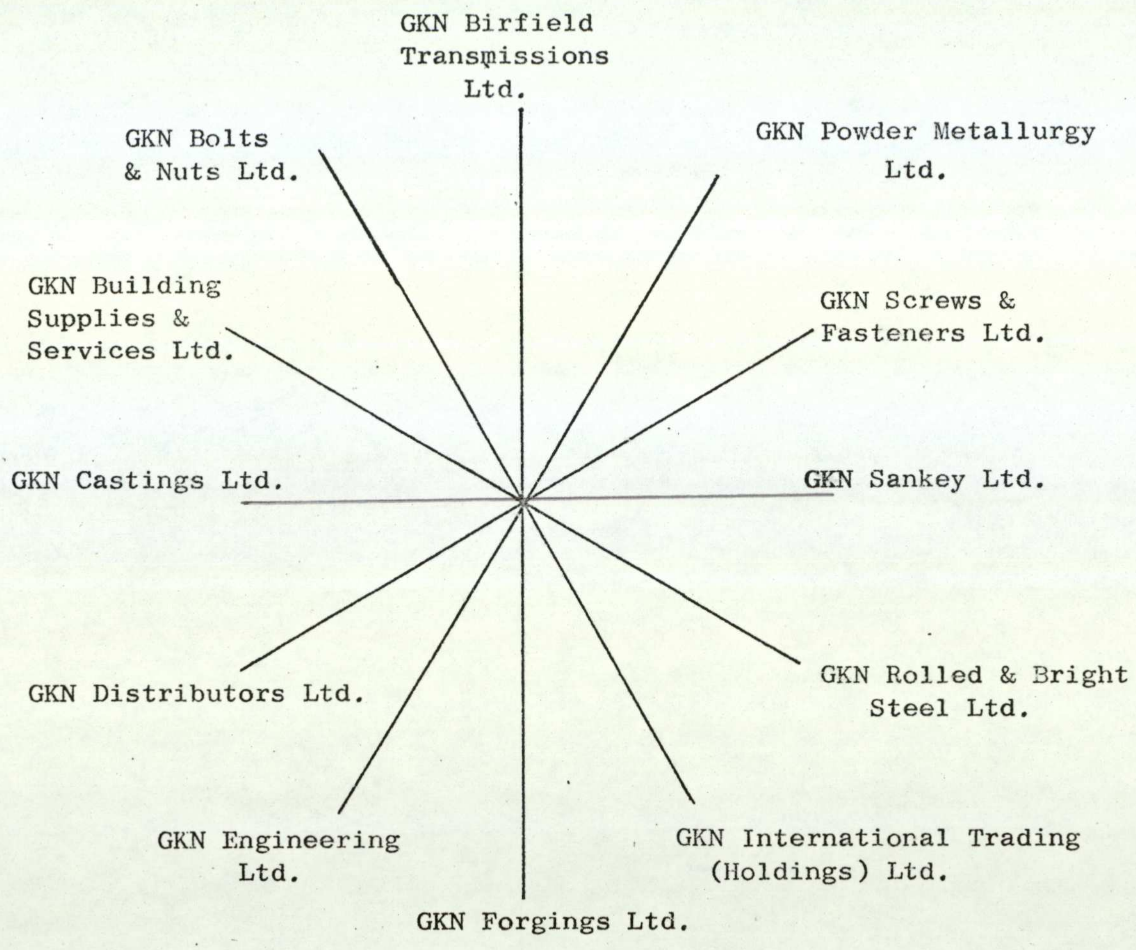


Fig 1. The twelve U.K. sub-groups.

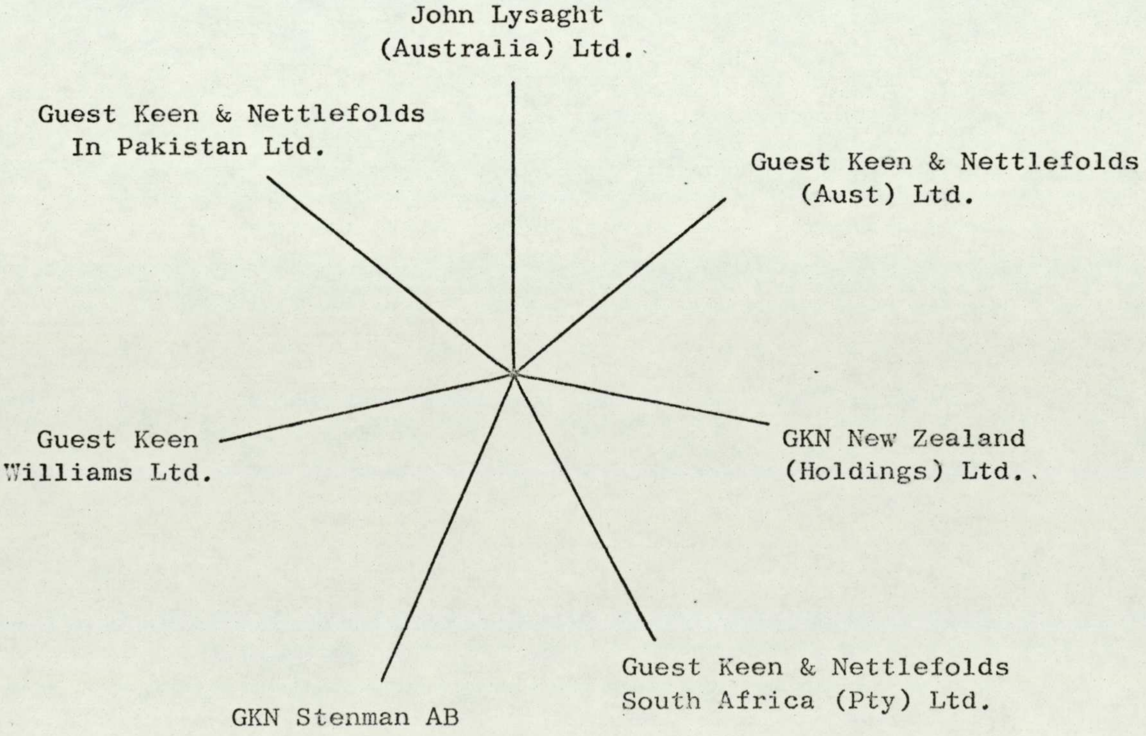


Fig. 2. The seven overseas sub-groups.

bright steel bar, extrusions of all kinds and bearings - a complete list would be out-of-place in this summary. In view of the subject matter of this thesis special mention should be made of the Group interest in sintered powder compacts, both for filtration and for solid shapes not amenable to fabrication from the solid, and of its interest in the use and production of metal forming tool materials. Other activities include steel stockholding and distribution of a wide range of assorted hardware and at another extreme, the design and manufacture of large one-off pieces of engineering plant such as rolling mills, furnaces and power station condensers. Although the above summary indicates that each operation has a large turnover, smaller operations, i.e. those with a turnover of less than £100,000 p.a. are not excluded if they are considered an essential complement to large volume operations.

The research and development needs of the Group are met in two ways. Each Sub-Group is an autonomous entity and is required to look after the short-term development of its current products and processes and to become expert in its specialised techniques. In addition, the Group Technological Centre, on an independent site, provides a service to the whole Group. It comprises the central library and information services, The Production Development Unit, concerned primarily with the development of special purpose automation equipment, and the Group Research Unit (GRU). It is the GRU that has supported the work described in this thesis. The GRU carries out long range and fundamental work that is concerned both with processes and materials relevant to any Sub-Group's operations. Its function is to be aware of developments in materials that may affect Sub-Groups and to investigate and develop processes and technologies that are beyond a Sub-Group's capabilities or short-term interests. In addition, the GRU administers specialised materials analysis services requiring expensive capital equipment. These are available to the whole Group, as is the service which handles large numbers of short-term technical enquiries. The project work covered by this I.H.D. thesis fits readily into this general framework.

Selection of Objectives

The selection of the objectives for the project had to be made with the interdisciplinary requirements of the thesis in mind. This meant the combination of disciplines from dissimilar fields. A study in the field of plasma chemistry was related to applications in powder metallurgy materials and evaluated both in a straightforward economic way and in its strategic value to the company. It had been previously decided that the GRU should investigate means by which the developing field of plasma technology could be exploited within GKN, either in an existing or new field of operations. (Plasma welding and plasma cutting were specifically excluded from the terms of reference of the investigation since these processes and the equipment to operate them were already commercially available). One of the projects that was undertaken forms the subject of this thesis. Prior discussions with a number of other institutions and companies had indicated that the wide choice of plasma-forming materials, high temperatures and fast quenching rates could lead to the production of new materials or of existing materials in a new form or with a previously unattained degree of purity. The GKN policy of examining and developing new materials and processes was applied to the possibilities of plasma chemistry, thus extending the plasma technology project to consider the production of ultrafine powders and their subsequent applications. This general objective led to the formulation of the following specific objectives either at the outset or at various stages as the work progressed.

A. The application of a plasma chemistry process as a specific method of producing ultrafine powders was to be studied. A comprehensive survey of the literature was also undertaken (Section 2.3) and experimental work carried out to gain experience of the process (Sections 2.5 and 2.6) in order that the important technical and economic factors might be identified (Section 5.2).

B. A known use for ultrafine particles is as a dispersed phase in a metal matrix for the purpose of strengthening that matrix (dispersion strengthening). It was decided to try and develop new materials, using as the dispersants, powder that had been produced by plasma torch methods. The results of the experimental work are given in Chapter Four and the market information in Section 5.1.2.

C. An extensive literature survey of dispersion strengthened materials was undertaken (Sections 3.4 to 3.7 and Appendix 5). This survey included a study of relevant powder metallurgical techniques (Section 3.2). Each one was costed where possible (Section 3.3).

D. Any benefit that the company might gain from the project was to be evaluated. Methods of evaluation are discussed in Chapter Five.

The aims of this thesis are primarily to answer the questions set by the company, but in such a way as to fulfil the idea of an interdisciplinary approach, and also satisfy the requirements of originality. Ideally, the originality of an I.H.D. thesis would arise from some synergism in the way two or more disciplines are combined to provide a novel, elegant solution. In the case of this thesis, the original work lies mainly in physical chemistry, but the combination of cost accountancy methods, thermodynamics and experimental results in the cost model of Section 5.2 provides a link between fundamental bench research and estimates of the economics of full scale production that could not be achieved in any other way. The interdisciplinary requirement is mainly satisfied by the broad approach to the problem, which has been tackled both from the technical and economic angles on two fronts - powder metallurgy and plasma chemistry. The way in which these aspects have been inter-related is shown schematically in Figure 3. The degree to which the questions have been answered is seen in Chapters Five and Six where the results are evaluated in the broadest terms and the final conclusions drawn.

Thermal Plasmas

Plasma has been described as the fourth state of matter, and may be defined as a gas which contains positively and negatively charged species but which is overall electrically neutral. Plasma physics is divided broadly into the study of high temperature and low temperature plasmas, where the temperature refers to the mean kinetic energy of the electrons. The study of high temperature plasmas is concerned almost exclusively with controlled thermo-nuclear reactions. Low temperature, or thermal, plasmas have many applications, e.g. mercury arc rectifiers, arc welding, M.H.D. generators and the Birkeland and Eyde Process.

A thermal plasma is so called because the energy balance is controlled by heat flow. The simplest way to produce one is to contain an easily ionised vapour, e.g. sodium, within a metal enclosure and heat it externally. Such a device is of academic interest only, and for most practical purposes the energy input is directly into the gas via an electric arc discharge.

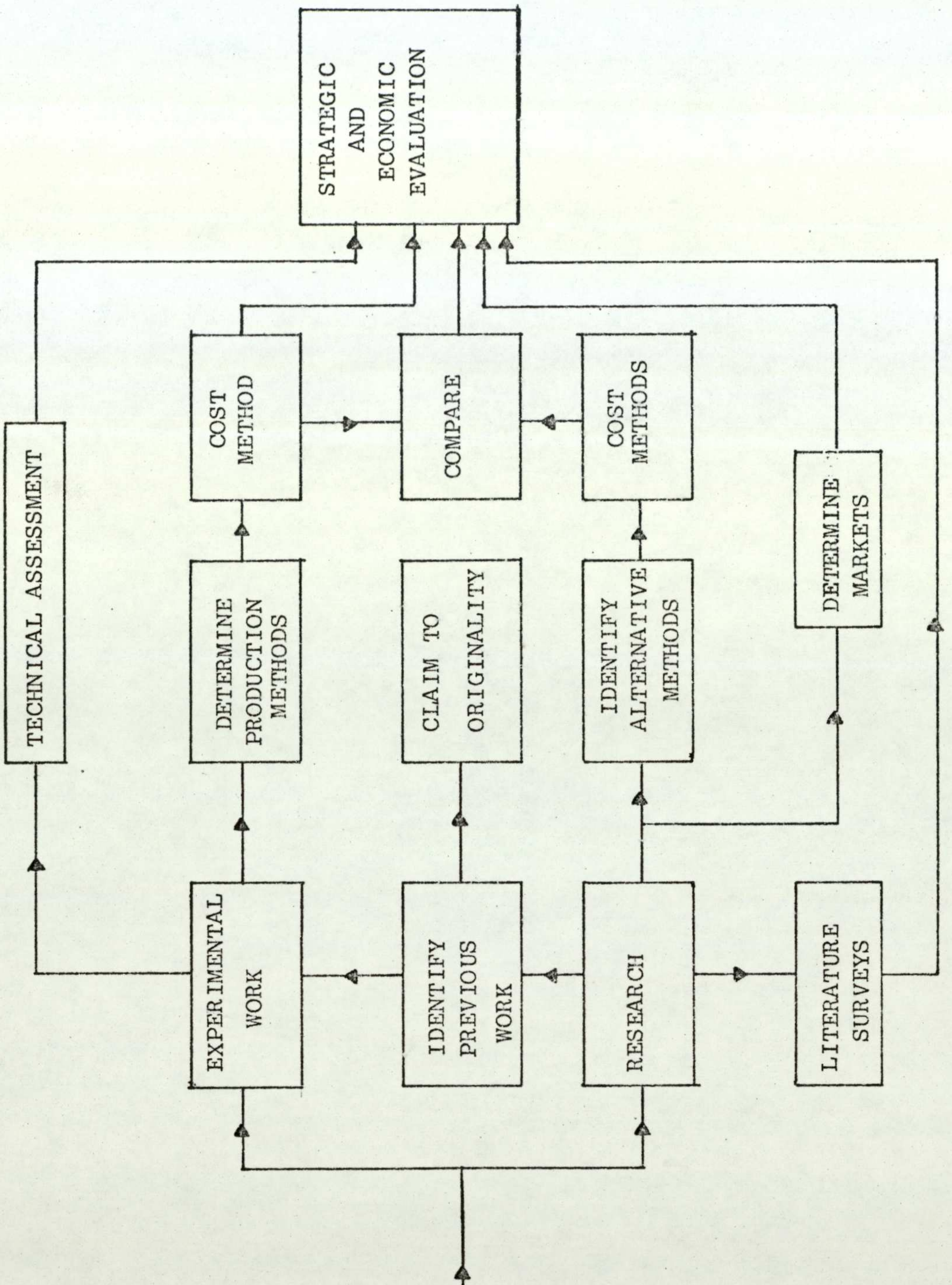


Fig. 3. Overall Scheme

In an arc discharge at atmospheric pressure, the current is carried by the electrons moving under the applied field. The energy supplied by the field is transferred to the gas atoms and molecules by the electrons as random kinetic energy during the very large (order 10^{10}) number of collisions per second. The gas is heated by the current as if it were a solid with a negative temperature coefficient of resistivity, and some of the neutral gas molecules become sufficiently hot to be ionised. Thus, the current is determined by the electron density and the applied field, and the electron density is controlled by the gas temperature, so heat lost to the surroundings is equivalent to loss of charge carriers. This amount of energy has to be replaced by resistive dissipation in the discharge.

In chemical applications, the plasma is required to supply heat to reactants, so a device is needed which is capable of dissipating far more energy than is required to sustain the discharge. Three devices are available, viz the carbon arc, the radio frequency plasma torch and the D.C. plasma torch. In the carbon arc process a stream of gas is blown between the two carbon electrodes of an arc (Figure 4). The resulting gases contain carbon vapour from the consumable electrodes, so the application of this method is restricted to reactions in which carbon is desirable or acceptable. The attraction is the simplicity of design, and the method has been used by IONARC to process minerals on a large scale.

The radio frequency (R/F) torch is based on the electrodeless discharge phenomenon, which has been comprehensively described by FRANCIS. A few turns of conductor, usually water cooled copper tubing, are wound onto a quartz tube of a few cm. diameter. Gas at atmospheric pressure is passed down the tube, and when a few kW of power at 1 to 10 MHZ are supplied to the coil, an R/F arc develops centred on the tube axis (Figure 5). The temperature falls with increasing radius, but it is usual to protect the walls of the tube by a locally higher flow of gas. The advantage is the absence of contamination of the discharge from electrode material, which must be considered against the high cost of R/F power supplies, and the low stability of the discharge. The issuing gas stream has a lower momentum and more even temperature distribution than is provided by the D.C. torch as it is not constricted, so it has been found more suitable for chemical processing than for applications such as cutting metals where intense local heat is required.

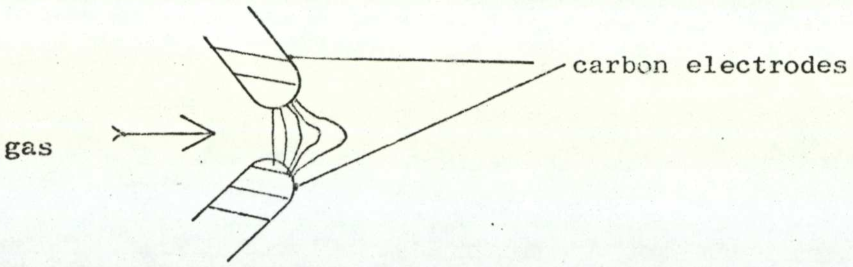


Fig 4. The Carbon arc

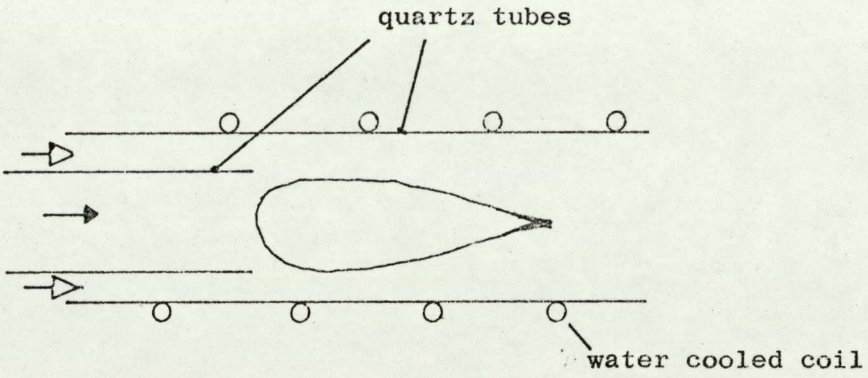


Fig 5. The radio frequency plasma torch.

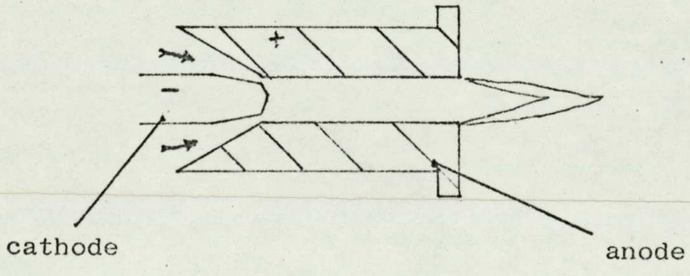


Fig 6. The direct current plasma torch.

The design of a typical D.C. torch is shown in Figure 6. A pencil shaped thoriated tungsten cathode is concentric with a cylindrical copper anode which is water cooled. The cathode may also be water cooled, but this is not essential. Gas, usually at atmospheric pressure, flows past the cathode and out through the anode via the throat and bore, or nozzle. An arc is struck using an ancillary spark generator, and the current builds up until the steady state voltage conditions are achieved, provided that they are within the operating range of the power supply.

There are two operating modes, governed by the fluid dynamic conditions. The non-fluctuating, or laminar mode describes the state when the arc anode root is stationary, and the gas flow is laminar (Figure 7). Fine stable jets up to several feet in length at atmospheric pressure may be produced, but at the expense of severe heat transfer conditions in the anode under the arc root. The fluctuating mode is associated with rapid cycling at several kHz, leading to a short, turbulent jet. The arc root is blown down the anode and the total arc voltage increases until a new root forms near the throat (Figure 8). Higher gas flows can be accommodated in the fluctuating mode, and more powder dissipated, as the heat transfer from the anode root is distributed along the anode.

The fluctuating mode is always associated with non-transferred torch operation, but the laminar mode may be achieved with an external anode, when the arc root is said to be transferred. A simple circuit allows such operation (Figure 9), which is ideal for metal working operations, but less suitable for performing chemical reactions. (Some Japanese work using this method is described in Section 2.3).

The temperature at the axis of the constricted arc discharge has been shown spectroscopically by MORRIS, RUDIS and YOS to be of order 10^3 to 10^4 K. DEMYANTSEVICH measured temperatures over 10^4 at the axis of a D.C. plasma jet running at 250 amp and 29 volts on 44 L/min argon.

As is described in Sections 2.2 and 5.2, it is important for economic use of the plasma torch, to make optimum use of the energy available. Depending upon the chemistry of the reaction to be performed, the reactants can be injected with the plasma gases or into the plasma jet. The experimental work described in Section 2.5 was confined to reactant injection into the jet of a fluctuating D.C. plasma torch.

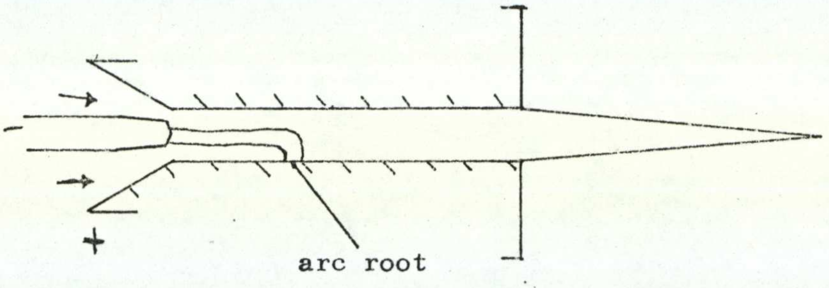


Fig. 7. Laminar mode

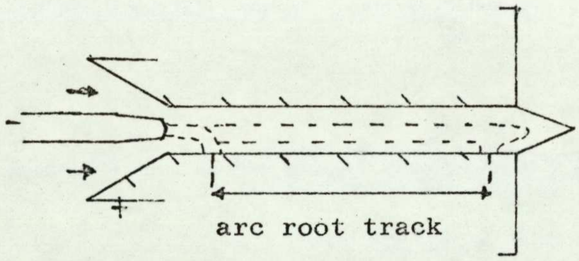


Fig. 8. Fluctuating mode.

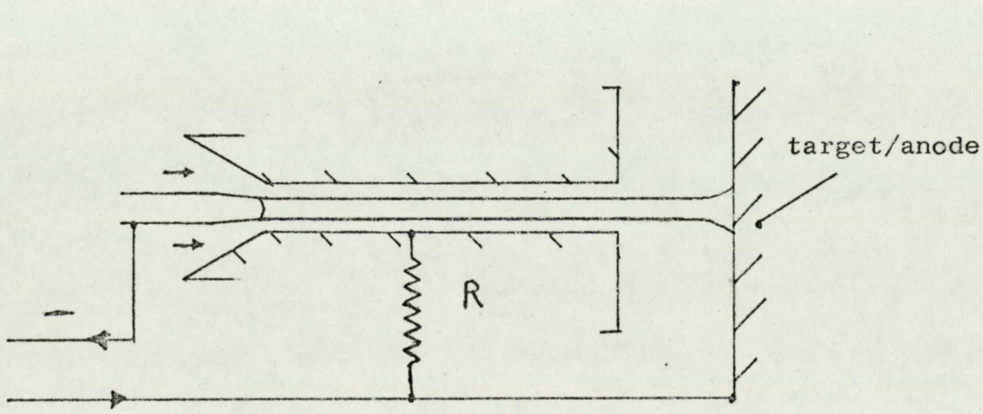


Fig 9. Transferred operation

Properties and Applications of Ultrafine Powders

The size range which is considered to be 'ultrafine' for the purpose of this thesis is from 1μ down to 1 mμ. The sizes of common substances in various degrees of subdivision are shown in Figure 10; naturally occurring particles which fall into the ultrafine category are viruses, clay particles and sea salt nuclei.

The most noticeable property of an ultrafine powder is its low density; 30 mμ powder can be only 2% dense - that is its bulk density is 2% of the theoretical density of the solid. Apart from the obvious transport problem, material in this form is difficult to handle. Particles once airborne will remain so in normal atmospheric conditions, so there is a danger from inhalation. At least powders in the 30 mμ range can be transported by gas flow, but the half micron range is too heavy for gaseous suspension and too light to flow down pipes or in a fluidised state. Mixed with coarser powders, such as ready mixed foodstuffs, a small ultrafine percentage promotes free flowing, anti-caking characteristics : 30 mμ silica is used for this purpose.

The fundamental characteristic of an ultrafine powder is its large surface/mass area - of order 100 m^2/gm. One resultant phenomenon is pyrophoricity, the property of elements and compounds to oxidise sufficiently rapidly in air that they heat up with consequent rapid acceleration of the reaction. The rate varies widely - a powder may become warm to the touch for a matter of minutes, or rise to red heat and oxidise completely. The chemistry involved is not novel, it is a matter of rates. The normal rate of heat release from surface reaction, usually resulting in a thin oxide layer may be sufficient with a fine powder to raise the bulk of the material to the ignition temperature.

A familiar danger to processors of resin powders, is the electrostatic charge which can build up in any metal components in contact with the moving powder. Fumed alumina and silica at 30 mμ have been made, with a nett positive surface charge. An application in the textile industry has allowed higher yarn spinning speeds, by neutralising the normally present negative charge, thereby reducing end breaks and increasing strength.

Fumed alumina and silica have thixotropic properties which are most marked in non-polar, non-hydrogen bonding liquids. These can be turned

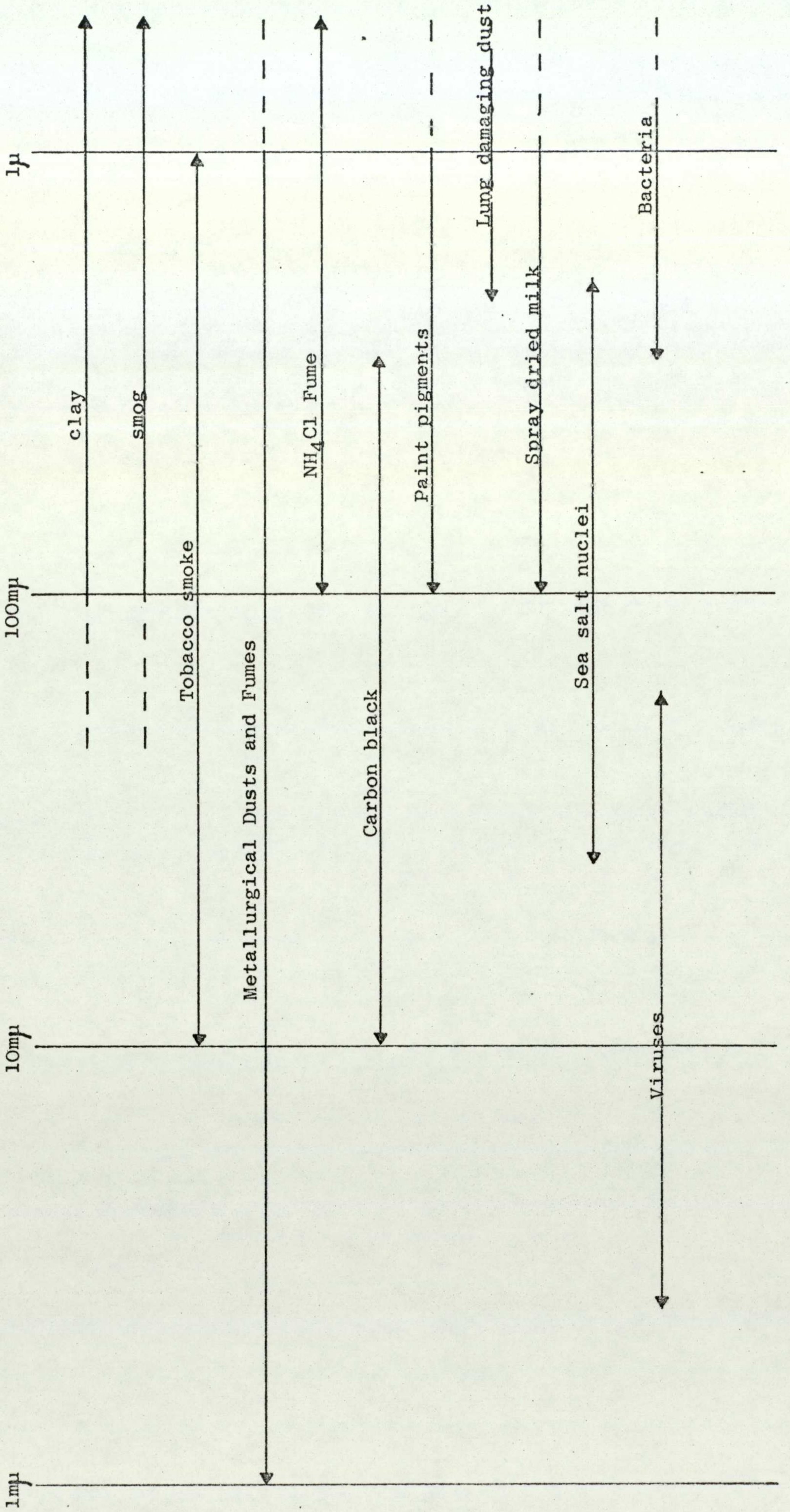


Fig. 10 Some Common ultrafine particles

to a gel by 1 to 3 weight % of powder. The cause is hydrogen bonding between hydroxyl radicals which form on the surface of the particles, forming a network which increases viscosity. Stirring breaks the bonds and viscosity falls. The presence of polar or hydrogen bonding molecules in the liquid tends to saturate the hydroxyl groups, so for instance water required $10^{w/o}$ silica to gel, and $33^{w/o}$ to become a free flowing powder. The stability of thickened liquid is maintained at elevated temperatures - sometimes until natural thermal decomposition. An example is the use of fumed silica in silicone greases for high speed, high temperature applications.

Another application in liquids is as an antisettling agent. Many suspensions such as paints, aerosols etc., tend to sediment on standing. Providing the liquid does not form hydrogen bonds, fumed silica lowers the settling rate, and keeps the eventual sediment loose enough to be dispersed easily by shaking.

The application of ultrafine particles to dispersion strengthened materials is described in detail in Chapter Three.

PART ONE

ULTRAFINE POWDERS

CHAPTER ONE

THE PRODUCTION OF ULTRAFINE POWDERS

Introduction

Because of the growing industrial interest in ultrafine powders, amongst which silicon nitride and titanium nitride appeared to be suitable models, it was decided to try and produce them using a plasma torch. Even if these nitrides were successfully produced, there would be no future in the process if a cheaper method were available. This chapter begins with a survey of possible alternative methods, which are discussed and summarised. The conclusion is that there is no alternative method which does not require the provision of the nitride in powder form.

Where sufficient information is available, the methods have been costed using the nomenclature and equation in Appendix Four. A table of commercially available powders is given.

It was known that the efficient collection of ultrafine powders in gaseous suspension is a major technical problem, so the second section is a survey of possible methods.

The various methods of producing fine powders fall neatly into classification according to the physical state in which the materials are processed. The solid state classification includes calcination, and all the methods by which large particles are mechanically broken down. The liquid state methods include atomisation from the melt, and the aqueous solution processes.

1.1. Solid State Methods

1.1.1. Ball milling

A ball mill consists of a horizontal cylindrical chamber, with 50% of it volume occupied by hard balls usually of two slightly different sizes (Fig 11).

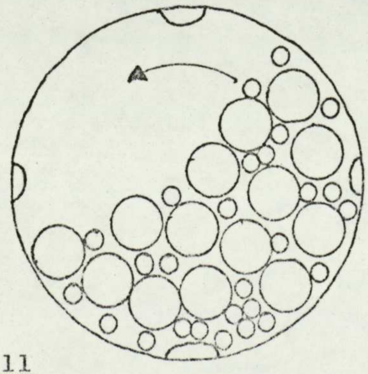


Fig 11. A ball mill

The interstitial volume is filled with the material to be ground so that the ball charge is just covered. When the chamber is slowly rotated on its axis, the balls exert a grinding action on the material between them. The form of the action depends on the properties of the material being ground - its hardness and malleability. The method is suitable for metals, alloys and refractory compounds according to KUHN, and is extensively used in the paint industry to grind and mix simultaneously.

The ultimate particle size depends on the balance between the rates of breaking down, and agglomeration which becomes increasingly important with finer particles. To reduce the agglomeration, the material is ground in the form of a slurry which includes a multivalent ion inorganic salt. This 'surfactant' allows particle sizes down to 0.1μ to be attained after grinding periods of 15 days.

The production of 0.5μ nickel from 2.5μ carbonyl nickel was described by QUATINETZ, SCHAFER and SMEAL, in a stainless steel mill at 48 r.p.m. There is no fundamental objection to scaling up their results, so to provide capital cost information, several manufacturers were asked to quote for stainless steel mills capable of holding;

a) 1000 kg of stainless steel balls.
b) 10,000 kg of stainless steel balls.

The cost components are:

Variable Costs - Materials - Electric power
- Surfactants
- Fluid
Consumables - Balls

Fixed costs - Capital, Maintenance Labour and Overheads

Let: Mass of the grinding balls = G kg
Cost of ball charge = £B
Powder charge/ball mass ratio = r
Life of grinding balls = x batches
Milling time = t hours
Emptying, cleaning, refilling time = 10 hours
Annual working hours = H hours p.a.

∴ Number of batches per year, $n = \dfrac{H}{t+10}$ p.a.

Surfactant cost per batch of powder = £S

Lubricant " " " " " = £L

Electrical " " " " " = £E

Annual maintenance = $\dfrac{£0.1C}{Y}$

With the standard notation given in appendix four, the cost equation is, in general terms;

$$P.C. = \frac{1}{Gr}\left[S + L + E + \frac{B}{x} + \frac{1}{n}\left(\frac{1.1C}{Y} + C_{LOH}\right)\right]$$

The quotations received were analysed to provide all the required cost information for a typical mill, and the following figures below are the results. The mill to which they are applied is jacketed, 6ft in diameter by 6½ ft long, and includes a steel support frame. It is driven by a 34 kW motor at 18 r.p.m., and holds 9000 kg of balls.

Ball mill operation is characterised by long periods needing no attention, so one third of a man per shift is required on average to run it. Assuming continuous operation,

C_{LOH} = £3000

Other costs are; C = £6,900

B = £13,800

with H = 8400 hrs p.a.

and G = 9000 kg

$$P.C. = \frac{1}{9000r}\left[S + L + E + \frac{13,800}{x} + \frac{t + 10}{8400}\left(\frac{1.1 \times 6,900}{7} + 3000\right)\right]$$

$$= \frac{1}{9000r}\left[S + L + E + \frac{13,800}{x} + 0.486\left(t + 10\right)\right] \quad £/kg \;......\text{eqn } 1.1.1$$

The data given for grinding nickel, by Quatinetz et. al. is;

Powder charge = 210 gms

Ball charge = 3000 gms

Surfactant = $(Al(NO_3)_3 9H_2O)$:- 70 gms

Fluid = Ethyl alcohol :- 300 ml.

Milling time, t = 50 hours.

The nitrate is 50p for 500 gms, so working on the ball charge ratio,

$$S = 0.5 \times \frac{70}{500} \times \frac{9000}{3} = £210$$

Industrial ethyl alcohol is £1 for 4546 ml, so similarly:

$$L = 1.0 \times \frac{300}{4546} \times 3000 = £198$$

$$E = .01 \times 34 \times 50 = £17$$

$$r = \frac{210}{3000} = .07$$

Let $x = 1000$

then

$$P.C. = \frac{1}{9000r}\left[S + L + E + \frac{13,800}{x} + \frac{2080}{n}\right] \qquad \text{........ (eqn 1.1.1.)}$$

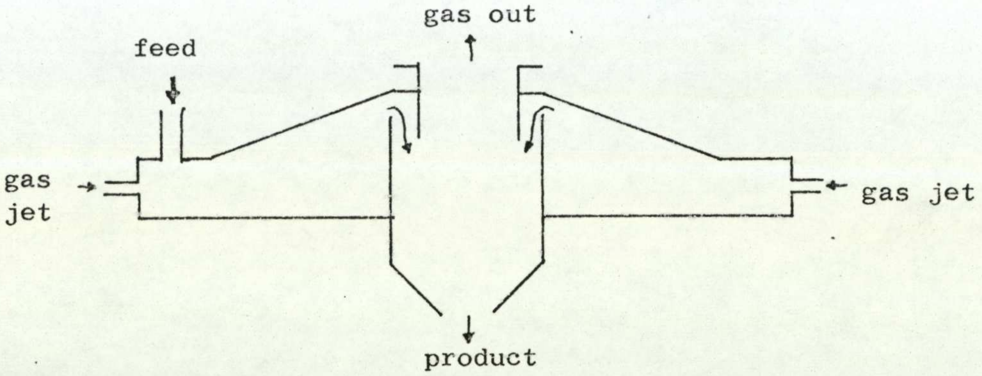
$$= \frac{1}{630}\left[210 + 198 + 17 + 13.8 + 14.9\right]$$

$= \underline{0.72 \text{ £/kg}}$ for reducing Ni from 2.5μ to 0.1μ, at a rate of 882 tonnes a year. Whilst the figures will vary depending on the material being ground, the above calculation gives a good idea of the processing cost which can be expected. As the grinding rate is most rapid at the beginning of the cycle, the time taken will not be significantly increased by a larger initial particle size.

1.1.2. Impact Pulverisers and Jet Energy Mills

These methods are described by TEMPERLEY and BLYTHE. The material to be ground in an impact pulverizer is fed into a stream of fluid which has been accelerated to a velocity such that the material is thrown forward and impacted onto a target surface. In order to achieve effective and efficient working the grinding fluid needs to have a velocity of the order of 300 m. sec^{-1}, and the material flow must be very uniform. Even then only a small proportion of the material is reduced to the desired size - the small particles needs to be removed and the larger ones recycled. The machine becomes bulky and is inefficient. This process has not been costed.

The jet energy mill combines the action of comminution between rapidly colliding particles with the separation process of a cyclone. The simplest geometry is a shallow cylindrical chamber (Fig 12), with jets inclined at 45^{o} to the outer wall. The fluid leaves the chamber along the axis in a vertical direction. The material is fed in near the outside wall. The outermost zone of the cylinder is where the grinding takes place, under periodic fluctuations and very high shear in the fluid: the velocity is zero at the outer wall but maximum a short distance away at the jet. The centre zone is the classification zone - only particles below a certain radius reach the inner or withdrawal zone where they are removed by the fluid and deposited in the cyclone. Larger particles are ground further or sent back to the outer wall. Radioactive or toxic products can be completely recovered by grinding with steam and condensing. Particles of sub-micron size may easily be obtained by this method.



cross section

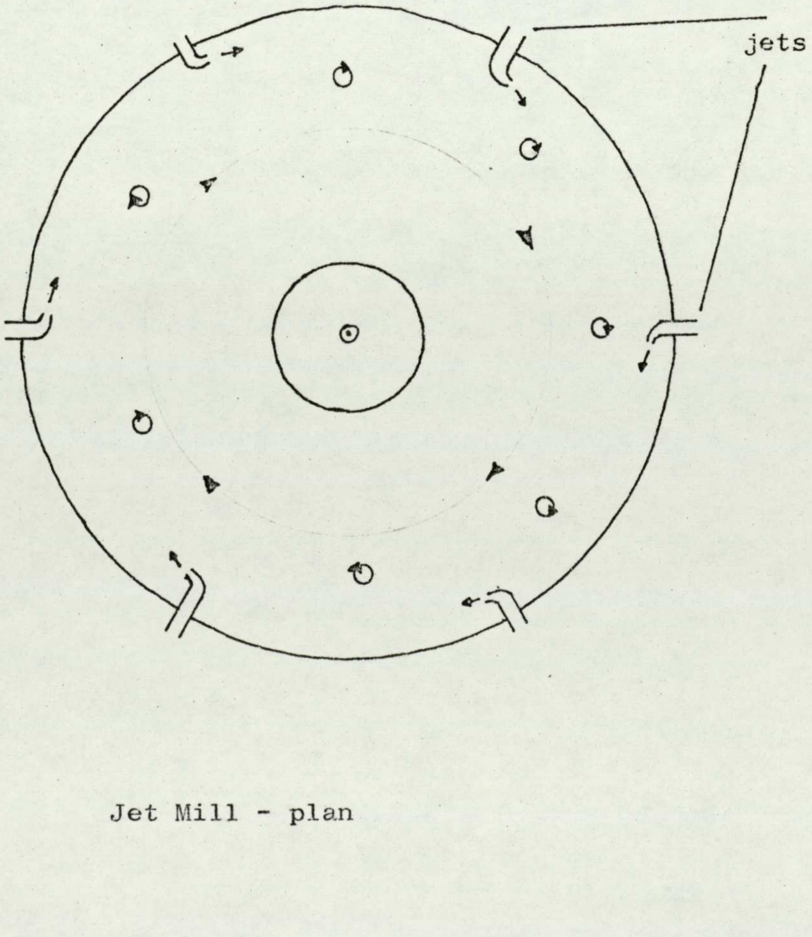


Fig 12 Jet Mill - plan

The cost components are:

Variable costs - materials - (compressed) gas
- electricity

Fixed costs - capital and maintenance
labour and overheads.

Let, Gas cost $= g(£m^{-3})$
Gas flow $= v(m^3hr^{-1})$
Electrical costs $= E(£hr^{-1})$
Capital cost $= C(£)$
Maintenance $= \frac{0.1C}{7}$

Production rate $= M(kg\ hr^{-1})$

The cost equation for a 2000 hour year, is:-

$$\text{Milling cost (£/kg)} = \frac{1}{M}\left[gv + E + \frac{1}{2000\eta}\left(\frac{1.1C}{7} + C_{LOH}\right)\right]$$

A typical mill has the following costs:

Mill and installation $C_1 = £10,000$
Compressor $C_2 = £\ 7,000$
Compressor motor power = 400 kW

$\therefore\ E \simeq £4\ hr^{-1}$ at 1p unit

Gas cost for air = zero
Let $\eta = 1$
Let labour be ½ man, $C_{LOH} = £1500$
Production rate $M = 90\ kg\ hr^{-1}$

$$\therefore\ \text{Milling cost £/kg} = \frac{1}{90}\left[4 + \frac{1}{2000}\left(\frac{1.1 \times 17,000}{7} + 1500\right)\right]$$

$$= £.07\ kg^{-1}$$

The milling cost is an inverse linear function of the production rate, and this can only be found for a particular powder by experiment.

1.1.3 Calcining

The calcination process involves the conversion of a metal salt to the oxide by the application of heat, according to HANCOCK. An example is the decomposition of ferrous sulphate heptahydrate to iron oxide in an indirectly heated rotary muffle kiln. Fe_2O_3 powders can be produced with a range of average particle sizes from 0.25 μ to 2.0μ, and are used to make ferrite components, whose magnetic properties are highly superior to those made from ground "natural" oxides.

1.2. Vapour State Methods

1.2.1. High Intensity Arc (see also section 2.3.3)

In the common convection stabilised arc, such as is used as a high intensity white light source, the electrodes become very hot by thermal conduction and convection from the arc plasma. If the current intensity is increased a point is reached where the mode of operation of the discharge changes, and very large amounts of energy are released at the anode. The anode temperature rises to above evaporation point, and its material joins the arc plasma as a vapour in the form of a well defined 'tail' or flame, as described by HOLMGREN, GIBSON and SHEER. The process is limited to anode materials that are electrically conductive or can be compacted with carbon, in which case carbon is present in the arc plasma. The anode material may be re-condensed downstream as a particulate, or undergo reaction with the arc plasma atmosphere and form a compound before condensation. The method cannot be used successfully if the presence of carbon interferes with the required reaction, or if the product decomposes before recondensation due to the arc temperature.

This method has been successfully used by the Vitro Corporation of America in the production of a variety of oxides, metals including aluminium, iron, tungsten, and molybdenum, and carbides including titanium and silicon carbides. The particle sizes range from 5 $m\mu$ to 200 $m\mu$; quenching with air caused a size reduction of 2.5:1 in the case of SiO_2, with a marked reduction of size dispersion.

Vitro claim that the process is 'at least comparable in cost to current chemical methods', and describe a small pilot plant which produces 5 to 10 kg. an hour of oxide. The consumable electrodes have to be prepared, and this constitutes the major part of the running costs. 65% of the electrical energy expended is utilised at the anode. The provision of an inert atmosphere adds to the running cost and if argon is required may be a significant factor. Oxides were marketed by Vitro from £35 per Kg. upwards for small quantities and contain carbon impurity of from 0.1 to 0.3%. They were produced in the pilot plant facility, that has since been closed down, presumably for lack of orders.

1.2.2. Evaporation under Low Pressure

Fine particles of various metals have been produced by KIMOTO et.al. in an ordinary vacuum evaporation unit using a tungsten wire basket heater. The atmosphere was Argon at pressures from 1 torr giving particles of 10 mμ, to 30 torr giving particles of 500 mμ sizes, which were collected on electron microscope grids. No attempt was made at 'bulk' collection, the experiments were for fundamental research and only a few milligrams of metal were evaporated at a time. It was noted that the ferromagnetic metals formed necklace-like agglomerates many microns long. The electron microscope beam power had to be kept down in order to avoid melting the specimens.

1.2.3. Flames

A flame may be treated as a chemical reactor, or simply as a source of heat. Exothermic reactions such as the oxidation of hydrocarbon fuels, usually produce fine particles known as soot. An example is the production of carbon black by burning fuel oil in an oxygen weak atmosphere.

Fumed alumina and silica are produced by injecting the chlorides into the tail, or luminous part, or an oxy-hydrogen flame, according to LOFTMAN. The flame acts as a source of both heat and H_2O for the reactions:

$$\mathrm{Si\,Cl_4 + 2H_2O \xrightarrow{1100^\circ C} SiO_2 + 4HCl}$$
$$\mathrm{2Al\,Cl_3 + 3H_2O \longrightarrow Al_2O_3 + 6HCl}$$

High yields are obtained, and the oxides, which are in the 10 mμ to 50 mμ size range, are marketed in bulk (see Introduction for applications and table 1 (section 1.3.4.) for prices).

1.3. Liquid State Methods

1.3.1. Allutriation and Freeze Drying

These methods are limited to the production of materials which are soluble in water or other solvents, or can be readily produced by a reaction between a gas and a material which is soluble.

In an allutriator, a gas is passed through the solution, and as the bubbles break the surface fine droplets are carried up in the gas stream. A vertical tube acts both as an evaporator and a size analyser, the finest droplets pass upwards and evaporate leaving the fine particle suspended in the gas stream. The larger ones are held in suspension until their size becomes insufficient to support their mass against the updraught, and they fall back. No references to the use of this method for bulk production have been found, but it is used to introduce a small controlled amount of a substance into a flame in spectroscopic studies of flame reactions and temperatures.

The technique of freeze drying has been described by LANDSBERG and CAMPBELL, and depends on being able to freeze the solution so rapidly as to restrict the extent to which the solute can agglomerate as it precipitates out. The particle growth may be diffusion controlled, or may depend on the conduction of heat through the solvent. This has been done by spraying the solution onto a rotary drum filled with a freezing mixture, or dripping the solution directly onto a freezing mixture in a stirred vessel. The frozen solution is then transferred to a vacuum chamber, where it is heated to a temperature below that required to melt or sinter it. The resulting powder may be reduced by hydrogen if necessary:-tungsten-rhenium alloy powders as fine as 5 $m\mu$ have been produced by the U.S. Bureau of Mines by this method.

1.3.2. Precipitation

HANCOCK has reviewed precipitation methods, and quotes the example of hydrated iron oxide. Seed nuclei are formed by the reactions:

$$4NaOH + 2FeSO_4 + H_2O \longrightarrow 2Fe(OH)_2 + Na_2SO_4 + H_2O$$

$$2Fe(OH)_2 + \tfrac{1}{2}O_2 \longrightarrow Fe_2O_3.H_2O + H_2O$$

and the $Fe_2O_3.H_2O$ nuclei are needle shaped, approximately 0.05μ thick and $0.5\,\mu$ long. They can then be transferred to a precipitator containing $FeSO_4.H_2O$ and iron, usually in the form of thin gauge stampings. The seed particles are circulated over the bed of iron in an oxidising environment and, as the iron oxidises, the reaction products precipitate on the nuclei causing the particles to grow. The final size can be controlled up to several microns, and these particles find applications on magnetic tape.

Another method is to dissolve a metal in an ammoniacal solution, which is necessary to keep the metal in solution at the high pH values experienced. The solution is heated up to 150 to 220°C at 2.1 - 4.9 MN/m^2 (300 - 700 lbs/in^2) pressure and hydrogen is bubbled through it. The metal is reduced, and forms a fine powder. In general the particle size is above 1μ , but certain refinements have been used to produce sub micron cobalt from cobalt hydroxide. The methods have been reviewed by BURKIN.

The Sol-Gel method starts by dissolving the metal in nitric acid. The nitrate ion is removed by solvent extraction or thermally, forming the Sol which is then injected into a liquid which removed some of the water (an alcohol) and leaves a Gel. The Gel is then centrifuged, and reduced by hydrogen to give the metal powder. Alternatively ths Sol could be freeze or spray dried. Tungsten powder of 0.1μ to 0.5μ size has been produced at Harwell from tungstic oxide by this method.

1.3.3. Atomisation

Metal is heated in an induction furnace and transferred to a zirconia lined funnel where its temperature is maintained by induction heating. It is allowed to run out through a zirconia nozzle; at the exit it is blown into droplets and cooled by fine jets of water or gas. In the latter case the stream is blown into a tank of water. The powder is filtered out, most of it is 50μ to 100μ size, but there is a small sub micron fraction which could probably be increased if particularly required.

1.3.4. Comparison of methods

In principle, all the solid state methods can be used to break down any solid material. In a ball mill, material being ground can become contaminated from the balls, the liner, and the surfactant and lubricant being used. Contamination from the balls and liner is especially likely if they are softer than the particles being ground. The impact pulverising method does not seem a serious contender for ultrafine particle production, relying as it does on momentum, which falls off with the cube of the radius of a particle. The jet energy mill suffers less from contamination, but if air cannot be tolerated the cost of the driving fluid could be serious, even with recirculation. For the attrition of nitrides, air would be tolerable. Calcination is widely used, but limited to oxides.

All of the vapour state methods have some limitation on the range of materials which they can produce. The high intensity arc process produces carbon vapour, which may interfere with a reaction to produce e.g. nitrides, if the thermodyamics favour the production of the carbide. Evaporation under low pressure is limited to the production of elements. Flames are a good way of producing oxides, but are unlikely to be useful for nitride or carbide production, and certainly not for elements, except carbon.

Of the liquid phase methods, allutriation depends on the material produced being soluble in water or other solvents, which does not apply to oxides, carbides or nitrides, although a salt could be produced which could later be decomposed to an oxide or element. Precipitation, hydrometallurgy, freeze drying and the Sol-Gel processes start with aqueous solutions, and the product is an oxide which can be reduced to the metal. Atomisation is limited in practice to metals.

Of all the available methods, only ball milling and jet milling are suitable for the production of ultrafine nitrides. Both methods are unproven below 100 mμ, and only process ready-made coarse powders. Chemical reactions are not generally performed in mills. The possibilities of producing ultrafine nitrides using plasma torches are examined in Chapter Two.

A stainless steel ball mill can grind 2.5μ Nickel down to 0.1μ at a calculated cost of £0.72 kg, and a jet mill working on air can produce sub-micron powders at a cost of £0.07 kg, subject to trials with a specific material.

The cost of commercially available powders are shown in Table 1. The Vitro range has been withdrawn from sale, but is included for comparison purposes.

1.4. The Collection of Ultrafine Powders

If the powders are prepared in the solid or liquid states, collection presents no unusual problems. If a vapour state method is used, the particles remain suspended in the gaseous medium, and continuous collection from a flowing system is difficult, as filters tend to become blocked. Electrostatic precipitation in a vertical column was attempted by workers at the NPL, but after a few minutes the corona discharge current fell to zero, although powder was apparently still settling on the column walls.

The following is a review of known methods of collection, which are discussed according to their relevance to laboratory scale apparatus. The operating problems which were encountered with filters and vertical tubes are described in section (2.5). As a result of this experimental experience, a low cost collecting system was sought with these properties:

1. Collection efficiency of over 95%, for yield measurements,
2. Determine the sample weight collected to within 5% of 100 gms.
3. No significant contamination of the sample.
4. Only one or two p.s.i. gas pressure required to operate it.

These are the criteria upon which the suitability of each method for laboratory scale operation was judged.

1.4.1. Agglomeration and Cyclones

The collection of fumed alumina and silica has been described by STEFANICK as depending firstly on a process of agglomeration in which 'the path of the particles is physically obstructed right after they leave the reaction zone (i.e. the furnace). The direction of the gas stream is rapidly changed in a snake like series of coils which causes the small particles to collide physically with each other more often. The particles 'stick' to each other through physical attractive forces (van der Waal's)'. These clusters are then large enough to permit efficient removal from the gas stream and are cycloned and filtered by coated dacron bags, which cause a pressure drop of 0.8" water gauge. This method is used on a widely marketed product (see flame hydrolysis table 1) so is presumably successful and economic on a production scale, but would require experimental verification for other powders. It does not appear suitable for laboratory work as the agglomerator is bound to need some pressure to drive it, which cannot be tolerated at the feed-in end of the apparatus.

1.4.2. Bag Filters

It is possible to construct a filter bag of terylene felt which collects particles below one micron. The problem is that the powder tends to clog the felt, and needs periodically removing. The solution offered by MIKROPUL Ltd is to apply a 1/10 th second pulse of gas at 100 p.s.i. pressure to the inside of the bag every second. The felt expands a little, and the powder is blown off by a combination of shock and reverse gas flow. The collection efficiency for particles below 0.1μ is unknown, and the amount of powder collected would be difficult to determine, so the method is unsuitable for laboratory scale yield measurements.

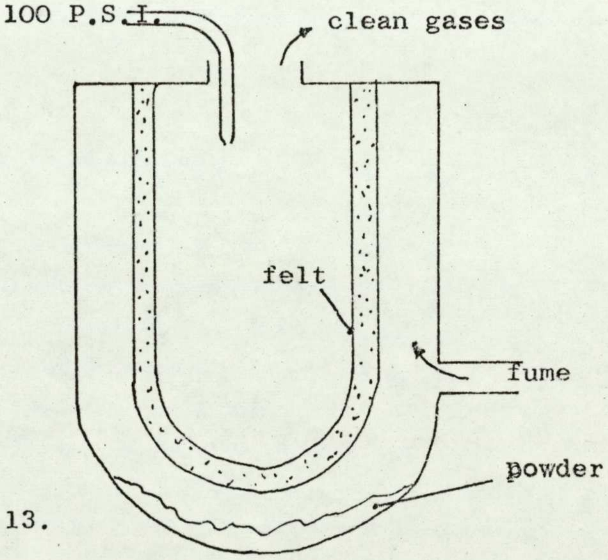


Fig 13.

1.4.3. Membranes

GELMAN HAWKSLEY LTD supply tri-acetate membrane sheets with an average pore size of .05μ, which should catch over 95% particles of 0.1μ size. The membranes are stable up to 150°C, may be made transparent for optical examination by application of certain oils, can be dissolved in methyl acetate, and are ashless. From the data supplied, for a flow rate of 40 l/min and a pressure drop on a clean membrane of 3 cmHg (0.6 psi) the required filter area is 1000 cm^2. A sample was obtained, but it was found to clog rapidly and very effectively, which was unsatisfactory.

1.4.4. Steam Condensation

This method has been thoroughly investigated by SCHAUER as a method of scrubbing out radioactive dusts produced by burning waste, where efficiences of 100% are required. A divergent/convergent/divergent nozzle was developed, in which steam condenses onto the particles and forms droplets. Steam is generated at 60 p.s.i. at a rate of 250 lb/hour, and passes through the arrangement shown in (Fig.14).

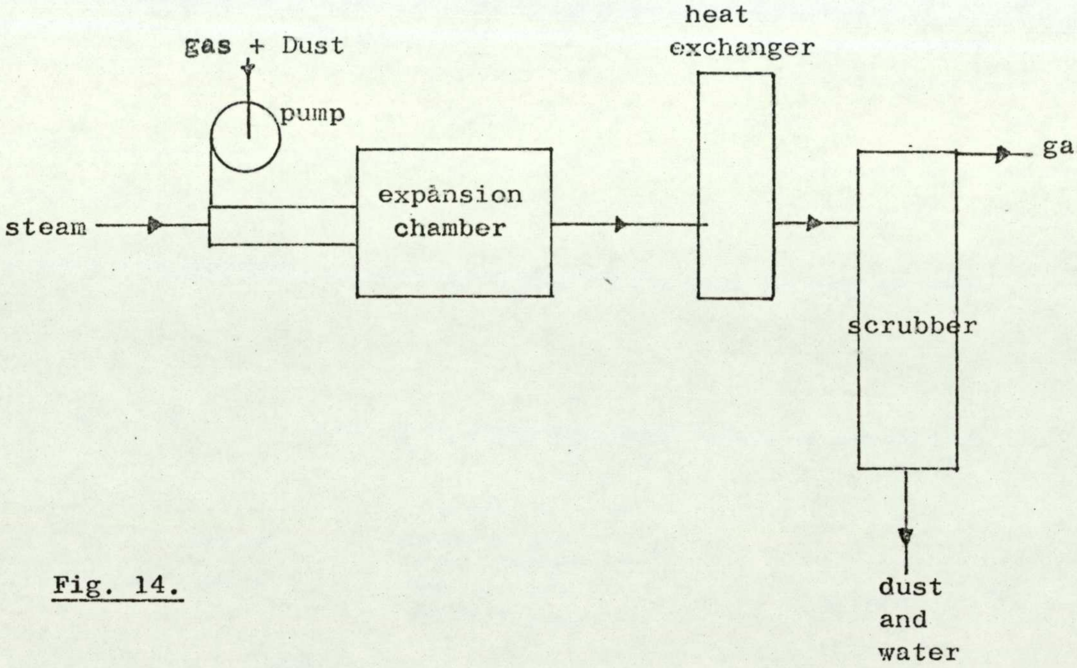


Fig. 14.

Approximately 2000 galls/hour of cooling water were required to deal with 25 cu. feet/min. of gas loaded with 0.3 μ dioctyl phthalate smoke at a concentration of 6.10^{11} particles per ft^3. Efficiency was 99.9%. The method was considered too complex and expensive for laboratory scale requirements, and included the disadvantage of soaking the powder, which would remove any soluble constituent, and make a total chemical analysis difficult.

1.4.5. Quenching on a cold surface

STOKES and KNIPE used freeze-out traps containing dry ice or liquid nitrogen to remove gaseous products such as cyanogen dioxide from plasma torch reactions. A 'cold finger' was used to quench certain reactions and also to collect solids formed during the reaction, when it was placed as close as 0.5" to the feed ring. TiN and Mg_3N_2 were collected in this way, but $Mo_2N$and W_2N could not be prepared.

HARNISCH et. al. collected TiN as a black powder on a water cooled copper drum which rotated at a distance of a few cm from the injection point of a plasma torch reactor (Fig.15). The TiN size range was not stated explicity but described as X-ray crystalline.

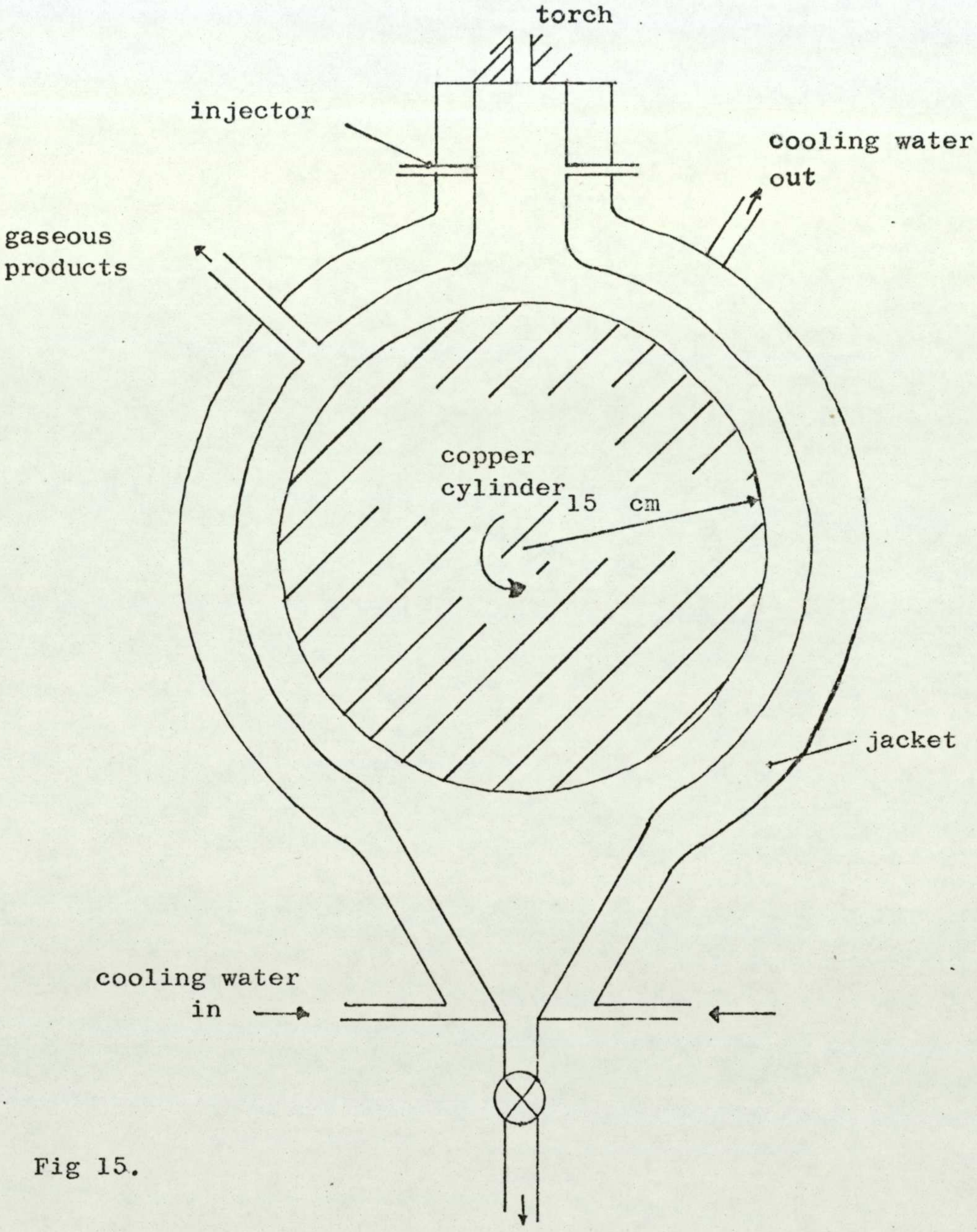


Fig 15.

The collection efficiency of this method is uncertain. The rotating drum may well be efficient when it is 'clean', but loses efficiency as the deposit builds up. A cold finger cannot collect all the powder produced as some will flow round it. The point in the

TABLE 1

COMMERCIALLY AVAILABLE SUB-MICRON POWDERS

Material	Average Particle Size(μ)	Supplier	Cost £/Kg	Nominal Purity	Remarks
Metals					
Co	1.0	Cerac	15.4		
Fe	0.05-0.5	Vitro	115	95 %	4.5% Oxygen
Mo	0.05	Ciba	38	99.7%	
Mo	0.05-0.5	Vitro	270	99.5%	
Ni	1.0	Sherritt	7.8	99.9%	Includes some Co.
Ni	0.05-0.5	Vitro	115	99.5%	
Ta	0.1	Ciba	38	99.9%	
W	0.8	London Scand.	5		All tungsten compound.
W	0.04	Ciba	38	99.9%	prices are tied to
W	0.05-0.5	Vitro	270	99.5%	the market price of W.
Carbides					
NbC	0.02	Ciba	38	99.9%	D.C. Plasma Torch ?
TaC	0.02	Ciba	38	99.9%	"
TaC	0.8	London Scand.	40		
WC	0.8	London Scand.	5		
WC	0.2-0.3	Ciba	38		D.C. Plasma Torch ?
Oxides					
Al_2O_3	.03	Cabot Corp.	1.5	99 %	90% γ form, other oxides 1 Flame hydrolysis
Al_2O_3	0.03	Vitro	60	99.3%	
Co_2O_3	0.02	Vitro	35	99.5%	
-Fe_2O_3	0.05	Vitro	35	99.5%	
Fe_3O_4	0.02	Vitro	35	99.5%	
MgO	0.02	Vitro	60	99.3%	High intensity arc
Mn_3O_4	0.03	Vitro	35	99.5%	
MoO_3	0.05	Vitro	115	99.75%	
Ni_2O_3	0.02	Vitro	35	99.5%	
SiO_2	0.005-0.01	Vitro	35	99.7%	
SiO_2	.007	Cabot Corp.	1.1	99 %	Flame hydrolysis
	.012	Cabot Corp.	0.9	99 %	
	.05	Cabot Corp.	1.2	99 %	
ThO_2	0.015	Vitro	160	99.5%	
WO_3	0.02	Vitro	115	99.75%	High intensity arc
V_2O_5	-	Vitro	60	-	
ZrO_2	0.05	Vitro	115	99.5 %	
Fe_2O_3	0.3-1.0	Ashby Morris	0.14	98 %	Paint Pigment. Calcining
Fe_2O_3	0.4x0.08	Bayer	0.7	99 %	Needles for e.m.tapes Precipitation
Miscellaneous					
Carbon		Morganite	0.075		Flame process
Boron	0.1-1.5	Borax	£295		Plasma method-amorphous

Notes

1. In the case of Vitro and Sherritt, carriage costs have not been included. Prices are lower for orders of 2 Kg and over. The Vitro range has been withdrawn.
2. Only major impurities are listed. Additional data on composition, particle shape and surface area are available.

production cycle at which the powder is collected should be selected so that any alteration in collection efficiency cannot alter the rate of production, and vice versa. Where the collector is also the quencher, this condition does not hold, and alterations in yield could be caused by alterations in the quenching conditions rather than in e.g. reaction zone temperature, flow rates etc. A situation where the operation of the measuring device can affect the phenomenon being measured, is intolerable for fundamental experimental work.

1.4.6. Inflatable sack

BOND, LADNER and McCONNELL collected the total gas sample from a D.C. plasma torch experiment on coal cracking, by allowing it to fill a thin walled polythene tube. It was rolled flat before the experiment to a 1 ft wide strip, and expanded to a 10 ft long cylinder holding 100 L at only a 'very small' pressure above atmospheric. PFENDER and BOFFA used a large inflatable plastic bag to collect ultrafine graphite particles generated at a transpiration cooled graphite anode in a D.C. plasma torch. The size distribution was analysed by a Whitby aerosol analyser.

Neither of these papers described the inflatable sack as a total collection method, but providing the particles are given sufficient time, they should all settle on the walls, allowing the gases to be evacuated and the sack folded and weighed. This method fulfulled all the experimental requirements, and its successful use is described in section (2.5.3.).

1.4.7. Choice of method for laboratory work

Agglomerators and cyclones were rejected because of the complexity, cost, and difficulty of collecting the powder which would collect on the inner surfaces. The required accuracy of yield determination could not be met, as was also the case with bag filters, which trap powder in the fabric. The filters have no guaranteed efficiency below Olu , so losses were inevitable. The tri-acetate membranes were impracticable because of clogging which completely stopped the flow of gas. The steam condensation method suffered from complexity, and therefore expense and would remove any soluble products from the powder, making total analysis difficult.

Cold quenching methods interfere with the reacting and condensing vapours by definition, which is intolerable in fundamental work, and are also of uncertain efficiency. The inflatable sack was accepted as it is simple, 100% efficient, can be weighed with the sample in, requires only 1 or 2 psi to inflate it, and is cheap.

CHAPTER 2

PRODUCTION OF FINE POWDERS FROM THE GAS PHASE AT HIGH TEMPERATURES

2.1. The Plasma Torch as a source of high enthalpy gas for chemical reactions

2.1.1. Choice of plasma torch

The relationship of the thermal plasma produced by a plasma torch to a chemically reacting system is simply that of a source of hot gas, and possibly some charged particles. In the Introduction the three common sources of thermal plasma were discussed, namely the carbon arc, the R/F plasma torch and the D.C. plasma torch. For the chemistry described in this thesis, the carbon arc is unsuitable because of the carbon vapour emitted, so the choice was between a radio frequency or direct current power source. A plasma spray gun powered by a D.C. pack had already been purchased (Metco type 3MB) so the choice had effectively been made. Consequently, the design and development of a D.C. plasma torch was initiated.

A D.C. plasma torch emits a jet of very hot gas, which rapidly cools from plasma temperatures as it leaves the nozzle, provided it is operating in the turbulent mode. A detailed account of the operating characteristics of a D.C. plasma torch and its power supply is outside the scope of this thesis. Suffice it to say that once a torch has been designed to work at a certain power with a certain gas, the mean enthalpy of the gas jet cannot be varied over a very wide range. The lower limit is set by the transition from turbulent to laminar mode as the gas flow is reduced (see INTRODUCTION) and the upper limit by the voltage characteristics of the power supply. The upper limit may be compared with arc quenching as practised in an air blast contact breaker, that is where the gas flow is sufficient to blow the arc out.

2.1.2. Thermal energy balance

The mean enthalpy of the plasma jet is obtained by measuring the power going into the torch, subtracting the heat loss in the anode cooling water, and dividing by the gas flow,

$$\text{i.e. Mean gas enthalpy (HNT3)} = \frac{IV - (\Delta T^{o} \times \text{water flow})}{\text{gas flow}}$$

where ΔT = increase in water temperature.

The temperature of the gas can be looked up on a temperature - enthalpy curve (Fig 16). The temperature profile in the arc column is very steep, but the degree of turbulence caused by the fluctuating arc mode assists in the rapid smoothing of the profile outside the torch. The subsequent temperature profile is determined by the geometry and thermal properties of the section into which the hot gas is passed - this will be treated in detail in section 2.5.

The plasma gas may or may not be used as a reactant. In either case its role as a provider of charged atoms or molecules cannot be ignored - it is known that charged particles can affect the nucleation of condensed phases (see 2.2.1). Whatever the chemical contribution made by the plasma gas to the reaction the thermal contribution is unaffected. At some suitable point chosen by measurements of temperature profiles in the reactor, the reactants are injected into the gas stream. Provided there is sufficient turbulence in the mixing region, heat is lost by the hot stream and gained by the reactants until an equilibrium is obtained. This is the temperature at which the reaction is considered to take place.

The reaction itself is predicted by considering all the possible reactions and then plotting the change in Gibbs function (ΔG_f^o over the temperature range experienced by the reactants to see which reactions are most likely or possible. An excellent treatise on chemical thermodynamics in S.I. units is given by WARN. The reaction scheme may have to be revised in the light of experience and the results of chemical analysis on the products. Once the reaction is determined, the heat absorbed (endothermic) or given off (exothermic) by the reaction is calculated from the change in enthalpy (ΔH_f^o) at the reaction temperature. The reaction temperature is chosen by inspection of the plot of ΔG_f^o as f (T) bearing in mind the stability of the desired product and any rival reactions. Ideally a temperature would be chosen which gives the highest equilibrium yield of desired products, or the highest rate of reaction, but in practice this is not possible as reaction rate data at high temperatures is scarce. Some work of this nature has been done by MILLER and AYEN, but not for the reactants involved in this work.

As described above, the reaction temperature is determined by the heat balance between the plasma gas and the reactants. In an experimental situation, the plasma gas flow and nozzle exit temperature is determined by the apparatus available, within certain limits. In order to begin

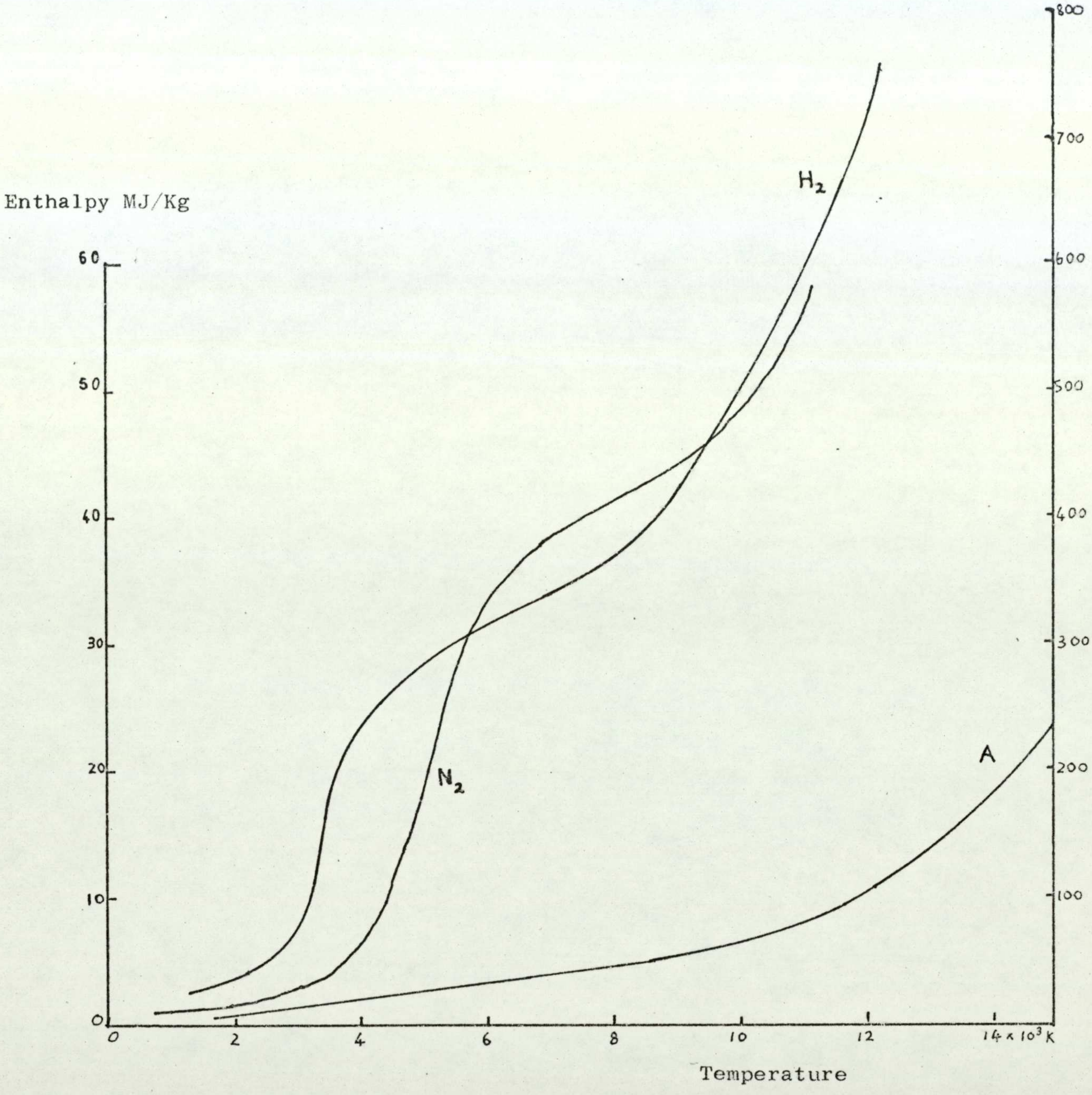


FIG. 16. Enthalpy-Temperature curves for Hydrogen (right hand scale) and nitrogen and Argon (left hand scale).

experiments, an approximate calculation of the heat required to bring the reactants to the correct temperature and perform the reaction must be made, or the experiment may fail completely and no desired products formed. The procedure is described in section 2.6.2, but is bound to be approximate at the initial stages as neither the reaction scheme or the product yield is known. When this information has been gained, the reaction efficiency can be improved by a process of re-iteration of calculation and experiment, using the experimental method described in section 2.5.3, and the equation derived in section 5.2.2.

Any heat contained in the products at the reaction temperature, or transferred by the plasma gas between the torch exit and the injection point, is considered to be lost, and must be accounted for in a cost analysis.

The energy balance of a reaction can be derived in general terms.

Let,

HNT3 = Enthalpy of the plasma gas at the torch exit

HNT2 = Enthalpy of the plasma gas at the injection point

HNT1 = Enthalpy of the plasma gas at the equilibrium with the reactants.

i.e. T1 is the reaction temperature.

The fraction of energy available which is utilised in the reaction will be known as the thermal loading factor, or TLF, and is given by

$$\mathrm{TLF} = \frac{\mathrm{HNT2} - \mathrm{HNT1}}{\mathrm{HNT3}}$$

The thermal efficiency of the torch is given by,

$$\mathrm{THEFF} = \frac{\text{Heat flow into the gas}}{\text{Power consumed by the torch}}$$

$$= \frac{IV - (\Delta T^{o} \times \text{water flow})}{IV}$$

I = torch current

V = mean torch voltage

ΔT^{o} = rise in water temperature

2.2. Nucleation and growth of fine particles

2.2.1. Nucleation

It is generally tacitly assumed in discussions on the condensation of matter from the gas state, that there must be a distinct point in space which is identifiable as a central point, or nucleus around which the condensation takes place. Whilst this is a useful conceptual ideal, there is no evidence that a nucleus as distinct as, say, a charged particle, is either necessary theoretically, or observed experimentally.

The most widely known work on condensation has centred on the tracks caused by energetic charged particles in cloud or bubble chambers. A volume of vapour being bombarded by such particles, e.g. protons, is put into a supersaturated state, and the path of a particle is clearly marked by the formation of condensed droplets. The droplets form on ionised molecules of the vapour, and the mechanism is discussed by BURCHAM in terms of positive ions acting as nuclei, and causing growth by electrostatic attraction.

The general case of condensation from the vapour to liquid phase was discussed in detail by FRENKEL, who showed that the existence of numbers of heterophase fluctuations is a natural consequence of a population distribution of aggregated molecules described by Boltzmann statistics. In other words, there is a finite probability of a number of molecules coming together, and if the vapour is sufficiently supersaturated condensation will centre on these 'nuclei'.

2.2.2. Theory of particle growth

FRENKEL'S theory of nucleation went as far as the derivation of an equation for the number of embryonic droplets formed per unit of time, that are capable of growth. HERMSEN and DUNLAP adapted this equation for the study of the formation of alumina droplets in flames, and combined it with a growth equation by Gyarmarthy which took the form of a driving force (supersaturation) divided by two resistances; diffusion and transfer of heat of condensation from the particle to the vapour. In the case of alumina in flames, the process was dominated by heat transfer, and diffusion could be neglected.

HERMSEN and DUNLAP took two distinct condensing systems, which were opposite extremes of practical situations, the steady system and the closed system. Using the equations mentioned above, they derived expressions for the particle size distribution as a function of time, initial aluminium partial pressure, and initial temperature. Solutions were derived numerically on a digital computer. The steady system involved assumptions of constant concentration and temperature, and has less relevance to plasma chemistry applications than the closed system, which includes the effect of depletion of condensing species and temperature changes on the degree of supersaturation. The two systems could be described as isothermal (steady) and adiabatic (closed).

The most significant result of the theory in its relevance to this work, was the relation obtained between final maximum particle radius, and initial temperature and concentration of condensing species (Fig 17). The dotted line representing .025 atm would seem to be a reasonable extrapolation, and represents concentrations of the order obtaining in the experimental work described in section 2.5.

The significant features of the functions in Fig 17, are the existence of a critical temperature, above which particle size is highly temperature dependant, and the increase in particle size as the concentration decreases. The variation of particle size with temperature is due to 'the highly non-linear dependence of nucleation rate on initial temperature'. The dependence of particle size with concentration is caused by the increased time for supersaturation to fall to 1.05, with decreasing concentration (Fig 18).

The authors state that the actual values of final particle size are probably not much more accurate than an order of magnitude, but that the qualitative relationships are correct.

2.2.3. Relation of the theory to observed phenomena

The characteristics of the particles produced in the works described in section 2.3. which are of greatest interest, are the size and shape. The theory outlined above says nothing about the shape or form, but its predictions on size appear to agree with experimental results. In particular, it is interesting that the particle sizes for lower initial temperatures converge to around .01μ, where a difference in concentration of one order of magnitude produces a difference in particle size of only a factor of two. It is realised that Fig. 17 applies specifically to Al_2O_3, but as the final size in this region is determined by growth, which is dominated by heat transfer, then other condensing systems are unlikely to show final sizes more than an order of magnitude different. In this case the distribution of particle sizes from 3 to 500mμ, which is typical of the papers described, is reasonable.

KIMOTO et al, studied fine particles of fifteen common metals produced by evaporating them in a tungsten basket under argon gas. They were

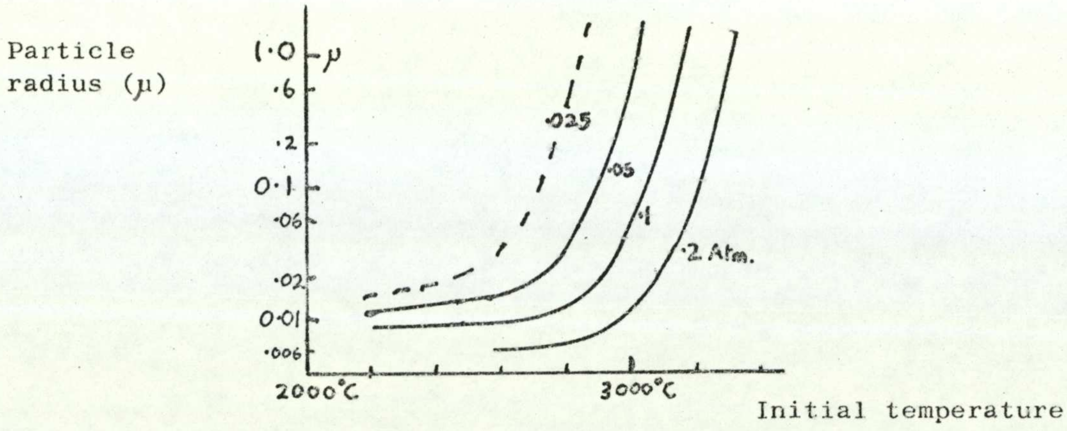


FIG. 17. Final maximum particle radius for alumina condensation in a closed system at P = 1.0 atm, and initial aluminium partial pressures as shown.

From HERMSEN and DUNLAP

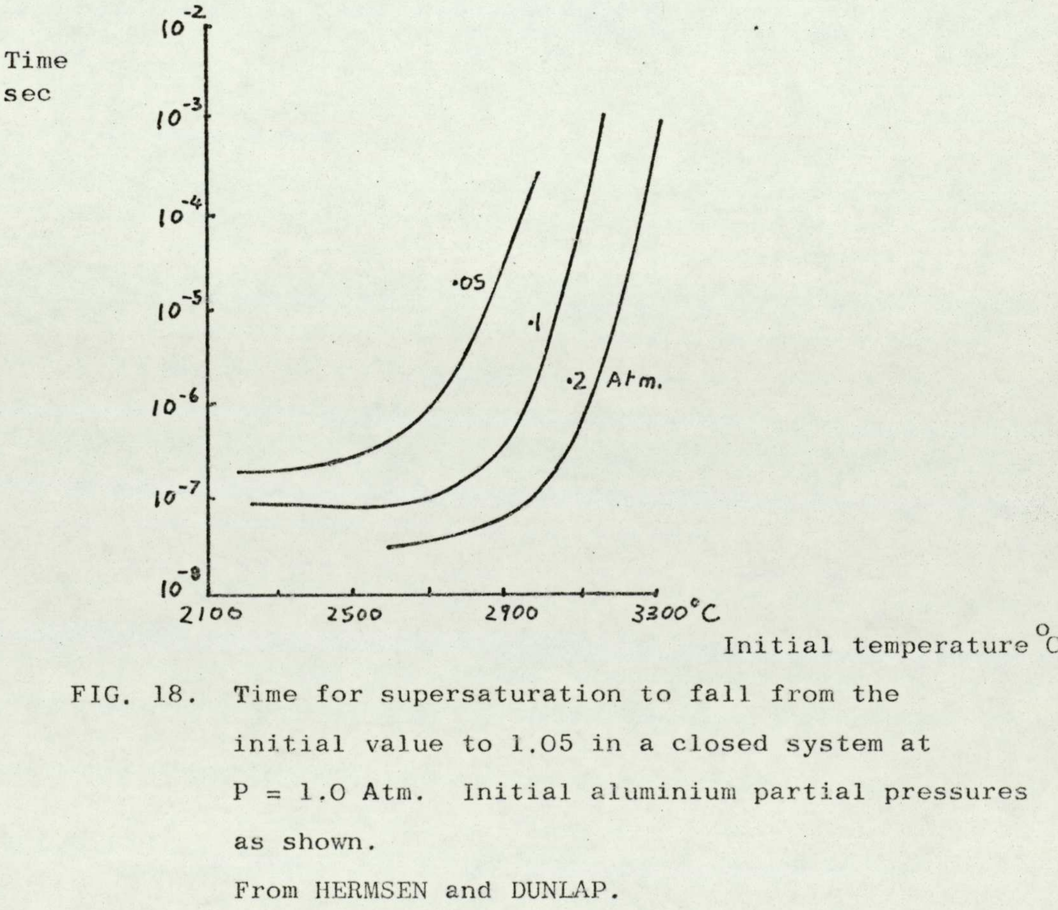


FIG. 18. Time for supersaturation to fall from the initial value to 1.05 in a closed system at P = 1.0 Atm. Initial aluminium partial pressures as shown.

From HERMSEN and DUNLAP.

collected directly onto microscope slides. The system is almost ideally closed, and particle sizes varied from 10 mµ in 1 torr argon (i.e. high concentration) to 500 mµ in 30 torr (low concentration). This is in direct agreement with the theory. A similar result was obtained by WADA using a transferred plasma torch to heat metal alloys (see section (2.3.3.).

HAMBLYN et. al. in their work on boron found an inverse relation between yield and flow rate of reactants. As their filter was ineffective below 1 µ particle size, the loss of the increased fraction of sub-micron particles at high flow rates (low conentration) agrees with the theory.

The only other worker to remark on the effect of concentration is SELOVER, whose observation that particle surface area was inversely proportional to reactant concentration, is in disagreement with the theory, and also with his statement that 'high ion concentrations create a high nucleation centre density which will lead to condensation of very fine particles from the supersaturated vapour'. Nickel has an ionisation potential of 7.63 eV, which at atmospheric pressure should have an ionised fraction of 10^{-3} according to the Saha relation (von ENGEL). As the boiling point is only 2820°C, it is possible that enough ions exist to change the nucleation process assumed by HERMSEN et.al.

2.2.4. Relevance of the theory to this experimental work

Electromicrographs of the powders produced are shown in Figs 41, 42 and 43. The silicon nitride contains a good proportion of long fibres, which appear to be tubular. That the nitride should have an extended form is not surprising, as the reactants are not injected in a strictly gaseous form. As described in section (2.4.1.) the di-imide has a polymeric form and all that is required of the hot gas in the reactor is to drive off ammonia, leaving nitride behind. The injection temperature is chosen so as to avoide breaking the Si-N bonds. Not all the di-imide can be expected to form polymerically, so the existence of very fine particles as well as fibres is likely.

Fibres were not seen on photographs of TiN, but experiments with different reactant concentrations have not been done in a controlled way with either TiN or Si_3N_4, so the theory has not been put to the test.

2.3. A survey of the production of fine powders using R/F and D.C. Plasma Torches

This section begins with a survey of the production of fine powders of radio frequency and d.c. plasma torches and then examines the chemistry of silicon tetrachloride and titanium tetrachloride, with particular reference to high temperature reactions. Many reviews on the subject of plasma chemistry have been published and of those which include the production of fine powders, the most notable are: KANA'AN and MARGRAVE, STOKES, KUBANEK and GAUVIN (1967), and VURZEL and POLAK. The various processes for the production of fine powders can be divided into three types.

1. The material, already in a coarse powder or rod form, is fed into the high temperature zone where it is volatalised and recondenses into a much finer powder form.

2. Reactants, in any physical state, are fed into the high temperature zone, where the products are formed, one of which is a finely divided powder. The plasma gas may or may not take part in the reaction, but this distinction is difficult to draw as the hot ambient gas may well take part in some intermediate step in the reaction, without appearing amongst the chemical products.

3. The reactant feed stock is present in the reaction chamber as a solid piece, and is heated by a plasma torch operating either in the transferred or the non-transferred mode.

The first two types of process can be operated continuously, whereas the third type is strictly a batch process. The processes within each class can be further sub-divided into production of elements, oxides, nitrides and carbides.

2.3.1. Type One Processing coarse powders

ENGELKE, HALDEN and FARLEY attempted to synthesise 'new high temperature materials' by feeding powders of mixed transition metal carbides, borides and nitrides into a d.c. plasma torch running on argon or nitrogen. The powder was fed at a rate of .05 to .7 grams per minute, into the cathode end of the nozzle so that it had to pass through the constriction. The products passed via the nozzle to a water cooled controlled atmosphere chamber, where they were collected on the outer edge of a rotating, water cooled copper disc. The residence time for particles of a diameter of 10 microns or less in the plasma, was calculated from a viscous drag equation to be a linear function of the particle diameter. Typical residence times varied from 1 millisecond to 10^{-2} millisecond. An equation based on simple conduction heating was developed to describe the heat transfer to the particles in the plasma. The equation predicted that only the very finest particles will be completely volatilised.

Examination of the material, which collected as a loosely adherent powder, showed the particle size to be considerably less than that of the starting material, which suggested that the volatilisation was at least partially effected. The phase changes in the collected material could be observed by X-ray analysis, but these phases could not be separated from the very large amount of unreacted material.

WALDIE has processed several feed materials in a radio frequency plasma including alumina, zirconia, silica, tungsten, iron, iron oxide, copper, boron carbide and barium oxide. The plasma was generated at a frequency of about 36 megacycles, at a power of 2.2 to 2.4 kilowatts, in argon. The powders were fed to the plasma through a central 2 millimetre bore quartz tube. Crushed silica, size 53 to 72 microns, was fed in at a rate of 15 grams per hour and about 15% of this was converted to ultrafine particles from about .003 to .1 microns diameter. Examination in an electron microscope showed these particles to be chain-like agglomerates. A sub-micron barium oxide powder was similarly treated and about 50% was converted to particles smaller than .1 microns. Unusual pattern structures were observed in a scanning electron microscope, on the surface of some of the particles of alumina and silica, which were spherodised but not vaporised during the process.

WHYMAN has developed a rotating wall furnace, in which a free burning arc contained in a tube is expanded and stabilised by rotating the wall. Many materials including aluminium, sulphur, silicon, alumina, silica and zirconia have been vapourised in argon arcs in the apparatus. The natural pumping mechanism of the arc is used to draw the reactant powders through the centre of the cathode and the products collect on the cool surface inside the furnace. For example γ - alumina was formed as small discrete single crystals, size 10 to 200 millimicrons.

2.3.2. Type Two Reactants are stored outside the reactor

ELEMENTS

RAINS AND KADLEC reduced alumina to aluminium by allowing it to react with either hydrogen, carbon dioxide or methane in an R/F argon plasma. The plasma was contained in a water cooled quartz reactor and produced by a 24 KVA, 3 MHZ generator. The plasma gas was introduced tangentially to provide vortex stability and the alumina was fed along this cylindrical axis into the hottest region of the plasma. To prevent the aluminium from re-oxidising, the products were rapidly quenched on the water cooled surface, positioned about $\frac{3}{4}$" below the coil. The yield of aluminium ranged from 3 to 30% and was generally found to increase with decreasing alumina flow rate and particle size and with increasing power input. The introduction of carbon monoxide or methane with the plasma gas was found to enhance the aluminium conversion rate but hydrogen was found to be ineffective. The highest conversion, 30%, was obtained by feeding 26 micron alumina into an argon plasma at 5 kilowatts at a rate of about 0.07 grams per minute. To achieve this result with 37 micron alumina, the flowrate had to be dropped to about .03 grams per minute. 250 micron alumina flowing at .2 grams per minute produced no aluminium at all. The aluminium produced in this way was found to be finally divided and highly pyrophoric. Similar work was described by CAPITELLI and others and BORGIANNI et al as the experimental part of a study of heat transfer to small particles in argon and argon/nitrogen plasmas. The plasma was generated by a 15 kilowatt nominal output R/F generator, operating in the 4 to 20 megacycles range. The alumina was injected through the triple walled, water cooled axial inlet, after fluidization in 5L/min of argon, and collected on a water cooled copper probe. Alumina flows above 72 gms/hour extinguished the plasma. Plasma gas flows were kept constant at 53 litres per minute and were either pure argon or pure argon and 4 to 8% nitrogen. The power dissipation was as follows:

16% radiated
30% conducted to the walls
54% carried away by the hot gas stream

This distribution in a pure argon plasma, was not significantly altered by addition of up to 8% nitrogen. Aluminium yields of up to 12% were obtained from 60 micron alumina fed into a 5 kilwatt argon plasma.

BIGGESTAFF et al produced elemental boron by reacting boron trichloride or boron trifloride with hydrogen in the nozzle of a d.c. plasma torch. The torch was connected directly to an 18" length of $\frac{1}{2}$" copper tubing which was water cooled. Boron was deposited as a cake on the walls of the tube and when ground was found to be between 100 and 200 mesh. The large particles size is presumably a result of elemental boron coming into contact with the cold walls of the copper tube before the processes of nucleation and growth had taken place. This is an extreme example of the effects of rapid quenching of a condensing vapour. Plasma gas was argon or argon/hydrogen mixtures at flows of 9 to 33 L/min and power settings from 4 to 23 kilowatts, with torch efficiencies in the range of 15 to 40%. The boron yield was found to be highest when the chloride was used, rather than the fluoride and increased linearly with plasma temperature up to the highest measured value of 60%. Considerable variations of reactant feed in geometry were experimented with, but a single radial port about 2/3 of the way along the nozzle was decided upon. With no hydrogen in the system, elemental boron could be produced by simple thermal decomposition of either the fluoride or the chloride, but in both cases yields were enhanced by the use of hydrogen. Whether the hydrogen was added through the cathode or through the halide injection port the yield of boron was the same. It was concluded that further development on the system could lead to a commercially feasible process with an efficiency of up to 95% (including recycling techniques) and a product of greater than 98% purity.

The same reaction was used by HAMBLYN and others to produce elemental boron by a 2 megacycle, 1 to 30 kilowatt radio frequency plasma contained in a water cooled silica tube. The boron trichloride was injected with the argon plasma gas and the hydrogen was injected into the tail of the plasma. The mixture of products and excess reactants was quenched by expansion into a vertical water cooled glass tube where the boron powder either collected on the walls or was carried through with the gas stream and filtered by a polypropylene bag. The filter was effective for particles down to 1 micron in diameter. Boron yield fell rapidly from 70% at a feed rate of about 5 grams per minute to 35% at a feed rate of about 20 grams per minute and then stayed roughly constant up to a feed rate of 60 grams per minute. The product was easily broken up to a brown powder with a mean particle size of ½ micron (measured by a Fisher sub-sieve sizer) and a specific surface area of 12.4 sq metres per gram. Electron microscope examination identified irregular platelets of boron typically 2000 anstroms in diameter and 10 to 50 angstroms thick. X-ray analysis of the powder showed a strong crystalline structure with low boron chloride feed rates, which became less crystalline as the chloride feed rate was increased. The purity of the product was found to be about 99%. Any ultrafine particles which did not agglomerate would presumably pass through the filter. If this were so, the observation that low flow rates gave higher yields would agree with the theory (section 2.2.3), which predicts that the mean particle size increases at lower concentrations of the condensing species.

SELOVER produced nickel fume by injecting nickel carbonyl into an argon plasma produced by a 48 kilowatt D.C. plasma torch. The plasma jet was run into a brass chamber maintained at roughly 0.2 atmospheres pressure during the injection period. The chamber was cylindrical, 20" high by 8" internal diameter, with water cooled walls. The nickel carbonyl was injected with the argon plasma gas. The nickel fume condensed out on the chamber wall and samples were taken from different areas. The torch was usually operated at from 10 to 15 kilowatts. The product was a fine black powder, the colour due to the presence of nickel oxide. The specific surface area of the powder varied depending upon its position on the chamber walls. The surface area was also found to be inversely proportional to the concentration of nickel carbonyl in the arc gas, varying from 170 to 50 sq metres per gram. The effect of rapid quenching was examined by suspending a nickel pipe-cap, cooled down to 65°C by a mixture of dry ice and isopropyl alcohol, 10 cm below the torch anode. The surface area of the powder collected in this way was found to be about one half of that formed on the walls of the chamber. Analysis showed the carbon and oxygen contents to be an order of magnitude higher than in powders collected on the chamber walls. The nickel fume with the surface area of 150 sq metres per gram was examined under the electron-microscope and found to consist of particles of a size range from 3 to 30 mμ.

The Russian workers ZHDANOVSKII and LOKOMSKII examined the reduction of niobium pentoxide and molybdenum oxide and the production of boron and titanium nitrides. Their very versatile apparatus consisted of a d.c. plasma jet followed by a reactor which could be of either copper or graphite and which was constricted before passing into the quenching chamber. Reactants could be fed either through the hollow cathode in the plasma jet or through four holes drilled in the nozzle. A water cooled copper quenching head could be varied in its distance from the reaction chamber, but the bulk of the products was carried away by the exhaust gases to two cyclones which were provided with glass cloth filters which could be periodically shaken. Alternatively the reaction could be collected in the quenching chamber from a removable water cooled plate. Oxide reduction was studied with methane supplied in the stoichiometric quantity, or with carbon black. Using methane in an argon plasma jet, the degree of reduction of niobium pentoxide was found to be 46% when the material was fed in via the cathode but only 36% when it was fed in via the jet nozzle. Substituting carbon black for the methane gave very similar results. The best results were obtained by feeding the oxide into the plasma jet nozzle with an argon hydrogen mixture. Increasing the hydrogen flow rate up to 2.3 times the stoichiometrically required rate produced a degree of reduction of molybdenum dioxide of 81%. This result was obtained with an arc current of 100 amps, voltage of 30 volts, that is 3.4 kilowatts, with 7.5 litres per minute of argon. The 5-30μ particle size oxide was fed in at the rate of 3.2 grams per minute with 2.6 litres per minute of reducing gas. The powders produced were in the size range 2 to 10 microns. The relatively large product size is presumably because the reactants were not volatilised and recondensed, but suffered reduction by hot hydrogen diffusing in from the surface. The degree of reduction could be substantially improved by ensuring a sufficiently high rate of quenching to prevent reverse reactions. Nitrides of boron and titanium were formed by feeding the elemental powders into a nitrogen plasma jet. The yield of boron nitride was found to depend very heavily on the mean mass temperature of the nitrogen plasma. With a plasma temperature of 4,800 to 5,200 K the product was found to contain a large quantity of the starting material, whereas with a plasma temperature of 5,600 to 6,100 K the product yield was as high as 70%. It is implied that the same applies to the production of titanium nitride. The X-ray diffraction pictures of the synthesised boron nitride differ from that of a standard specimen, which was attributed to the formation of a nitride similar to pyrolitic boron nitride.

Oxides

BARRY BAYLISS and LAY prepared mixed chromium and titanium oxides and mixed chromium and aluminium oxides, by passing halides into a radio frequency oxygen plasma. The plasma was produced by a radio frequency of 5.8 megacycles and a power of 17 kilowatts. A central feed tube was used to introduce the reactors into an argon plasma, which was contained by an intermediate tube and surrounded by a fast annular flow of oxygen, which both separated the argon plasma from the outer quartz tube and also supplied oxygen for the oxygen for the oxidation of the halides. The products were collected by passing the effluent gases with their suspended powders, firstly through a pyrex tube and then into an aluminium ducting, followed by an electrostatic precipitating unit. With an argon flow rate of 11 litres per minute and an oxygen flow rate of 42 litres per minute, the rate of production of solid was 0.28 milligrams per second. Electron microscopy showed that the particles were in the size range 0.01 to 0.15 microns. A pure chromia specimen was produced which contained some thin hexagonal platelets, probably of alpha chromia, with diameters up to 0.4 microns. Detailed examination using X-ray diffraction techniques showed that the solid solution of chromium in titania and titania in chromia was extensive. It was concluded that the titania condensed as a liquid in droplet form in a temperature range of 2,400 to 2,200 K, forming the solid phase anatase below 1096 K. In contrast, the chromia was concluded to condense as solid particles, probably in the temperature range 2,100 to 1900 K. These conclusions were reached by consideration of melting points and partial pressures, and are supported by the electron micrographs, which show that the chromium particles have angular shapes whereas the titania particles were spherical. It is suggested that as a general principle only those particles which form initially as liquids will be spherical in shape, but if the super saturation and rate of condensation are very high, this rule may not always hold. The major difference in the results obtained for alumina/chromia preparations was that the degree of solid solution achieved was very much lower. This was attributed to the fact that the alumina could begin condensation to liquid droplets at temperatures as high as 3,000 K, whereas the chromia condensed directly to a solid phase at a relatively low temperature of about 2,100K. Also during the temperature range at which the chromia is condensing, the alumina is rather viscous, so that incorporation of the chromia into the alumina is unlikely.

The oxidation of silicon tetrachloride to silica and chlorine, was investigated by AUDSLEY and BAYLISS using a radio frequency torch. Four different torch designs with varying injection methods were examined. The hot gases with their load of fine powder were exhausted via a silica tube 10 cm in diameter by 70 cm long, and then into a fume extraction system. The silica tube was fitted with sampling ports through which gas samples were drawn by aspiration. The gas sample was filtered, then drawn through N/2 sodium hydroxide solution to adsorb unreacted silicon tetrachloride. The yield of silica was obtained by comparing weights of silicon tetrachloride and silica collected in this way. When the silicon tetrachloride was injected into the tail flame region of the plasma by means of radially position ports, a yield of over 99% was obtained from a reagent feed rate up to 67 grams per minute, which was the maximum rate which could be obtained from the reagent delivery apparatus. This result was obtained using a power of 22½ killowats, and oxygen flow rate of 56 litres per minute. If the silicon tetrachloride was injected so that it was allowed to come into contact with the plasma, the plasma was extinguished at very low reagent flow rates. The form of the silica produced by this method is not discussed.

DUNDAS and THORPE (1970) produced TiO_2 paint pigment by oxidising $TiCl_4$ in a 1Mw induction heater running at 4MHZ on oxygen. The $TiCl_4$ was injected after the very hot plasma gas had been allowed to mix with a higher flow of sheath oxygen, giving the required mean enthalpy. No information is given on collection method or particle characteristics, except that contamination was less than 5 p.p.m. Some costs are given in terms of energy consumption in kWH/lb of product, which show the beneficial affect of high sheath gas flow rates in this respect.

The commercial importance of titania as a pigment is demonstrated by the number of Patents concerned with its manufacture. ZIRNGIBL, GUTSCHE and WEIDMANN injected $TiCl_4$ and air into the exit end of the nozzle of a D.C. torch running on 20L/min N_2 with an efficiency (THEFF) of 55%. Titania (150mμ) was produced in a cylindrical ceramic reactor, and collected via cyclones. $TiCl_4$ utilisation was 96%, using 50% more air than stoichiometry demanded. The same authors used an R/F torch at 10 MHZ to react $TiCl_4$ and steam, the reaction being started by an auxilliary flow of a combustible mixture, e.g. CO and air.

Patents describing processes essentially identical to the above for the production of TiO_2 by oxidising $TiCl_4$ have been filed by FREEMAN, BRITISH TITAN PRODUCTS, and DUPONT DE NEMOURS.

CHARLES, DAVIES, JERVIS and THURSFIELD subjected various minerals to thermal dissociation in a radio frequency plasma torch. The reactions studied were:

1) $MnSiO_3 \xrightarrow[\text{heating}]{} Mn + Si + 3O \xrightarrow[\text{cooling}]{} MnO + SiO_2$

2) $ZrSiO_4 \xrightarrow[\text{heating}]{} Zr + Si + 4O \xrightarrow[\text{cooling}]{} ZrO_2 + SiO_2$

3) $FeTiO_3 \xrightarrow[\text{heating}]{} Fe + Ti + 3O \xrightarrow[\text{cooling}]{} FeO + TiO_2$

4) $FeS + 7O_2 \longrightarrow 2Fe_2O_3 + 4SO_2$

5) $MoS_2 + 2O_2 \longrightarrow Mo + 2SO_2$

Two vortex stabilised torch designs were used, each with central powder feed tubes. The smaller, 3.7 cm diameter torch, could produce a plasma at anode circuit power levels from 2 to 22 kilowatts, for flow rates of argon from 20 to 60 litres per minute. This torch operating at a frequency of 5 MHZ was found to suffer from heating of the confining tube from the plasma. A larger torch of 5 cm diameter was constructed to obtain higher efficiencies. This torch produced stable plasmas with power levels from 3 to 29 kilowatts at a frequency of 5.4 megahertz. A wider range of operating conditions was obtainable with the larger torch. As might be expected, the overall processing efficiency was dependant upon a high rate of heat transfer from the plasma to the particles, in order that the required particle temperature might be reached during passage through the plasma. The critical variable was found to be the residence time of the particles in the plasma environment, and fine powders were found to be more easily processed than coarse powders. Products were deposited on the inner wall of the confining tube in the form of agglomerates and particles, starting from near the centre of the work coil. Using a feed rate of 40 gms per hour of 50 micron rhodenite particles and a plasma power of 15 kilowats, 20 grams per hour of manganese oxide were produced. Particles produced by a similar treatment of 50 micron zircon, showed a leaf-like dendritic pattern of particles ranging up to 10 microns diameter. This was taken as clear evidence that the zircon powders had been melted during their passage through the plasma. Molybdenite was converted to molybdenum in the 37 millimetre diameter torch with a conversion efficiency of 60 to 70%. The oxidation reaction of iron sulphide, being exothermic, absorbs very little energy from the plasma, so comparatively high feed rates can be tolerated without extinction. Feed rates as high as 400 grams per hour were used and for a feed rate of 250 grams per hour a 10% oxygen in argon plasma gave a conversion rate of iron sulphide to iron oxide of 72%, and a 95% oxygen in argon plasma gave a conversion efficiency of 86.5%.

Nitrides

STOKES & KNIPE used a D.C. plasma jet to prepare titanium and magnesium nitrides. The torch had a $\frac{1}{8}$" thoriated tungsten cathode and a copper anode with a pure tungsten insert in the nozzle and throat. The torch was run on nitrogen and the nitrides were prepared by reaction between the metallic powders and the nitrogen of the plasma jet. The powders were injected by fluidising in nitrogen and injecting just underneath the nozzle. When preparing magnesium nitride the power to the plasma torch was between 12 and 15 kilowatts and the nitrogen flow 2.5 litres per minute. The problems of erosion of the copper anodes and even the tungsten inserted anodes were almost certainly caused by the low plasma gas flow. A 40% yield of nitride was obtained. The free energy of formation of this compound is positive at temperatures above about 1700 K, so it was collected on a quenching cold finger device, set immediately below the injection point. The form of the powders prepared in this was is not described. A patent granted to CIBA Ltd (1965), described the preparation of finely divided non-pyrophoric nitrides of zirconium, hafnium, niobium and tantalum. These were prepared from the metal halides in the highest stage of halogenation by injecting the halides in a stream of nitrogen into the exhaust of a hydrogen plasma torch. The torch was run at about 10 kW on 25 litres per minute of hydrogen. Alternatively the halides were injected in a stream of argon, at a few centimetres from the torch exit, and a stream of nitrogen was injected into the plasma gas immediately outside the torch exit. The reactor and the collection mechanism is not described in detail, but is shown on a diagram to be a large cylindrical body, in which up to 500 grams of nitride are collected in a run. A production run of hafnium nitride is described under the following conditions:

Torch power 11.5 kW in a hydrogen throughput of 25 litres per minute, giving a mean plasma gas temperature of 3,300°C at the anode exit. 0.6 grams per minute of nitrogen were injected at the anode exit, and at 1.5 cm from the anode, 5 grams of hafnium tetrachloride in argon. The reaction mixture formed a brilliant jet of 10 to 15 cm length. 2.8 grams per minute of hafnium nitride were formed which corresponds to a yield of 93%. The specific surface area measured by the B.E.T. method, was 20 to 30 sq metres per gram, which assuming equally large spherical particles means a particle size of .02 microns. The electron microscope showed the particles sizes to be between .01 to .05 microns, which shows good agreement.

Carbides

NEUENSCHWANDER produced tantalum carbide, niobium carbide, titanium, carbide, tantalum nitride and tungsten, by reacting the chlorides in a jet of hydrogen, produced by a d.c. plasma torch. The plasma gas was injected tangentially to perform vortex stabilisation, and a magnetic field was superimposed causing the arc to rotate. The chorides were injected at the anode exit and either methane or nitrogen was injected about half way down the anode nozzle. The reaction chamber was a large cooled cylindrical vessel, from which the rest of the products were passed to a settling tank. The torch was run with a current of 200 amps and a voltage of 117 volts on 74 litres per minute of hydrogen, which with a thermal efficiency of 45%, corresponds to 10.5 kilowatts into the gas. The mean temperature of the gas stream at exit to the reaction chamber was 3,000°C. A bright luminous jet 15 to 20 cm long was observed. Specific surface areas of the powders formed ranged from 8.7 sq metres per gram for titanium carbide, to 6.1 sq metres per gram for tantalum carbide determined by a simplified B.E.T. method. Grain size and grain size distribution was measured with a Zeiss semi-automatic grain size analyser and found to have a logarithmic-normal distribution. The specific surface area was determined from these measurements and compared with that obtained by the B.E.T. methods. In this way a 'form factor' was calculated, from the direct ratio between the two specific surface areas. The published micrographs show the particle sizes to vary from .01 to .05 microns. C.I.B.A. (Aug 1964) made carbides of boron, silicon, and the metals Ti, Zr, HF, V, Nb, Ta, Mo, W, Th and Uranium, by reacting the relevant halide with a hydrocarbon gas (usually methane) in the jet from a D.C. plasma torch. The plasma torch was run at 115 amps and 100 volts on 25L/min of hydrogen, and 7 gm/min of WCl_6 and 0.3 gm/min of CH_4 were injected via a quartz tube 1 to 2 cm from the nozzle. The product was α - W_2C with 93% yield, size .02μ, and collected on the walls of the reaction chamber. There is no mention of a collector as such - the only outlet from the reactor is the waste discharge tube. It is difficult to understand how such high yields were obtained, or even measured, if the products were free to be carried away by the waste gases.

2.3.3. Type Three: Reactants are present inside the reactor

The high intensity arc process was patented by BECK in Germany in 1910. In 1921 KOHLSCHÜTTER and TÜSCHER prepared oxides of seventeen metals including chromia, alumina, magnesia and silica by making the metal one electrode of an arc, and oxidising its vapour by means of a current of air. Mixed oxides of fifteen different pairs of metals were similarly prepared. The oxides were separated from the vapours or fumes by precipitation in a corona discharge. On the size of the particles, the abstract states that it 'corresponds with the upper limit of the colloidal state'. A translation of this long paper is not available.

SHEER and KORMAN (see also section 1.2.1.) vapourised electrodes made of 80% silica and 20% carbon in air, collecting a fine fume of silica in a commercial dust filter. The particle size was 30 to 40mμ. A chlorine atmosphere in the arc was used to convert metal oxides to their chlorides, and carbothermic reactions were used to reduce metal oxides. Processing costs of the order of a few pence per kg were claimed for this process, but it is difficult to reconcile this with the high price (e.g. £35/kg for SiO_2) charged by Vitro Corp. for materials produced by this method. A companion paper on the electrode requirements summarises the problem as the 'efficient exploitation of minimal proportions of carbon in the electrode' as carbon 'imposes limitations upon the rate of production of all the electrode components in the vapour of the discharge because of the relatively high energy of sublimation of carbon'. There is evidently a conflict of interest between the amount of carbon required to maintain the current density and the energy expended in vapourising it. The method is limited to reactions in which carbon can be tolerated - and is therefore unlikely to be useful in producing nitrides.

GIBSON and WEIDMAN used the same method to produce aluminium from alumina, the metal condensing as spherical liquid droplets with diameters from 20 to 100mµ. The product was pyrophoric. An interesting application was the production of uranium carbide spheres for use as fuel elements in a nuclear reactor. The sphere size ranged from 2,500µ to 44µ at 99.95% purity. A uranium-Zirconium carbide powder was similarly produced. Tantalum carbide was made with an average particle size of 4mµ (700 atoms), which was very easy to sinter.

A considerable amount of Japanese work has centered on the production of nitrides using a transferred plasma torch. MATSUMOTO and HAYAKAWA synthesised molybdenum and tungsten nitrides by heating a slice taken from a high purity rod of the metal with a transferred plasma torch. The metal slice was placed on a shallow, water cooled copper crucible which was made the anode of the arc, and was converted to nitride by the nitrogen plasma produced by the torch. Black powders were collected from the cool surfaces inside the reaction chamber, and the efficiency of nitrogen fixation was no higher than 0.13%, depending on the conditions. A number of curves showing the relationship between various pairs of variables were given, including one showing the 'relationship between the energy used to the formation of Mo_2N and N_2 flow rate'. Plotted on the same curve is the free energy change for Mo_2N formation at 3000°C, which is positive, and considerably less than the energy utilised. The conclusion is that 'it is considered that energies sufficient for the nitride formation were supplied'. It is not surprising that yields of nitrides were so low - the nitrides are not stable at the very high temperatures in the vapour above the anode arc spot, making the method highly unsuitable for this application. A companion paper by MATSUMOTO describes the production of TiN by an identical method, with similar results - in 5 mins a 10 gm button of titanium yielded 0.34 gms of TiN. A simple costing exercise using these figures, a nitrogen flow rate of 3L/min and torch power of 7kw with fixed costs of £1 hour gives a processing cost, i.e. excluding the titanium charge, of £70 kg. MATSUMOTO, SHIRATO and MIYAZAKI prepared aluminium nitride using similar apparatus, but a graphite anode crucible was used, and reactant dies made from alumina and graphite by mixing powders, binding with pitch, and baking at 1100°C for four hours. The optimum ratio was found to be three times as much carbon as alumina. Yield efficiences of AlN up to 30% were reported.

HAYASHI, OKADA and KOIDE used the same method with a copper anode crucible, and made nitrides of aluminium, silicon, titanium, zirconium and hafnium from metal plates. The percentage conversions and times to react are given, but no weights of reactant or product. The electron micrographs show particle sizes from 0.1μ for TiN and Si_3N_4 to a range from 0.5μ to 5.0μ for ZrN.

WADA fired a transferred plasma torch at an angle of about 45° to the surface of a copper crucible anode, on which he placed a button of Fe-Co-Ni alloy. He found that to produce very fine particles, it was necessary to reduce the pressure in the reaction chamber e.g. particle size was 10mμ at 250 torr and 100 mμ at 760 torr. This agrees with the observations of KIMOTO et al (section 1.2.2.). It was found that argon plasma jets blow the molten metal off the anode, but helium or helium plus hydrogen jets did not. The Fe-Co-Ni alloy powders were collected as long chains. A gram of particles were produced in 5 mins.

A novel device invented by GROSSE et al, called the Liquid Wall Furnace, was used by SAYCE. A D.C. plasma jet was mounted horizontally and fired along the axis of a rotating ceramic tube. The ceramic melted and was retained by centrifugal force as a stable layer on the inner wall of the ceramic tube, and distilled out as a vapour. Cold gas quenching downstream controlled the particle size from 5mμ to 20mμ. Silicon carbide was made from a tube of mixed silica and carbon;

$SiO_2 + C \longrightarrow SiO + CO$

and quenching with methane gives

$SiO + CH_4 \longrightarrow SiC +$

This work is being patented.

SHEWARD used the liquid wall furnace to produce fine oxides of aluminium, Zirconium, magnesium and cerium.

2.3.4. Summary

Ultrafine powders have been produced by all three of the types of process described above. There is a disadvantage inherent in type one. When the feedstock or reactants are injected in coarse powder form, there is often incomplete conversion to an ultrafine form. This is due to finite heat transfer from the plasma gas to the powder, associated with residence times of the order of milli-sec. The rotating wall furnace has gone some way to improving the situation by increasing residence times.

Two commercially interesting processes have resulted from the application of electric arc heating to materials stored inside a reaction chamber (type three). The high intensity arc process has produced a range of oxides which have been offered for sale. They have since been withdrawn, presumably because the high prices (around £35 kg) have discouraged the growth of applications. (The range of uses of fumed alumina and silica described in the Introduction show that if the powder is cheap enough, say less than 50p kg, applications will be found). The limiting cost is presumably that of producing the electrodes. It is difficult to see any clear advantage of the Japanese work with transferred torches over the high intensity arc process, but the work on nitride production is marred by a lack of understanding of the thermodynamics. Perhaps later work will rectify this and allow a comparison to be made. The second device of commercial interest is the liquid wall furnace. The reactants have to be prepared into cylindrical shape, but as the current does not flow through it, no carbon is required, making for a simpler and presumably cheaper fabrication. This work is being backed by an unspecified company.

The most popular method has been to introduce reactants in either powder or vapour form (type two), the vapour usually being a volatile halide, because there are halides of many elements which are available at room temperatures or just above. Chlorides are often available in bulk at low prices, because elements are often extracted from their ores by hydrochloric acid. A further advantage of injecting chlorides is that if hydrogen is present in the reactor, HCl gas will be formed. HCl is a highly stable molecule, and so may reduce the rate of back reactions.

There is no clear preference for either D.C. or R/F torches, the volume of work being fairly equally divided. No authors have made a systematic comparison for a specific reaction, and in theory, considering the torch as a source of hot gas, the only differences are of cost and electrical and thermal efficiencies. It is possible to extinguish an R/F torch by allowing reactants (particularly chlorine) to mix with the core gases of the electric arc. In practice this is no disadvantage, as there is nothing to be gained by allowing such mixing. The degree of turbulence, and the flow patterns, in the exhaust streams of the two types of torch must be different, as the D.C. torch emits a fine jet and the R/F torch does not. The mixing and heat transfer to reactants injected into the tail flame may be better for one torch than another, but there is no experimental evidence.

Yields cover the complete range from 3 to 99%, but are not very meaningful unless considered in relation to the other running costs, and fixed costs. It may be easy to produce high conversion of reactants at very low concentrations. The particle sizes vary from less than 10mμ to over 1μ. At the upper end of the sub-micron scale is boron. In one case this is due to very severe quenching, and in the other to agglomeration. Sizes over 1μ are produced when reactants are introduced in solid form, as in the case of processing mineral ores. The form of the various particles which have been produced may be spherical, platelet, dendritic, chain like agglomerate, or something in between. This is clearly a most interesting feature of the process, and one on which very little work has been done.

The production of nitrides of silicon and titanium appears feasible using a D.C. plasma torch. Silicon nitride has not, according to the literature, been so prepared, but titanium nitride has. Virtually no work has been done on the factors which affect the cost of such processes.

2.4. PREVIOUS WORK ON PRODUCTION AND PROPERTIES OF Si_3N_4 and TiN

2.4.1. The production and properties of silicon nitride

The chemistry of silicon and nitrogen has been studied extensively in the last fifteen years, and has been reviewed by WANNAGAT in 1964. The only well established solid phase in the silicon-nitride system is Si_3N_4, according to KAISER and THURMOND, who made it by reacting nitrogen with molten Si in a floating zone apparatus. A silicon rod was heated by an R/F coil, and a molten zone produced which was held in position by surface tension between the two solid parts of the rod. The rod was enclosed in a fused silica jacket, so that a controlled atmosphere could be introduced. In an atmosphere of nitrogen, very little reaction was observed except at pressures of a few torr, when a glow discharge was induced by the R.F. field, and needles of Si_3N_4 covered the surface of the melt. A similar effect occurred in a nitrogen-helium atmosphere, but a nitrogen-hydrogen ambience showed no reaction, and no glow discharge. This effect was ascribed to the presence of active nitrogen. Whereas helium, with its well known metastable states, would be expected to enhance the production of active nitrogen, hydrogen would have the reverse effect. An atmosphere of ammonia at atmospheric pressure reacted rapidly and violently with the molten silicon, producing large quantities of the nitrides. CORDES produced Si_3N_4 films on silicon wafers held at 200^oC to 300^oC using a sputtering technique at low pressures of nitrogen. He concluded that the films contained excess silicon, which could not be nitrided even with subsequent heating in nitrogen - an effect which represented a fundamental limitation of the technique.

The usual method of preparing a solid piece of silicon nitride is to heat compressed silicon powder in dry, oxygen free nitrogen at 1300-1400°C. FRIESER tried to produce silicon nitride films by the direct nitridation of silicon wafers at up to 1400°C, but found that a surface layer of nitride effectively stopped further diffusion of nitrogen, and concluded that direct nitridation was practicable only of silicon powder, and that films were best prepared by a vapour deposition method. This pyrolytic silicon nitride, as it is known, was first prepared by STERLING and SWANN inside a fused-quartz reaction tube heated by a 500W, IMHz R/F generator. A mixture of silane and ammonia deposited Si_3N_4 onto a heated potassium bromide substrate, which if held at 700-900°C acquired a silicon nitride film with similar properties to the conventional bulk material.

COLEMAN and THOMAS examined amorphous Si_3N_4 films made in the same way, and concluded that the optimum reactant ratio was 3 moles ammonia to 1 mole SiH_4 which produced particles of 0.8 to 1.0mμ, determined by electron diffraction. A similar study was made by DOO, KERR and NICHOLS, who performed the reaction in a hydrogen atmosphere.

A German patent by JENKNER and SCHMIDT describes the reactions:

$$3\ SiH_4 + 4NH_3 \longrightarrow Si_3N_4 + 12H_2$$

(which is performed with a x 2 to x 10 excess of NH_3) and

$$3CH_3SiH_3 + 4NH_3 \longrightarrow Si_3N_4 + 9H_2 + 3CH_4$$

The reactants are passed through a heated quartz tube at 800 to 900°C in the case of the silane reaction, when very fine particles of silicon nitride of a light to dark brown colour are produced, the colouration being caused by elemental silicon. The colour is lighter if a lower temperature (600°C) is used. The particle size is not given.

GRIECO, WORTHING and SCHWARTZ deposited silicon nitride films by reacting $SiCl_4$ and NH_3 in a quartz reaction chamber heated by an R/F field, the nitride being deposited on a silicon substrate at 550°C to 1250°C. They successfully produced films up to 2μ thick.

In 1903 BLIX and WIRBELAUER, experimenting with the reaction between silicon tetrachloride and ammonia, suggested that the products were ammonium chloride and silicon di-imide because the ammonium chloride could be washed out with liquid ammonia. The reaction has been extensively studied by BILLY, who firmly established the relation,

$$SiCl_4 + 6NH_3 \longrightarrow Si(NH)_2 + NH_4Cl$$

and it is on this work that the method of preparation of Si_3N_4 described in this thesis is based. The silicon di-imide was formed as a 'very fine white powder, amorphous to X-rays, without vapour tension', stable under vacuum up to more than 600°C and extremely sensitive to the effect of moisture - 20 to 25% of the imide is hydrolysed after a few minutes in air with evolution of ammonia and formation of silica'. The di-imide was prepared in an evacuated chamber by reacting silicon tetrachloride and ammonia liquids. At room temperature the reaction, which 'seemed slow', occurred between the vapours, as the $SiCl_4$ was so volatile. At temperatures below the boiling point of NH_3 the reaction was very rapid, and exothermic. In all the experiments, the di-imide was found to be the only stable end product. Later work by BILLY (1960) on the detailed structure of the di-imide concluded that it was polycyclic, 'probably a higher polymer with a disordered network of $Si(NH)_4$ tetrahedra'. The existence of two intermediate was proved, and the reaction between the di-imide and hydrogen chloride considered. The overall scheme is;

$$\overset{\xrightarrow{\qquad\qquad (HCl) \qquad\qquad}}{(SiN_2H_2)_x \text{ ——— } Si_2N_3H_3Cl_2} \text{ ——— } \underset{\xleftarrow[(NH_3)]{\qquad\qquad\qquad\qquad}}{(SiCl_3)_2NH \text{ ——— } SiCl_4}$$

The reaction between HCl and $Si(NH)_2$ was shown by BILLY (1958) to be,

$$Si(NH)_2 + 6HCl \longrightarrow SiCl_4 + 2NH_4Cl$$

which at room temperature began violently liberating heat, and then proceeded very slowly for about three days.

The thermal decomposition of the di-imide was studied in a nitrogen atmosphere and found to proceed according to,

$$Si(NH)_2 \longrightarrow Si_3N_4 + NH_3$$

the equilibrium ratio $NH_3/Si(NH)_2$ increasing linearly with temperature beginning at 75°C and reaching a plateau at 550°C. The silicon nitride formed was amorphous to X-rays, but crystallised very slowly when heated in nitrogen at 1450°C, after which it gave a normal X-ray pattern. During the process of thermal decomposition a series of ill-defined amorphous states occured, probably polymeric in chains or cycles.

Silicon nitride in its massive state is a very hard substance of density 3.18 gms/cm^3 and a sublimation point of 2040°C. It has good oxidation resistance up to 1200°C, but it can be used in air up to 1650°C. A phase change from the α form to the β form takes place at about 1500°C, and was studied by BRADLEY, MUNRO and WHITFIELD over a wide range of temperatures and pressures. GRIEVESON, JACK and WILD (Report No. 1) have shown that the α form is in fact silicon oxy-nitride, and resolved the conflicting data on $\alpha - \beta$ transition temperatures by showing that the two phases were not merely low-temperature and high-temperature structure forms of the same compound, but high (α) and low (β) oxygen potential modifications. The oxidation kinetics of powdered Si_3N_4 of 100µ size were studied by HORTON in dry oxygen and dry air at 1 atm. pressure. They concluded that a protective oxide film formed which prevented further oxidation. A similar result was obtained by KRASOTKINA, Si_3N_4 has very good thermal shock resistance, because of its low thermal expansion (2.5×10^{-6}/°C) good dimensional stability, electrical insulation and resistance to chemical attack, notably from molten aluminium. Common practice when forming components is to give an initial partial nitriding to the pressed silicon part, machine it to size and then complete the nitriding process. A dimensional accuracy of 0.1% can be achieved, compared to 2% with alumina. Applications in the gas turbine field are described by PETERS.

Silicon nitride can, under certain circumstances, react with iron. GLEMSER, BELTZ and NAUMANN showed that the reaction

$$Si_3N_4 + Fe \longrightarrow Fe + 3Si + 2N_2$$

took place above 700°C, the silicon apparently going into solution in the iron. The Si_3N_4 was mixed with iron powder, and the reaction measured by the amount of nitrogen given off in a sealed system connected to a mercury manometer. The authors give no idea of the time scale involved.

The formation of Si_3N_4 by nitriding silicon iron alloys has been studied by PEARCE, who showed that precipitation of the nitride took place below 770°C, and that above 770°C silicon nitride was unstable. GRIEVESON, JACK and WILD (Report No 4) investigated the nitriding of 14% Si in Fe alloys at 1290°C for 16 hours with different nitrogen potentials. A gas composition of at least 97% N_2 (3% Argon) was required to precipitate β-Si_3N_4.

Providing the service temperature is below 750°C, the Si_3N_4 should remain stable, and it appears that the rate of solution of Si_3N_4 into iron is slow compared to the times needed to sinter or hot forge compacts.

2.4.2. The production and properties of titanium nitride

The only nitride of titanium sufficiently well characterised to permit preparation of a thermodynamic table is TiN, but there is some evidence for Ti_2N. TiN is readily prepared by burning titanium metal in nitrogen at above 800°C. This method is considered expensive as the preparation of titanium metal itself is expensive. Titanium nitride is a crystalline substance, normally a golden-bronze colour, but in the finely divided state is dark violet or black. It has a cubic structure of the NaCl type with lattice parameter 4.2Å, and a melting point of 2950°C ± 50°C according to AGTE and MOERS. The vaporisation rate and thermodynamic properties have been studied by RYKLIS et al, and the dissociation energy of gaseous TiN examined by STEARNS and KOHL.

TiN was first produced with a plasma torch by STOKES and KNIPE in 1960. Titanium powder at 200 mesh was fluidised in nitrogen and fed into the exhaust of a D.C. plasma jet from an injection ring at 1.72 gms/min. The torch was run at 12 kW on 5 L/min of N_2, and products collected on a cold finger situated ½" below the injection ring. The product was 100% TiN, with a size range of 0.75 to 7.5μ (large for a plasma method - there is probably some crystal growth due to the proximity of torch and collector) but the large particles 'broke down easily'. The yield was 30%.

ZHDANOVSKII and LOKOMSKII also produced TiN by feeding titanium powder into a D.C. plasma jet running on nitrogen. The apparatus is described in detail in section (2.3.2.).

MATSUMOTO took a different approach using the reaction between the plasma gas of a transferred plasma torch and the target or anode. A titanium button was placed on a water cooled copper crucible, and a nitrogen (3 L/min) transferred arc played on it. The current was 110A at 63 V, i.e. 7 kW power. After 5 mins TiN collected on various parts of the apparatus.

In 1909 Ruff showed that TiN could be prepared by reacting titania and ammonia:

$$TiO_2 + NH_3 \longrightarrow \frac{1400\text{-}1500^{\circ}C}{} \; TiN + (3H + 2O)$$

but this method has not yet been tried with a plasma torch.

Franklin reported the existence of titanium amide, formula $Ti\,(NH_2)_4$, and ROSENHEIM and SCHUTTE produced an amorphous yellow powder by bubbling dry ammonia through a conc. solution of $TiCl_4$ in ether. They gave the powder the name 'Titanium tetrachloride hexammine,'

$$TiCl_4 + 6NH_3 \longrightarrow TiCl_4 \cdot 6NH_3$$

This reaction is discussed later in section (2.6.3.)

HARNISCH, HEYMER and SCHALLUS used a D.C. plasma torch but with a slightly different reaction scheme:

$$TiCl_4 + H + NH_3 \xrightarrow{3000^{\circ}C} TiN + 4HCl$$

or preferably

$$1)\ TiCl_4 + \tfrac{1}{2}H_2 \longrightarrow \overset{(gas)}{TiCl_3} + HCl$$

$$2)\ TiCl_3 + NH_3 \longrightarrow \overset{(95\%)}{TiN} + 3HCl$$

the remaining 5% solids being titanimides which were removed by dilute HCl.

The torch was typically run at 100-250 A, 100-200 V, or 15-30 kW. The gas flow was 50 to 83 L/min. The reacted gas stream was quenched (a few cm?) after leaving the torch by impinging on a rotating water-cooled copper drum. The TiN produced was X-ray crystalline, and black due to its very finely divided state. Sometimes golden yellow, compact crystals were produced. The analysed nitrogen value varied from 49.3 to 50.5 atom %.

BICHOWSKY reacted ferrous titanate with carbon under a nitrogen atmosphere in a furnace.

$$2FeTiO_3 + 6C + N_2 \longrightarrow 2Fe + 2TiN + 6CO$$

This reaction has not been attempted in a plasma torch, but the production of TiO_2 by CHARLES, DAVIES et. al. (Section 2.3.2.) from the reaction,

$$FeTiO_3 \longrightarrow Fe + Ti + 3O \longrightarrow FeO + TiO_2$$

suggests that the nitride may be formed in a similar way.

The most convenient way of introducing titanium to a reaction in vapour form, is as $TiCl_4$, which is readily available in tonne quantities.

Miller and AYEN reduced $TiCl_4$ to $TiCl_3$ using hydrogen injected into an argon plasma produced by a 4 MHZ R.F. generator with a maximum output of 10 kW. The plasma was confined by a 2.8 cm I.D. water cooled quartz tube, and the $TiCl_4$ injected with the argon. Without hydrogen injection, very little $TiCl_3$ was produced, with or without quenching on a cold ring which could be raised to within 5 cm of the bottom of the work coil. Typical values were 10 L/min Argon containing 0.2 mole % $TiCl_4$ and a torch power of 5 kW. When hydrogen was introduced with the argon and $TiCl_4$, $TiCl_3$ of over 95% purity was deposited on the tube walls below the plasma. Conversion efficiency was calculated by weighing the confinement tube before and after a run, including a small correction for collection efficiency. Conversion efficiencies up to 87% were obtained, and the highest production rate was 12 gms/hour at 7kW, giving an electrical consumption cost of about £1 per kg. The production rate was limited by the amount of $TiCl_4$ which could be injected without extinguishing the plasma. The thermodynamic equilibrium gas-phase compositions for the systems Ar-$TiCl_4$, Ar-Ti-Cl-Mg and Ar-Ti-Cl-H were calculated.

OPFERMANN produced TiN by dissociating $TiCl_4$ and nitrogen and allowing the mixture to cool rapidly:

$$TiCl_4 + N_2 \xrightarrow{\text{HEAT}} Ti + 4Cl + 2N \xrightarrow{\text{COOL}} TiN + Cl_2 + \text{Titanium chlorides}$$

He used a D.C. torch running on 23.3 L/min of a $64^{v/o}$ A plus $36^{v/o}N_2$ mixture (His torch could not be run on nitrogen alone). No electrical data is given. The plasma nitrogen was first bubbled through $TiCl_4$, when small golden crystals appeared in the anode bore, eventually blocking it -- these were identified as TiN. A 7% yield of TiN from the $TiCl_4$ was achieved, and in all 1450 LA, 810 LN_2 and 40 gm$TiCl_4$ were used in producing 1 gm TiN. The yield would certainly be improved by the addition of hydrogen to form the highly stable HCl gas.

2.5. Apparatus and Experimental Method

Introduction

The apparatus required to produce ultrafine powders from the gaseous phase using a plasma torch falls naturally into five sections.

1. The plasma torch, which was described in the Introductory Chapter.
2. A device for delivering controlled flows of reactants.
3. An injector, through which the reactants are brought into contact with the hot gas.
4. A reaction vessel, which confines the reactants in a suitable environment.
5. A collector where the fine particles are separated from the gas stream. The possible methods of collection were reviewed in section (1.4).

The account of the evolution of the apparatus for the production of silicon nitride is divided into two sections, as originally the aim was to inject $SiCl_4$ into a mixture of hot nitrogen and hydrogen, so that it would be first reduced then nitrided. This method was unsuccessful, and when the work of BILLY on the ammonolysis of $SiCl_4$ was discovered, a different method was tried based on the production of an intermediate, silicon di-imide, which demanded a different injection method.

The third sub-section describes the experimental method of making yield measurements.

2.5.1. Development of apparatus for the first reaction scheme

Silicon tetrachloride is a readily available silicon compound, which is volatile at room temperature, boiling at 57.57°C. (Fig 19). It was decided to try and produce Si_3N_4 from the two reactions;

$$SiCl_4 + 2H_2 \longrightarrow Si + 4HCl$$

$$3Si + 2N_2 \longrightarrow Si_3N_4$$

after plotting the relevant values of free energy changes (Figs 20 and 21). The choice of gas for absorbing the $SiCl_4$ vapour and conveying it to the injector was between H_2, N_2 and argon. Argon was chosen for its low specific heat, so that its presence in the thermal balance at the injection point could be ignored.

The first rig is shown in Fig 22. The delivery vessel, in which argon was bubbled through $SiCl_4$ held at a steady temperature by an oil bath, is shown in Fig 23. The reactor was a water cooled, 3" I.D. copper tube with two welding-glass covered viewing parts, and a steam injection nozzle pointing downstream at the far end. Injection (Fig 24) was via three ceramic nozzles facing radially inwards, being fed by an annular gap in the two parts of the brass body. The glass sections were all standard Q.V.F. components (Fig 22), comprising a 90°C bend leading to a condenser and collection jar. The object of the steam injection was both to collect any ultrafine particles by condensation and droplet formation (see section 1.2.4.), and to dissolve the (by-product) HCl gas. The method was found unsuitable for the production of Si_3N_4, as water vapour passed upstream to the reactor, and only SiO_2 was formed. The particles were very thin, regular platelets, as shown in Fig 25.

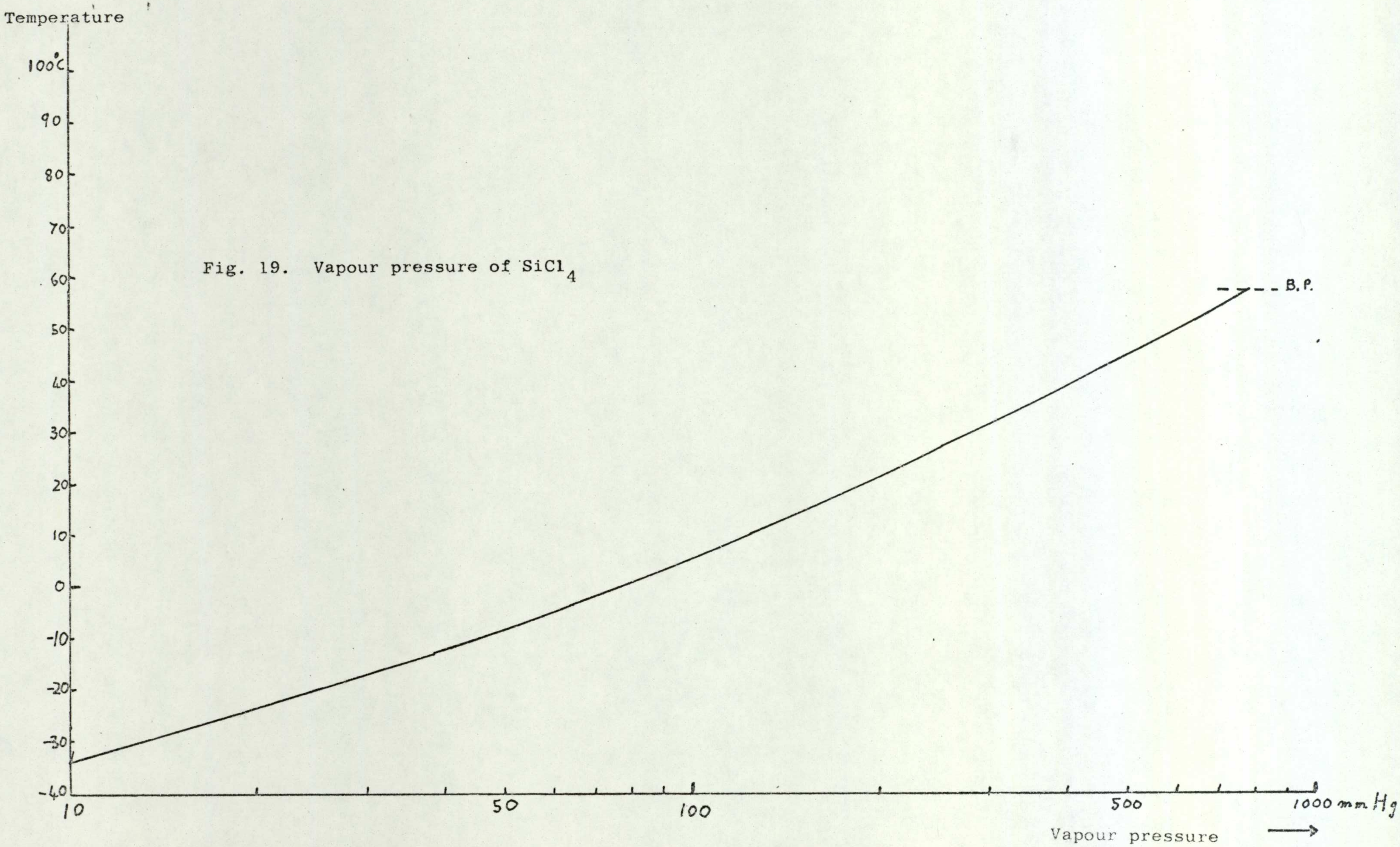


Fig. 19. Vapour pressure of $SiCl_4$

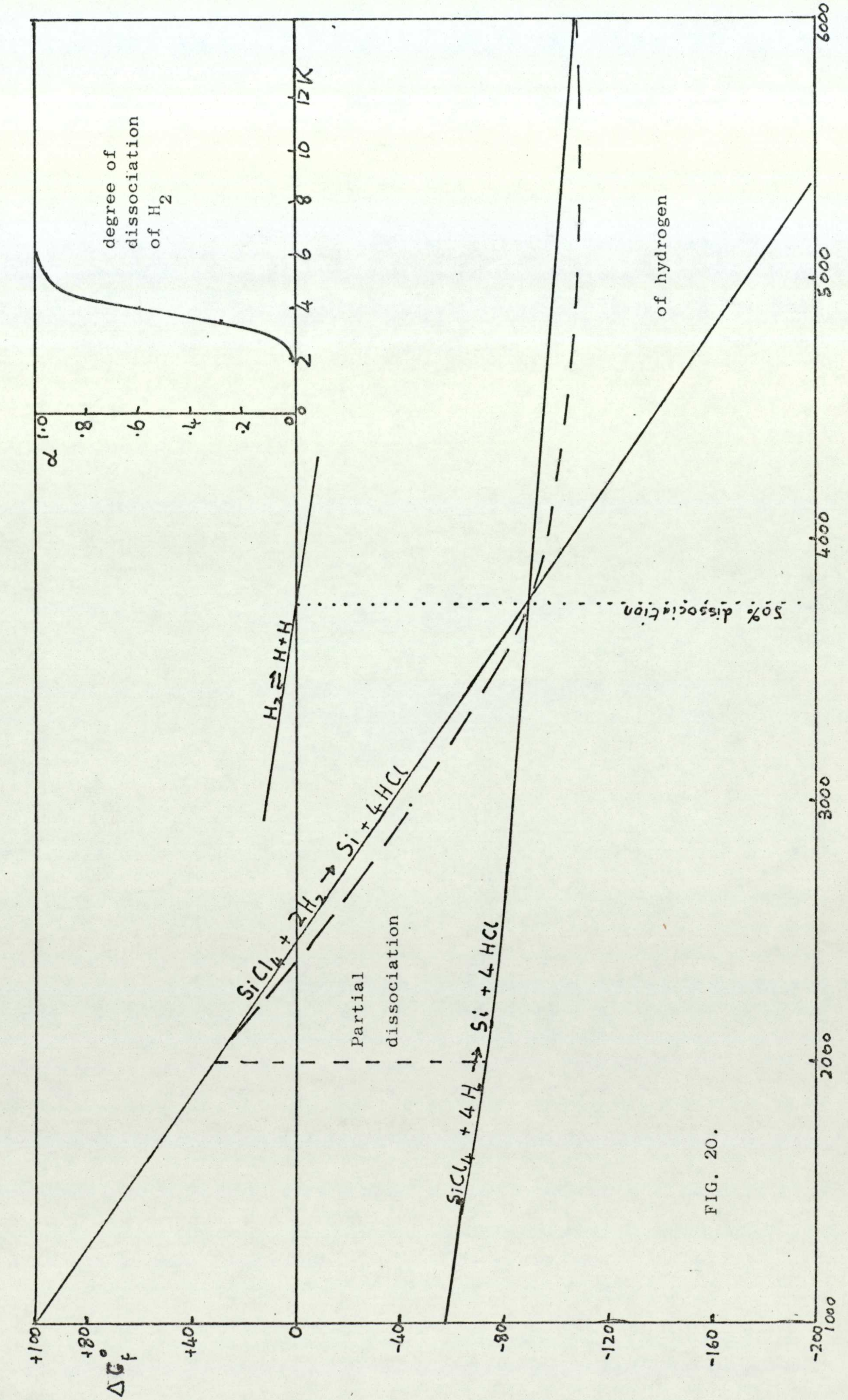
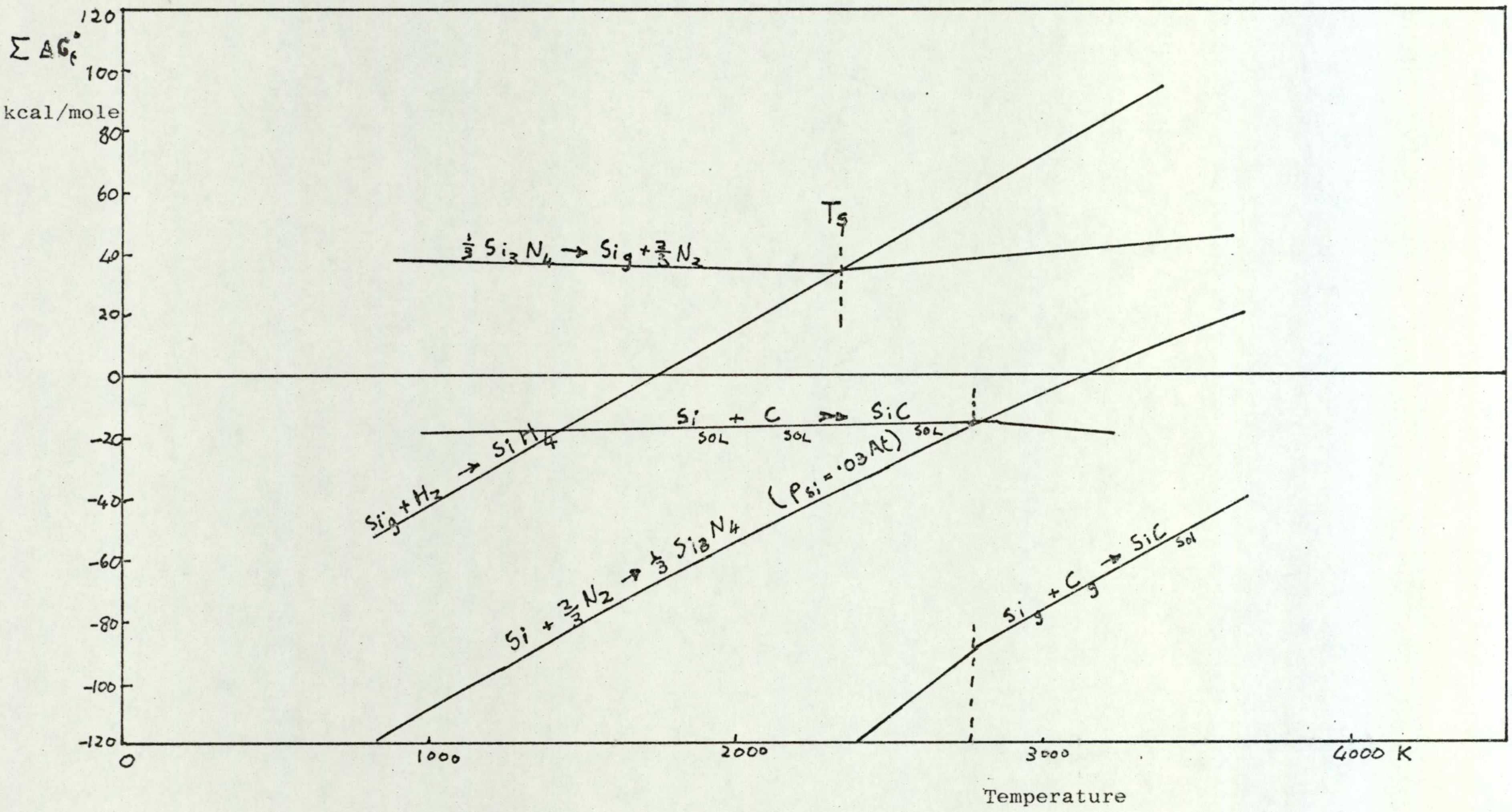

$\Sigma\Delta G^\circ_f$
+100
+80
+40
0
-40
-80
-120
-160
-200
1000
2000
3000
4000
5000
6000 K
α
1.0
.8
.6
.4
.2
0
0
2
4
6
8
10
12 K
degree of dissociation of H_2
$H_2 \rightleftharpoons H + H$
$SiCl_4 + 2H_2 \rightarrow Si + 4HCl$
$SiCl_4 + 4H \rightarrow Si + 4HCl$
Partial dissociation
of hydrogen
50% dissociation

FIG. 20.



$\Sigma\Delta G_f^\circ$
kcal/mole
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
0
1000
2000
3000
4000 K
Temperature
T_g
$\frac{1}{3}Si_3N_4 \rightarrow Si_g + \frac{2}{3}N_2$
$Si_{SOL} + C_{SOL} \rightarrow SiC_{SOL}$
$Si_g + H_2 \rightarrow SiH_4$
$Si + \frac{2}{3}N_2 \rightarrow \frac{1}{3}Si_3N_4 \quad (P_{Si} = \cdot 03\,At)$
$Si_g + C_g \rightarrow SiC_{sol}$

Fig 21.

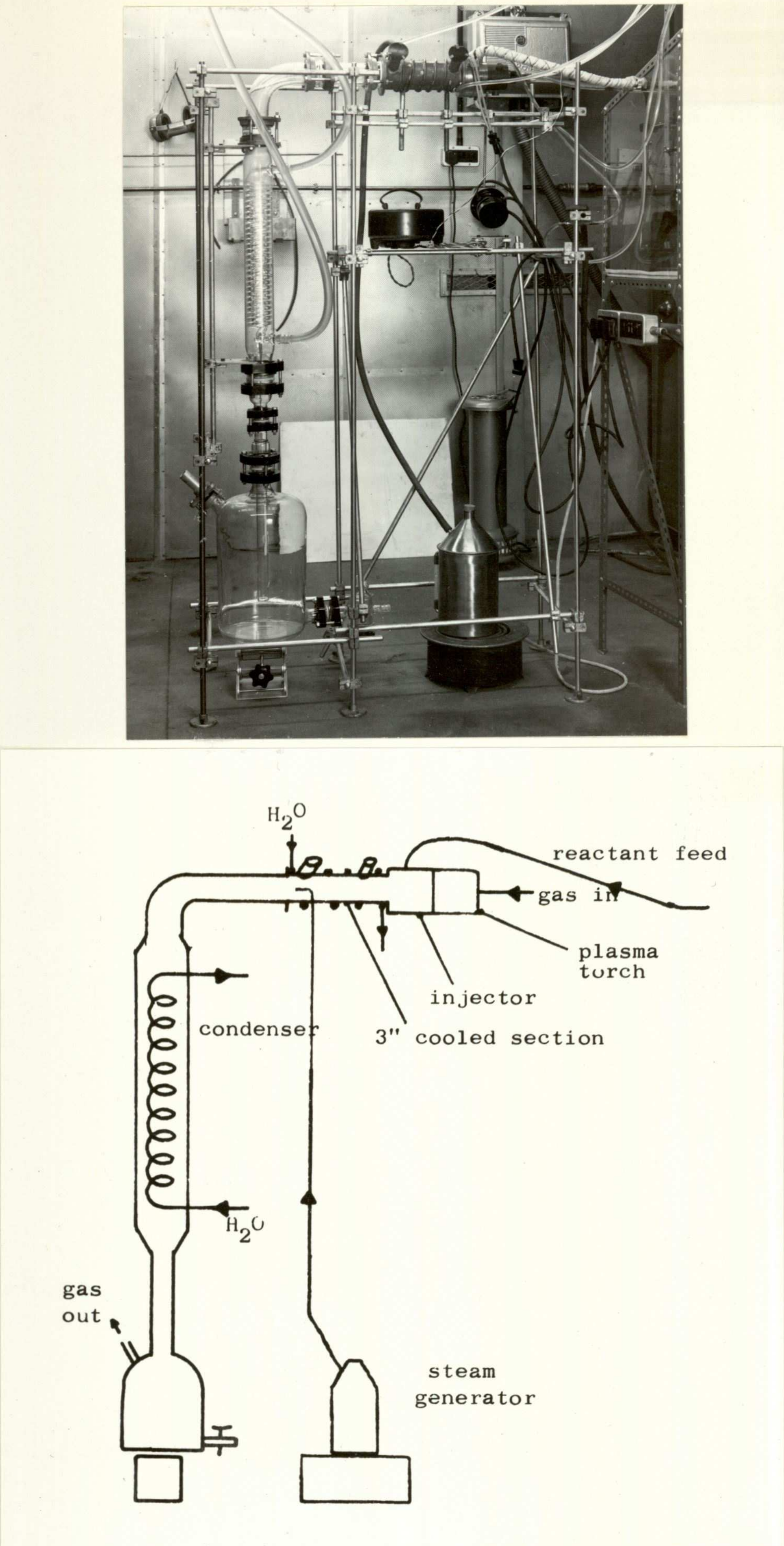


Fig. 22. The first rig for the production of silicon nitride.

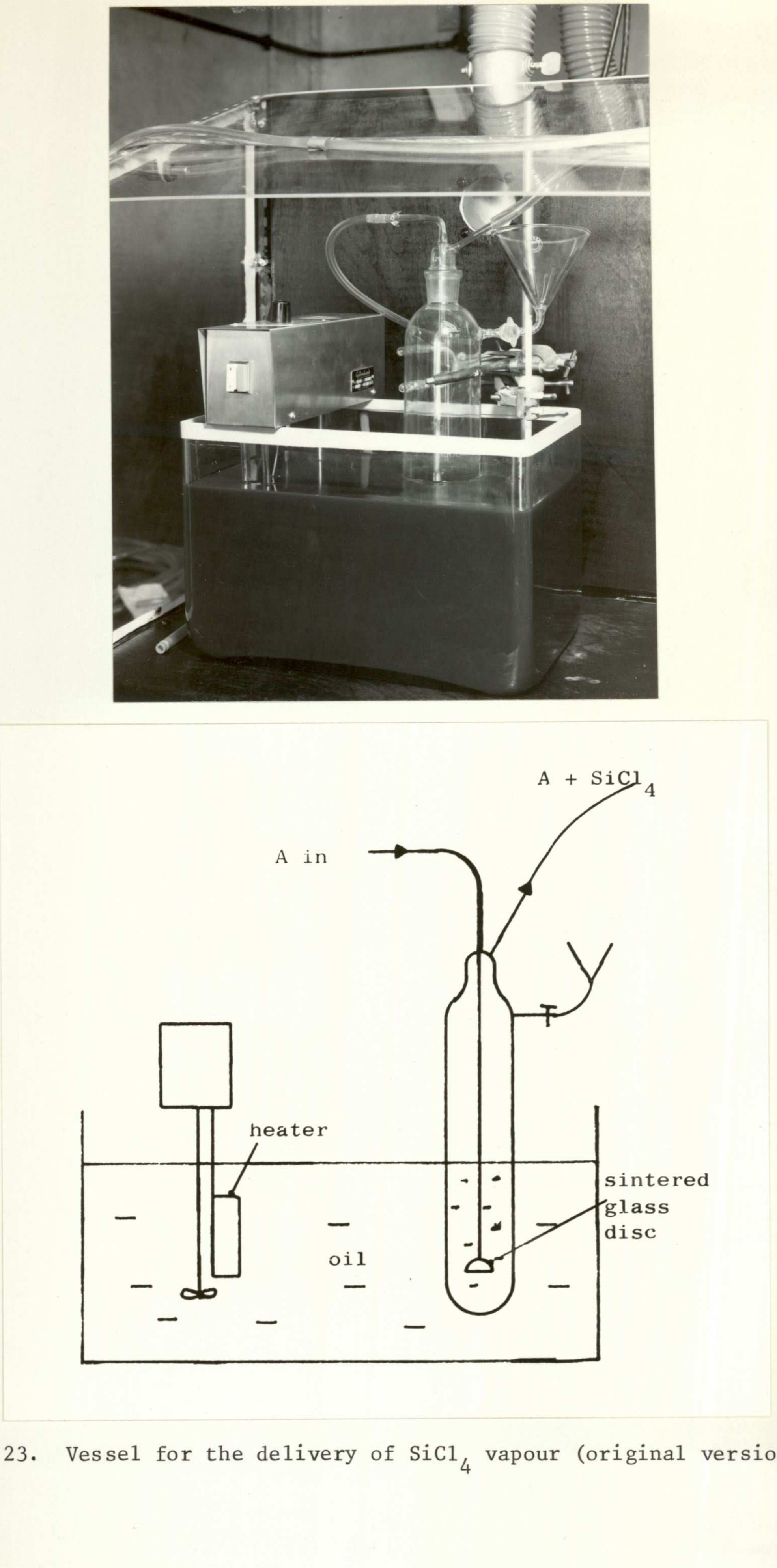


Fig. 23. Vessel for the delivery of $SiCl_4$ vapour (original version)

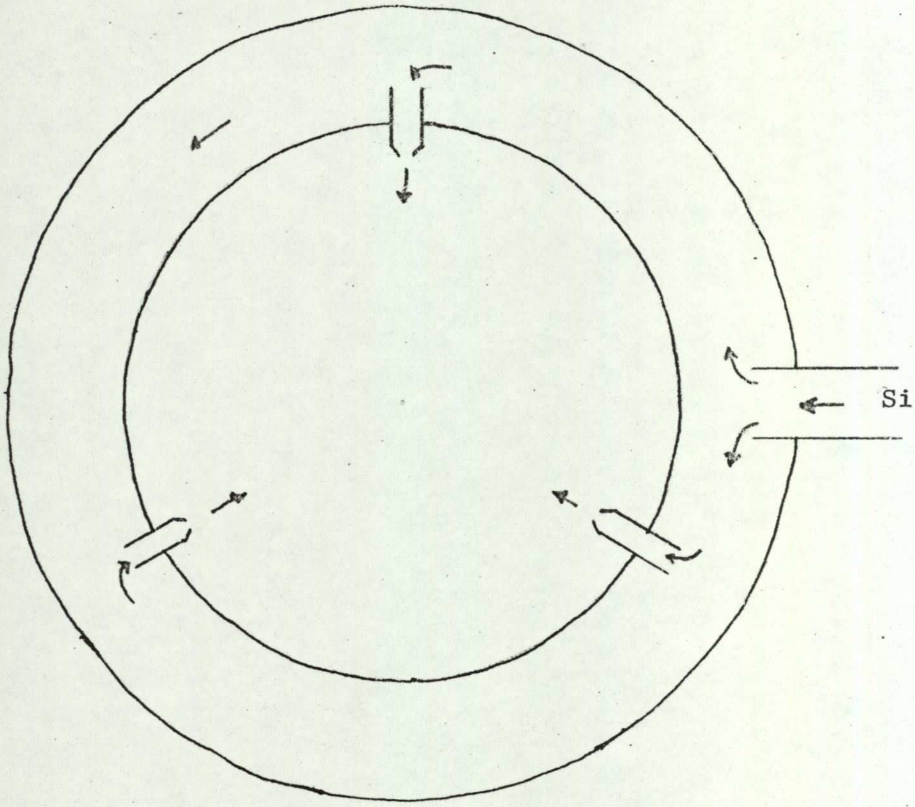


Fig. 24. The annular injection ring with radial nozzles.

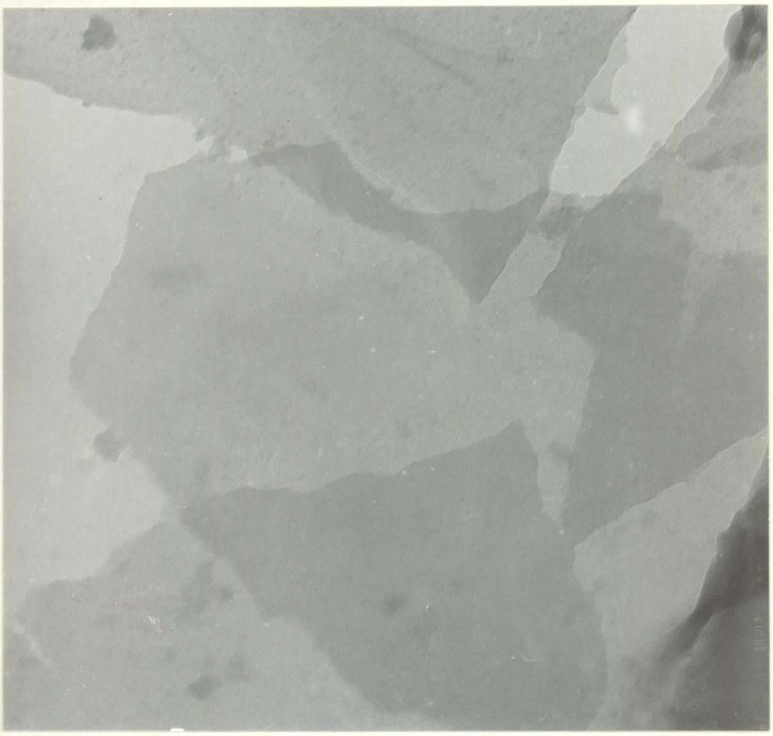


Fig. 25. Thin platelets of silica produced with the first rig.

The steam injection and collection system was taken away for the second rig, and replaced by an additional section of cooled copper tube, this time 2" I.D. (Fig 26) intended to cool the gas stream before it passed through a stainless steel filter element.

The oil bath temperature was set to 36°C, giving a vapour pressure of half an atmosphere of $SiCl_4$ in the bubbler vessel. The argon flow was one L/min, and the delivery tube was heated to 50°C to prevent recondensation. The torch was run at 250 amps and 63 volts, on 12 L/min of N_2 and 3 L/min of H_2. The run lasted 15 mins, during which some 'vapour' was visible entering the filter.

When it had cooled, the filter element was examined but very little white powder was found inside it. The reactor was dismantled and a black sticky residue was found on the walls of the 2" I.D. section. On exposure to air it turned white with an exothermic reaction. This was probably due to the condensation of unreacted silicon tetrachloride with some powder, which was hydrolised by the moist air.

The residue in the 3" reaction section consisted of dark coloured flakes, which when scraped off combusted spontaneously with an orange flame, leaving behind a white vapour. The flakes were probably pyrophoric silicon powder which had condensed on the cold walls, and formed a dust explosion when dispersed in air.

A qualitative analysis of the residue inside the stainless steel porous collector showed no nitrogen. The conclusion was that the cold walls of the 3" I.D. section were too close to the reacting gases, and the reaction was interrupted halfway through. The silicon was being produced by the reduction of the silicon tetrachloride, but was then deposited on the walls of the reaction vessel before it could combine with nitrogen. It was decided to construct a new reactor with a very much greater diameter, to overcome this problem.

For the third rig, a reaction chamber was made from a large steel drum with a clip on lid, coated internally with a varnish. The drum was mounted horizontally on a stand and fitted to the torch and injector ring (Fig 27). The reaction chamber was purged for 30 minutes by 20 litres per minute of nitrogen. The torch was started and the drum allowed to warm up. $SiCl_4$ was injected under conditions identical to those described in the previous experiment. When the drum had cooled the lid was removed. A thin layer of white fluffy powder was seen to be covering the whole of

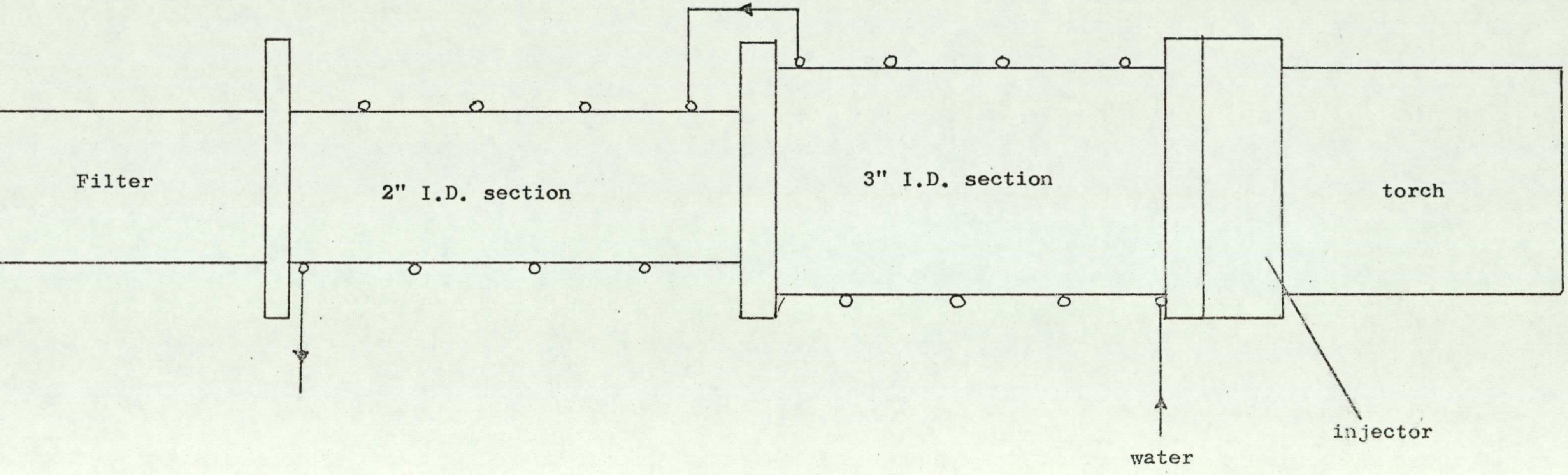


Fig. 26. Second rig for the production of Si_3N_4

the internal surface of the drum (Fig 28), but no powder was found inside the stainless steel filter element. No brown deposit was visible inside the drum and there was no smell of silicon tetrachloride. The cold surface of the drum where it was bolted to the injection ring was covered with a sticky layer, probably caused by condensed and unreacted silicon tetrachloride. The white powder was later analysed and found to be 75% silica with 2% nitrogen present as nitride, and some ammonium chloride and iron.

The experiment was repeated and a sample of the gaseous products taken, via a small tube welded through the lid. The gas sample was analysed for chloride. All the chloride was present as HCL, to a concentration consistent with complete reduction of the $SiCl_4$, taking into account the dilution caused by the plasma gas.

The presence of so much silica in the sample was not expected so provision was made to mount an oxygen probe into the drum. This probe has a ceramic electrolyte and was specially designed for measuring the oxygen concentrations down to very low levels furnace gases. With this instrument partial presures of the order of 2 x 10(-13) atmospheres were recorded, which were considered to be orders of magnitude too low to account for the amount of silica in the drum. It was eventually found that iron oxides formed on the drum were the source of oxygen.

2.5.2. Development of apparatus for the second reaction scheme

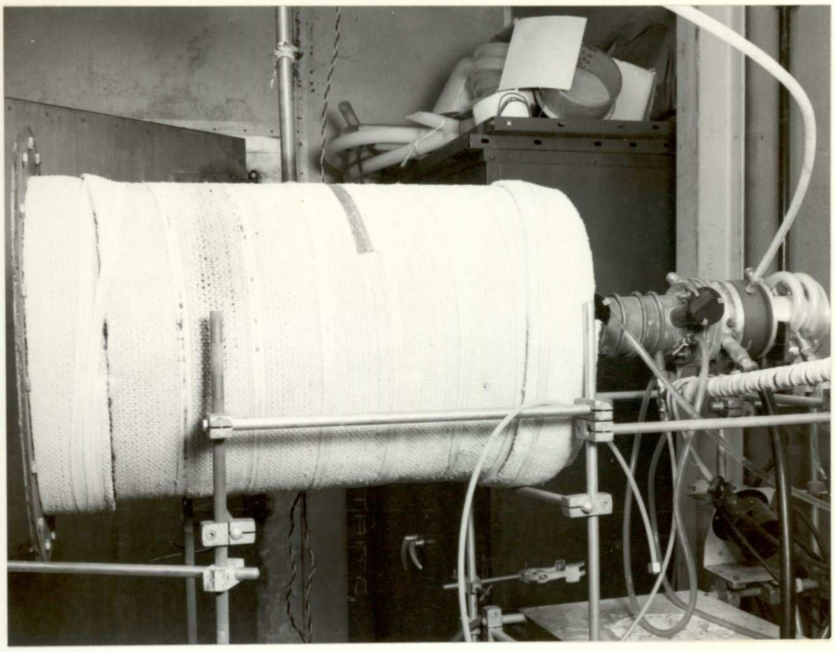
The reaction scheme given by BILLY was,

$$SiCl_4 + 6NH_3 \longrightarrow Si(NH)_2 + 4NH_4Cl$$

$$3Si(NH)_2 \longrightarrow Si_3N_4 + 2NH_3$$

There was no data on the rate of formation of di-imide, so until experiments could be performed a simple double co-axial tube arrangement (Fig 29.) was made, and fitted to the 3" I.D. section, which was inserted between the torch and the drum (Fig 30). The oil bath was at 40°C, and 1 L/min argon passed through the bubbler and into the central coaxial tube, whilst $\frac{3}{4}$ L/min ammonia passed down the outer tube. The torch was run at 300 amps and 60 volts on 20 L/min N_2, for 6 minutes.

When the drum had cooled, the lid was removed and exposed a small amount of fluffy white powder which analysed to 0.2% nitrogen as nitride, 4% SiO_2, 24% chloride and 18% iron. This amount of iron showed that the drum



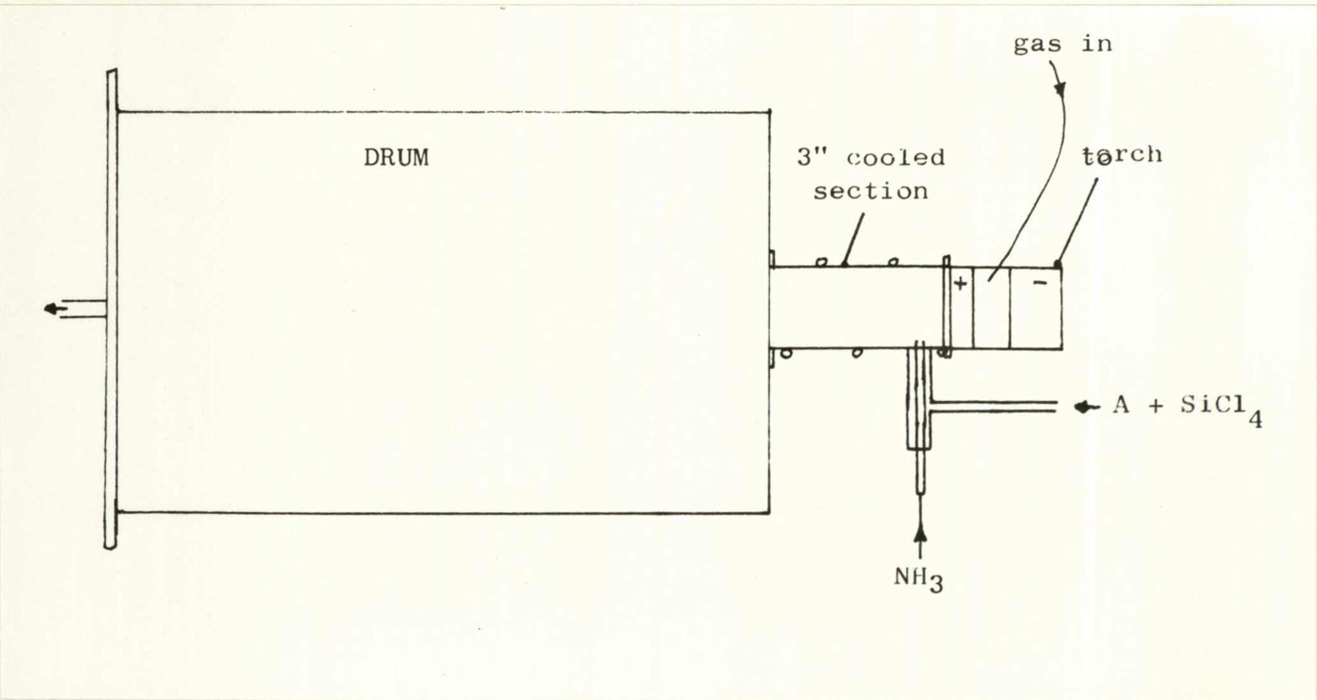


Fig. 27. Third rig for the production of silicon nitride. including Figs. 29 & 30.

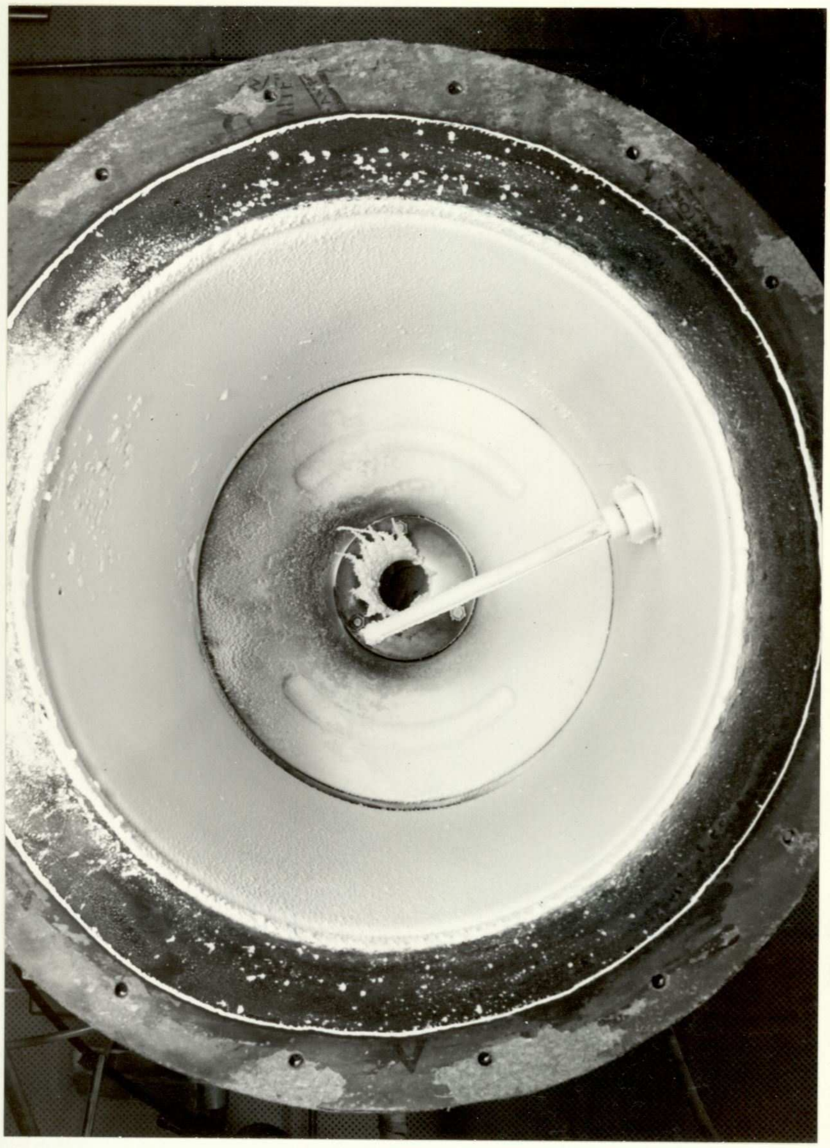
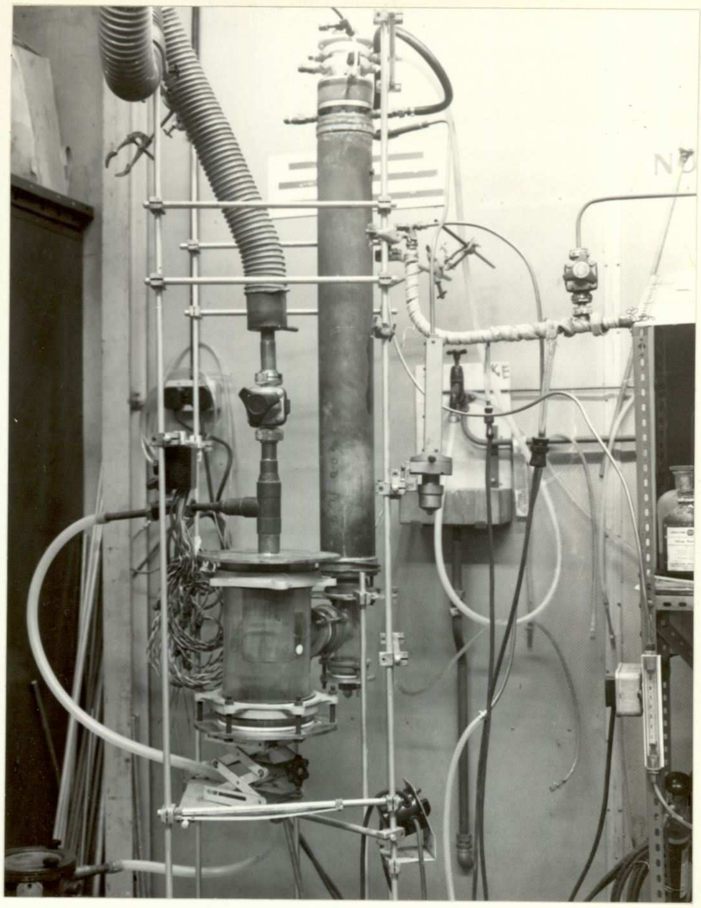


Fig. 28. View inside the drum after a run, showing the oxygen probe in position.



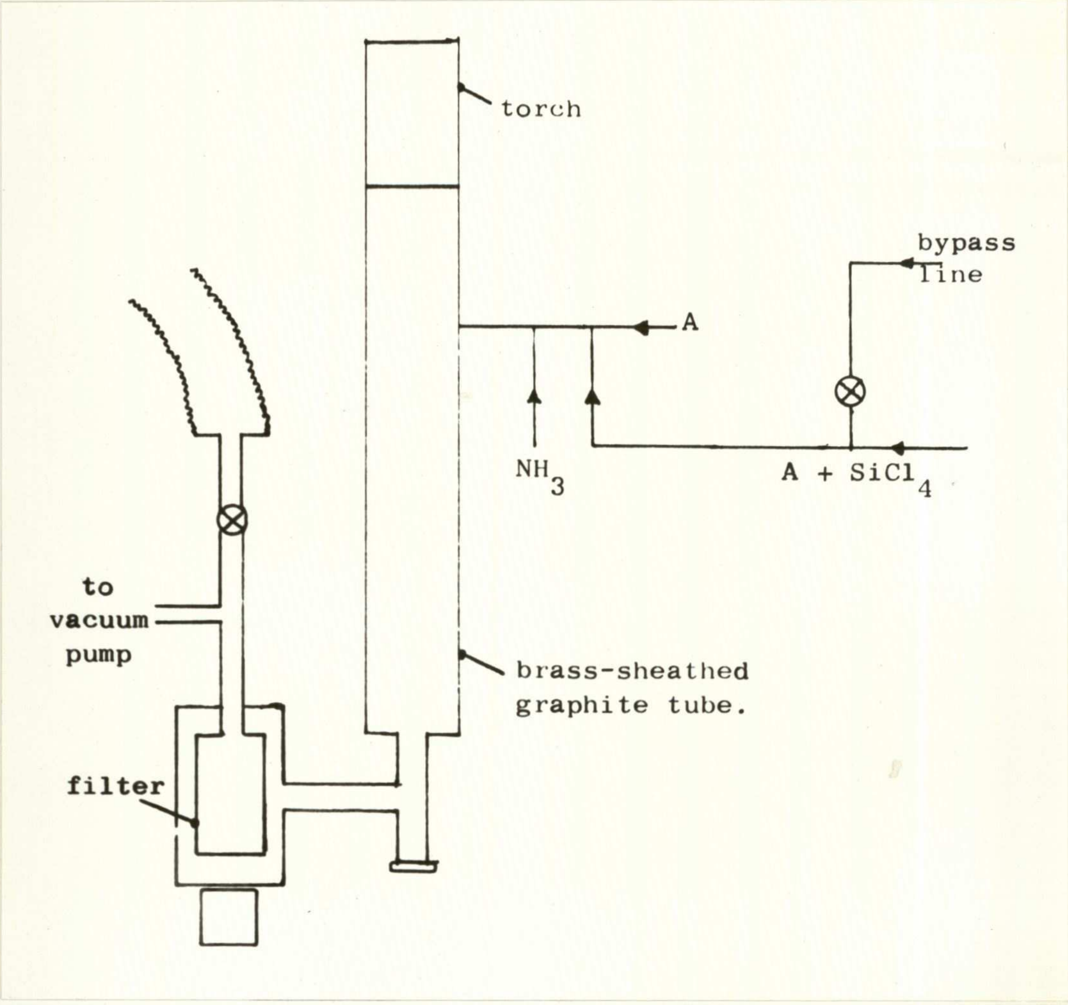


Fig. 31. Fourth rig for the production of silicon nitride.

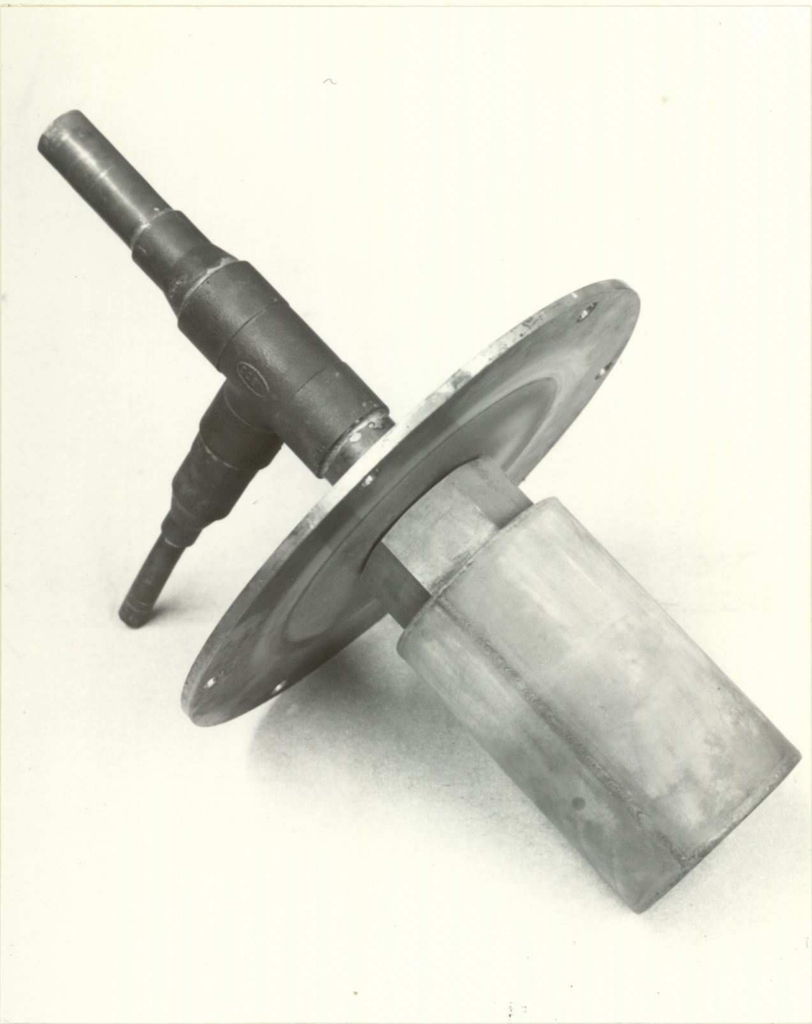


Fig. 32. Stainless steel filter element used as a powder collector.

was so heavily contaminating the powder samples that it was unsuitable as a reactor. Its use had proved that the presence of cooled surfaces in the previous rig had caused premature condensation of silicon. Temperature measurements inside the drum showed temperatures over most of the volume lower than the desirable range of over 800°C for the formation of Si_3N_4 from $Si(NH)_2$. A smaller diameter reactor was required, made from a refractory, unreactive material, which would give higher temperature profiles and hot walls.

The fourth rig (Fig 31) was built round a graphite tube 34" long, $3\frac{1}{2}$" I.D. and $\frac{3}{4}$" thick. It was set up vertically with the torch at the top separated from the reactor by the 3" I.D. cooled section to avoid damage to the graphite. A series of blind holes were drilled at 10 cm vertical intervals in the graphite wall, to take chromel/alumel thermocouples. The torch was run at 250 amps and 60 volts on 20 L/min N_2, and the highest temperature was 470°C, showing that the graphite was not in danger of overheating.

The lower end of the reactor was connected by standard Q.V.F. glass components to a glass vessel in which the filter element was mounted so as to collect the powder on the outside (Figs 31 and 32). An attempt was made to produce silicon nitride by injecting silicon tetrachloride and ammonia via the coaxial injector which was positioned at the upper end of the 3" cooled section. During the run a white layer was observed on the outside of the filter element, and great difficulty was experienced in holding the reactant flows constant. This was due to the filter becoming blocked by the powder.

A sample from the filter surface was soluble in caustic soda solution, proving it was not Si_3N_4 (which is insoluble) so no further analysis was made.

Two major modifications were made to the rig, to increase the reactor temperature and seal the graphite tube, for the following reasons. A platinum-rhodium thermocouple was inserted through the lower part of the 3" I.D. section, and a temperature of 1400°C was measured with the torch running as above. A hole was then drilled through the graphite wall about 4" below its top and temperatures of about 1130°C were measured at the axis of the tube. It was decided that the graphite reactor was operating at far too low a temperature so the 3" I.D. cooled section and injection ring were removed and the torch connected directly to the upper flange of the graphite reactor. At the same time the graphite reactor tube was sheathed by a $\frac{1}{8}$" thick brass tube which was brazed to the upper and lower brass flanges.

While these modifications were underway, apparatus was set up to examine the reaction rate of $SiCl_4$ and NH_3 vapours. A spherical flask (Fig 33) was connected to a rotary pump and mercury manometer, a flask of $SiCl_4$ and a small cylinder of an hydrous NH_3. The flask was evacuated, tap A shut, then tap B opened for a few seconds, then shut and the manometer pressure noted. Tap B was opened, dense white fumes were immediately visible, and the flask became warm. The manometer level varied too rapidly to be read, settling to a slow rate of pressure reduction in less than ten seconds. A similar experiment was performed with $TiCl_4$, with a similar result, except that the fumes were yellow.

The speed of the reaction in the flask was probably diffusion controlled, as the dense fume appeared at the mouth of the tube carrying the NH_3 as soon as tap C was opened, accounting for the rapid initial pressure movements. As the vapours mixed more intimately, the slower final pressure fall was caused. This conclusion indicated that if an injection device were built which brought the vapours into intimate contact while flowing down a few cm of tube, the first part of the reaction could be completed before the reactants entered the graphite tube. The silicon-nitrogen bonds would be firmly established before the ammonia was dissociated by the hot nitrogen stream. The free energy changes for the overall reaction were calculated, and are shown in Fig 34.

An injector was built based on the gas entrainment principle, to promote mixing and propel the di-imide into the reactor, preventing it sticking to the injector walls and causing a blockage (Fig 35). Test firings into the ventilation ducting showed a cloud of white fume issuing from the injector tube. The free energy curves (Fig 34) suggested injecting the di-imide at a point in the reactor where the temperature (T_1) was normally 2000°C, as Si_3N_4 sublimes at 2040°C. The equilibrium temperature of the reactants and nitrogen stream (T_2) was to be 1200°C, and the reactant flow rates were set to give approximately this temperature.

The point of injection was chosen from temperature measurements made by a tungsten/tungsten-rhenium thermocouple which was mounted on a sectional brass tube which could be pushed up from the bottom end of the graphite tube. At the 2000°C level, a hole was made through the brass sheath and graphite tube, and the injector was fixed to the sheath

(Fig 36)

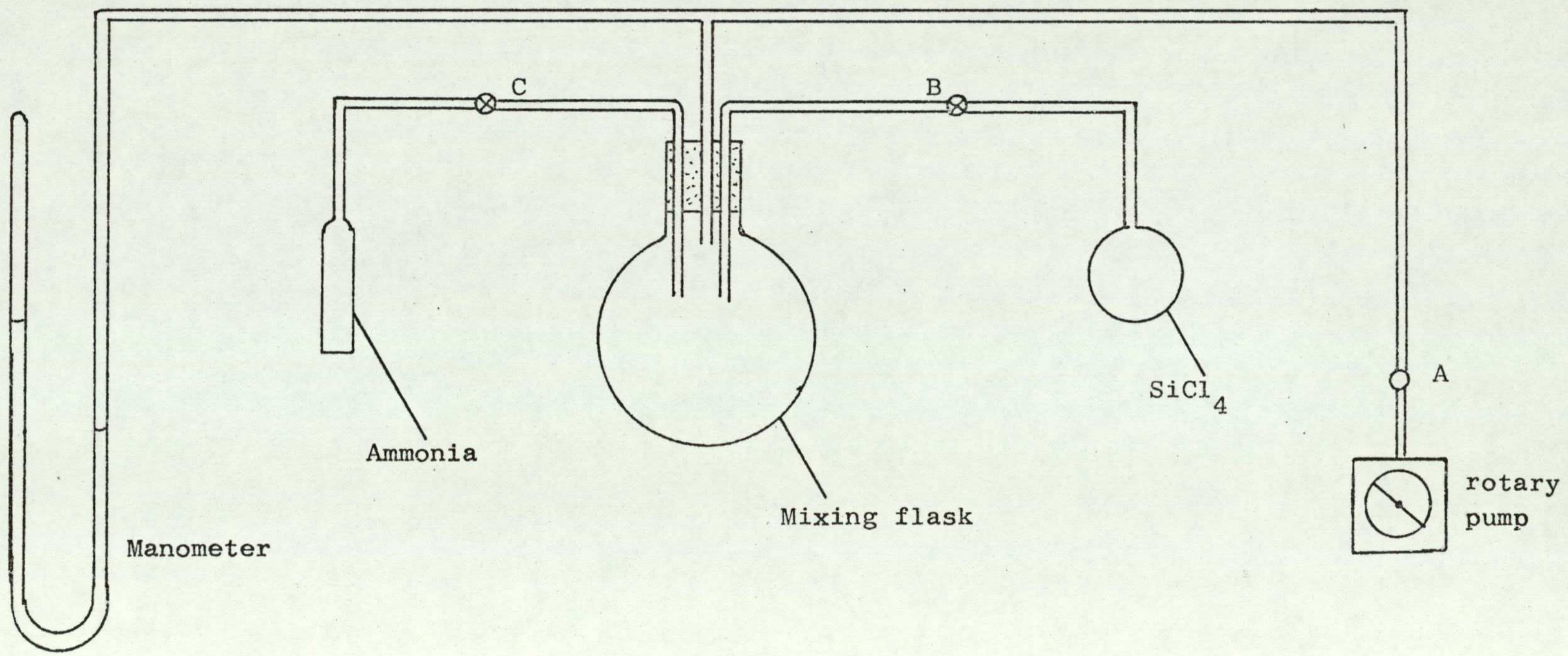


FIG. 33. Apparatus for the qualitative determination of the reaction rate between $SiCl_4$ and NH_3

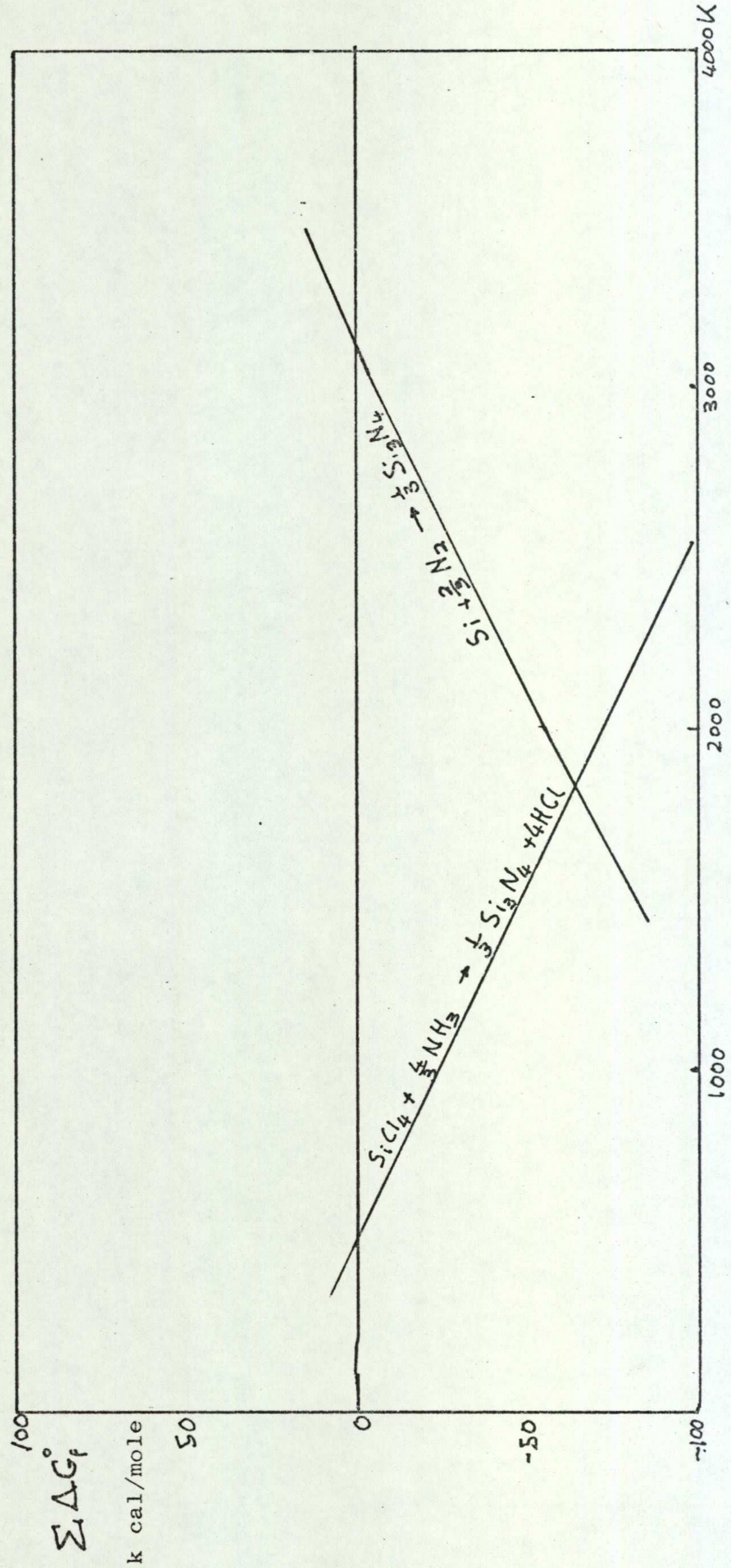

$\Sigma \Delta G^\circ_f$
k cal/mole
100
50
0
-50
-100
1000
2000
3000
4000K
Temperature
$SiCl_4 + \frac{4}{3} NH_3 \rightarrow \frac{1}{3} Si_3N_4 + 4HCl$
$Si + \frac{2}{3} N_2 \rightarrow \frac{1}{3} Si_3N_4$

Fig. 34.

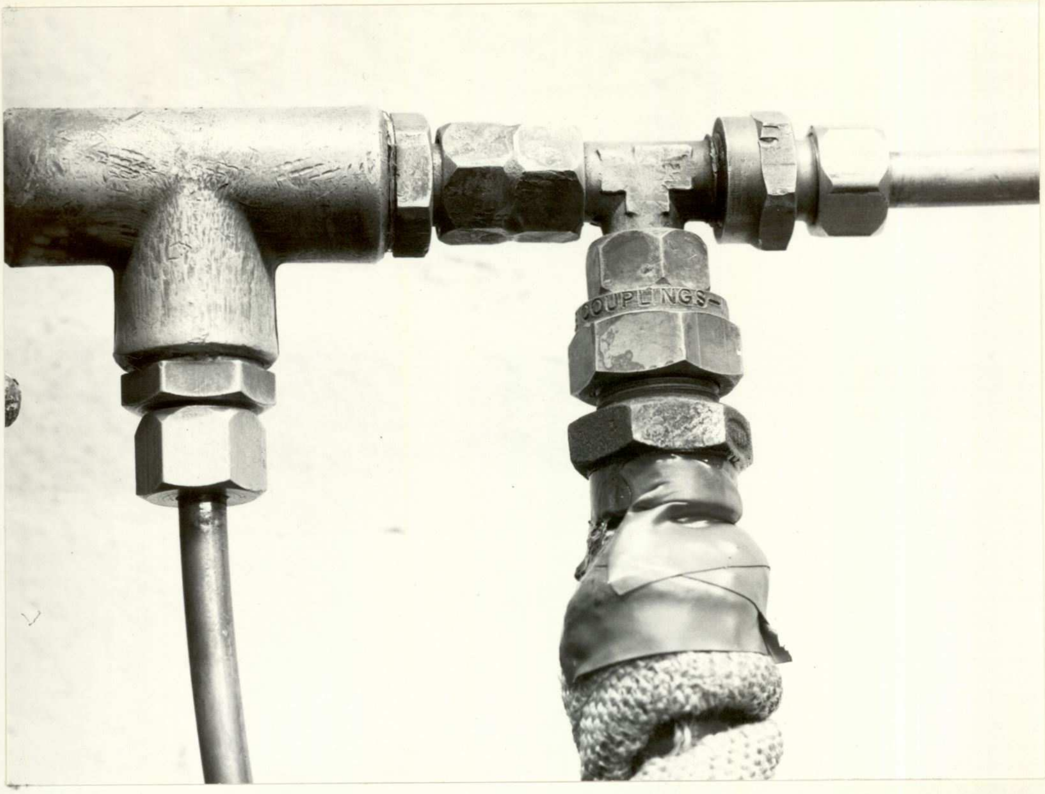


Fig. 36. Injector mounted to the graphite reactor.

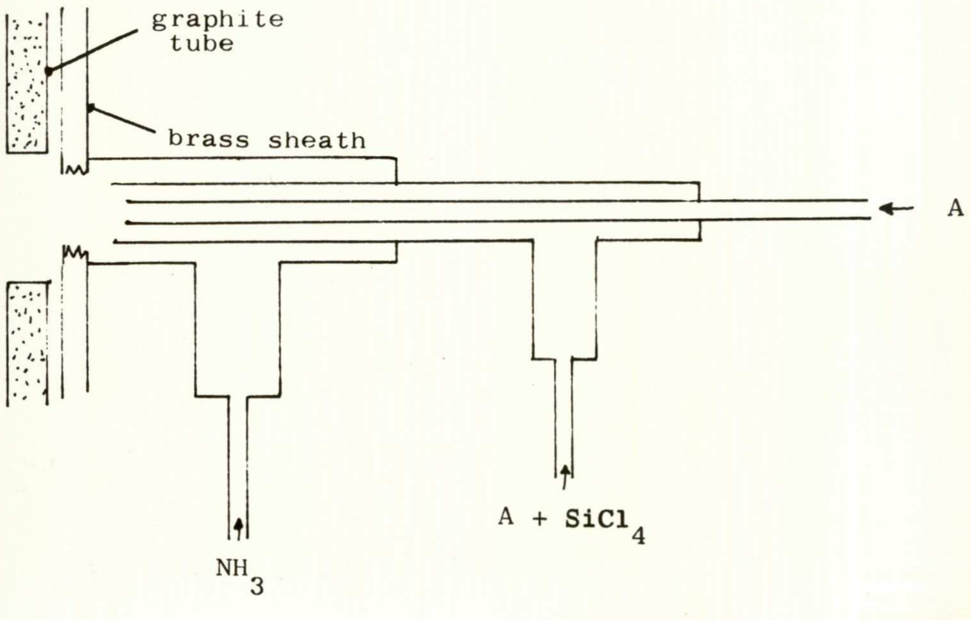


Fig. 35. The gas-entrainment injector

The first successful production of Si_3N_4 was carried out with the torch running at 300 amps and 50 volts on 20 L/min of N_2 which fell to 16 L/min as the filter clogged. One L/min of argon picked up $SiCl_4$ at 38°C, and mixed with a 4 L/min of NH_3 in the injector where it was propelled by 20 L/min of argon. After five minutes the filter was so blocked that the reactant flows were well down, so the run ceased.

Samples taken subsequently from the filter surface and from the inner wall of the glass chamber surrounding the filter had nitrogen as nitride percentages of 26 and 32% respectively. The sample also contained ammonium chloride and about .7% of carbon and some silicon, which if calculated as silica gave a total analysis of 97%. It was concluded that the fundamental problem surrounding the production of silicon nitride by this plasma method had been overcome. Experiments were therefore discontinued until a suitable collection method could be devised which would allow measurements of the yield to be obtained.

The filter element was removed, and the first part of the flexible tubing to the ventilation system replaced by a glass tube 150 cm long and 5.5. cm I.D. The $SiCl_4$ in the gas bubbler was replaced by $TiCl_4$, and the oil bath heated to 110°C. The vapour pressure curve for $TiCl_4$ is shown in Fig 37. The torch was run at 300 A and 45 volts on 20 L/min of nitrogen. When 2 L/min argon was passed through the gas bubbler, and 4 L/min NH_3 added in the injection gun, dense bluish/grey fumes were produced and passed up the glass tube. Some settled on the walls and the glass chamber, and a sample was analysed. An electron micrograph of a sample is shown in Fig 37a.

The results were as follows:

Titanium = 12.6%
Total Nitrogen = 21.6%
Ammonia = 75% (agrees with loss on ignition at 350°C of 77.1%)

Which give:

Nitrogen as NH_4 = 19.6%
$\therefore$ Nitrogen as nitride = 2%
$\therefore$ Titanium nitride = 8.8%

2.5.3. Apparatus used for yield experiments

No modifications were made to the reactor except to drill a series of

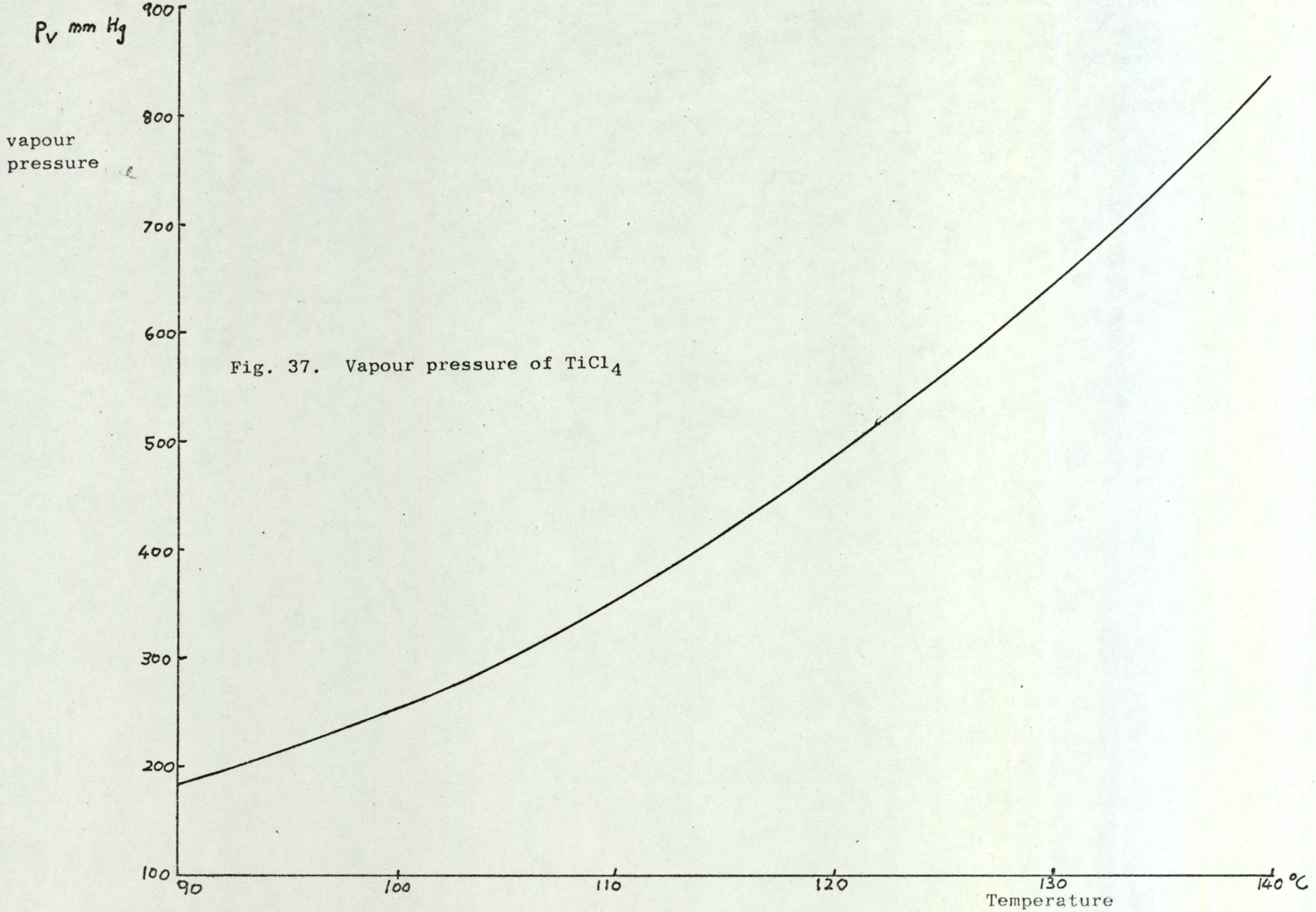


Fig. 37. Vapour pressure of $TiCl_4$

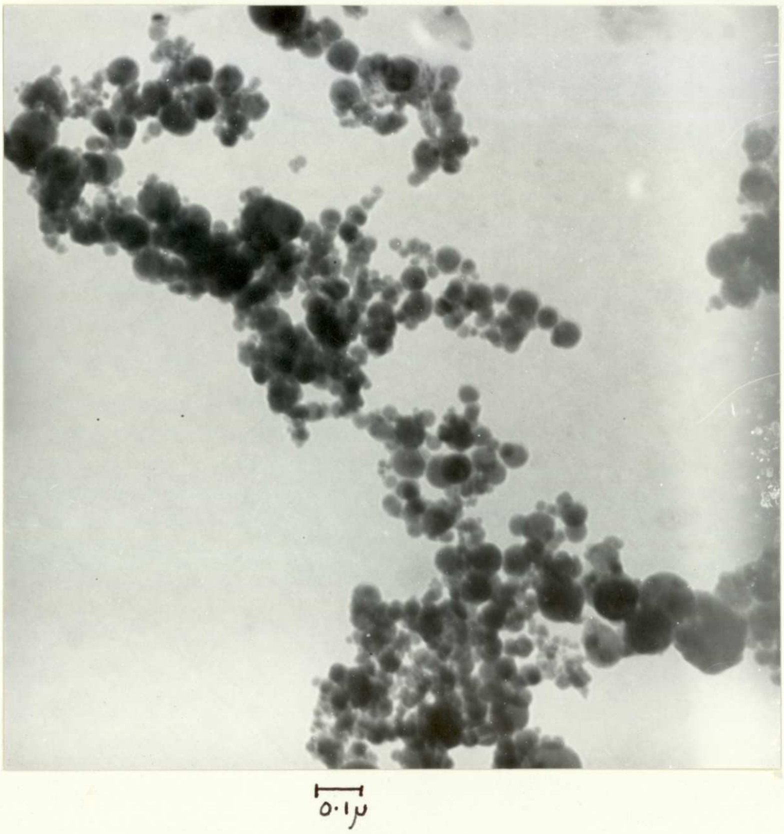


Figure 37a. Electron-micrograph of a TiN sample

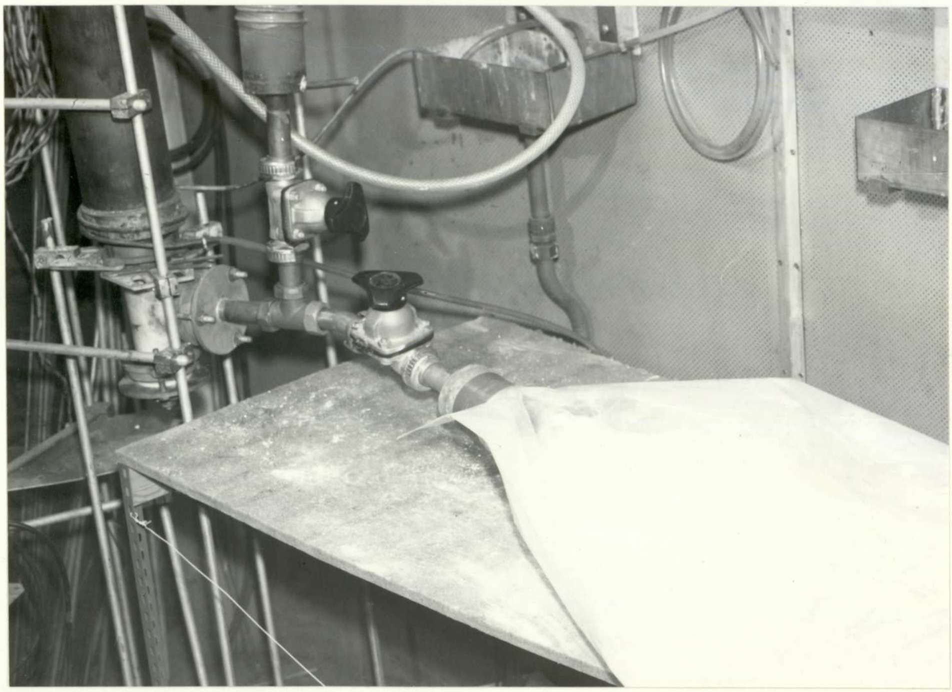
blind holes in the sheath as had been done previously for the graphite tube. The object was to record the temperature profile when a production run was in progress as a check on the reproducibility of the operating conditions. A differential thermocouple was connected across the torch, to measure heat lost to the cooling water.

The filter element and its vessel were removed, and replaced by an inflatable polythene bag with an arrangement of large vacuum taps (Fig 38) allowing the bag to be sucked flat by the ventilation system, inflated via the reactor, or by-passed.

A volumetric reactant delivery vessel was constructed from modified standard parts (Fig 39), which included a Q.V.F. crescent ring seal. This allowed the delivery tube to be removed if the glass sinter became blocked. Cone and socket joints cannot be separated after they have been exposed for a few days to $SiCl_4$ (see appendix III). For the same reasons, weir type vacuum taps were used, with viton diaphragms. The oil bath could be raised and lowered by hand to allow the reactant liquid level to be read. A by-pass tube was fitted to the delivery vessel to allow purging of the delivery tube with argon.

The mode of operation to perform a yield experiment was as follows:

A polythene bag which was used as a collector was folded up and weighed, then connected to the apparatus and sealed on with plastic tape. The ammonia container was weighed, and the level of $SiCl_4$ in the graduated cylinder noted. The silicon tetrachloride delivery tube (which was wrapped with heating tape) was heated to prevent condensation. The various gas bottles were checked to ensure that they contained sufficient gas for the experiment, then any lines that had been opened were purged. The ventilation system was switched on and used to evacuate the air from the collection bag. The bag was then filled with nitrogen via the reactor and torch, evacuated again and its tap closed. The anode and cathode water cooling circuits were switched on, argon was passed through the torch which was then started. When it was running satisfactorily the plasma gas was changed to nitrogen, and adjusted to 20 litres per minute. The torch was run through to the ventilation system for about 20 mins to warm up the reactor. The thermocouples on the brass sheath were read periodically until the temperatures steadied, and then the readings were compared with the previous run. The injector propellant gas was switched on, usually argon at a flow of 5 litres per minute. Argon flow was switched through the by-pass tube at a flow of 1 litre per minute. The



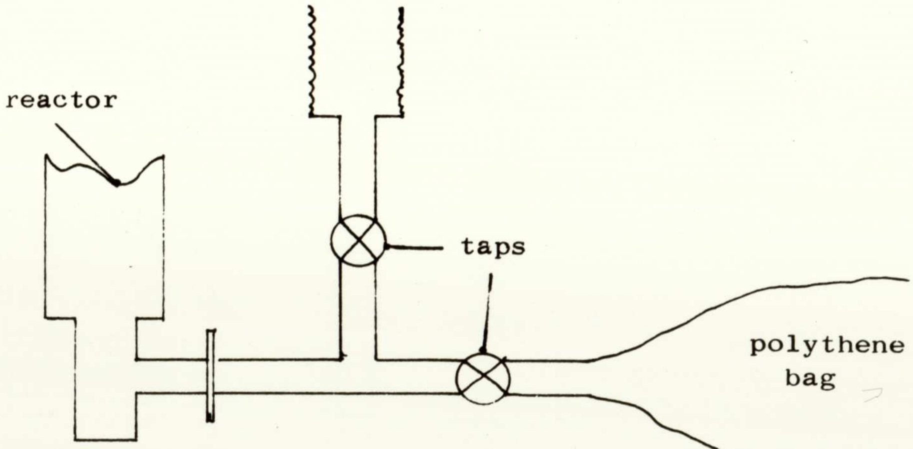


Fig. 38. The collection system used for the yield experiments.

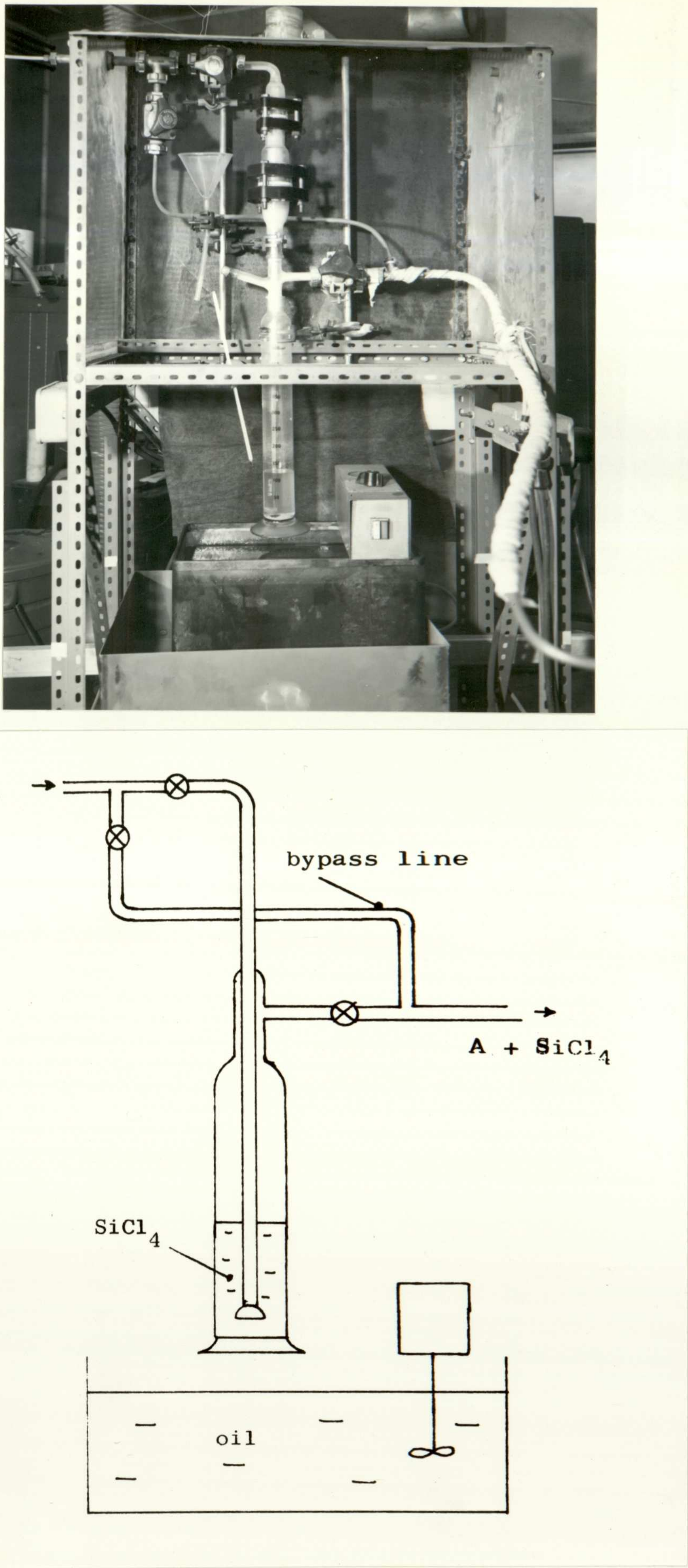


Fig. 39. The volumetric reactant delivery vessel.

ammonia flow was switched on and adjusted to 3 or 4 litres per minute, then the by-pass valve was closed so that the argon passed through the bubbler. The tap to the collection bars was opened and that to the ventilation system closed. The reaction was allowed to procede until the collection bag was full, which normally took about 10 minutes. During this time a constant check was kept on all the gas flows to maintain them at the required value. When the bag was full the tap to the ventilation was opened and that to the bag shut. The reactant flows were turned off and the thermocouple reading across the torch taken. The torch power was then switched off, and the milli-volt meter which was giving the differential thermocouple reading watched closely. The needle fell and after a few seconds settled to a new steady value. This value was recorded, and represents the amount of heat which was flowing into the coolant water from the reactor.

The difference between these two values represented the amount of heat which was flowing into the cooling water via the torch nozzle. The cooling water had to be kept on for up to three quarters of an hour, while the reactor cooled down.

The powder in the collection bag, which was present as a suspended fume or fog was given time to settle out. This took up to three or four hours. When the gas in the bag had cleared it was gently evacuated via the ventilation system. The bag was then removed and reweighed, put back on the apparatus and filled with nitrogen, when the powder was brushed and a sample taken for analysis.

The ammonia bottle was reweighed, and the new level of silica tetrachloride noted. The amounts of reactants used during the experiments were calculated from the differences in the readings.

2.6. EXPERIMENTAL RESULTS AND THEIR INTERPRETATION

2.6.1. Measurements of yield and properties

The experimental data is recorded on a duplicate sheet as it is taken, to avoid confusion. A specimen record sheet is shown in (Fig 40). When a specimen has been taken for analysis, it may be divided into three parts - one, the largest, for chemical analysis, another for measurement on the nitrogen absorption surface area meter and a third for dispersion in liquid and display on a carbon grid in the electron microscope.

Chemical analysis is made for Chlorine, Ammonium ion, total nitrogen and silicon in the first instance. The difference between the total nitrogen

Run No Log Book p Date

Object of Expt.

Plasma Torch

	Gas Flow L/min.	Pressure p.s.i.	Corrected flow (S.T.P.)
N_2			
H_2			
A			

Position of injector from torch cm Mixing length cm

Current I =	A
Volts (-2.5)=	V
Power W =	kW

Differential T-C, V_1 =	mV
" V_2 =	mV
$\therefore \Delta V$ =	mV
Power to water L =	kW

$(\times 31.65 \ \frac{kJ/sec}{mV})$

$$THEFF = \frac{W-L}{W} = \qquad = \qquad \%$$

$$HNT3 = \frac{W-L}{N_2 \ (L/min)} \times 1.34 \times 10^3 \ kJ/mole$$

$$= \qquad kJ/mole$$

T2 = °C. ∴ HNT1 = kJ/mole
T1 = °C. ∴ HNT2 = kJ/mole

	Gas Flows	Pressure p.s.i.	Corrected (S.T.P.)
Injection A			
$SiCl_4$ A			
NH_3			

$SiCl_4$

Bath Temp. = °C.

Partial p = mm

Volume $SiCl_4$

Before =	ml
After =	ml
Used = x	ml

Wt. of NH_3

Before =	gm
After =	gm
Used = y	gm

$$\frac{SiCl_4}{NH_3} = \frac{1.48x}{y}$$

Density $SiCl_4$ = 1.48

Stoichiometric mass ratio = 1.665

Si_3N_4 weight assuming 100% reaction of $SiCl_4$ = x x 1.22
= gms.

Collection Bag wt.

After =	gms
Before =	gms
Collected =	gms

Yield (UF1) = %

Reactor surface T profile °C.

T_1	T_2	T_3	T_4	T_5	T_6	T_7

Sample Analysis

Solid

Gas

ig. 40

and the nitrogen as ammonium ion is assumed to nitride of silicon, which allows the silicon bound to nitrogen to be calculated. Any silicon left over, as there usually is, may be present as elemental silicon or silica. From this point each sample has to be treated in an individual manner, the object being to obtain a total analysis figure of over 95%. The detailed methods of analysis are described in Appendix Two.

The method of dispersion of the sample for examination under the electron microscope is as follows.

A drop of ethylene glycol is put onto a glass microscope slide, and some powder sprinkled over it. The powder is stirred into the liquid. A second slide is pressed over the mixture to spread it out. The slides are separated, and an electron microscope support grid already covered with a carbon film, is dropped onto the film so that some of the mixture adheres to it. The film is then allowed to dry in air, and is then ready for examination.

The surface area, measurement is made with an 'AREA-meter' manufactured by STROHLEIN & Co. About 0.5 gm powder is degassed by heating to 350°C under vacuum or dry nitrogen flow in a small glass vessel. The vessel and a comparison vessel of equal volume are filled with nitrogen at ambient pressure and cooled down to liquid nitrogen temperatures. A manometer connected between the vessels measures the pressure differential caused by adsorption of nitrogen by the powder. The amount of nitrogen adsorbed by the sample can be calculated from the pressure difference and the filling pressure (ambient). The surface area of the sample is determined by a single point evaluation using a supplied nomogram.

If the individual powder particles are assumed to be spheres of equal diameter, their diameter can be calculated. The electronmicroscope is used to check this assumption.

One further measurement may be made on a sample, and that is the loss of weight when heated to 350°C for an extended period (two hours) Ammonium chloride dissociates at 325°C, giving an independent measurement of this substance. However, as it was noticed during the absorption measurement above, the ammonium chloride is considerably adsorbed onto the huge specific surface area of the powder. and is not easily dislodged by heat along. This method is liable to grossly underestimate the amount of ammonium chloride in the powder unless the heating is performed under vacuum.

A summary of three experimental results is shown in Table 2, and electromicrographs of the powders in Figs 41, 42 and 43.

TABLE 2 SUMMARY OF SIGNIFICANT EXPERIMENTAL RESULTS

Reference Number	Torch Power/kW	Torch Efficiency %	Plasma Gas and Flow L/min	$SiCl_4$ flow L/min	NH_3 flow L/min	% Yield of Si_3N_4 by collection	Powder surface area m^2gm^{-1}	Powder size and Shape
R9	15.5	53	N_2 22	0.5	8	19	41	Mostly agglomerates of 20mμ particles. See Fig 41.
R10	16.0	55	N_2 22 H_2 1	0.5	9	11	47	Agglomerates of 10 to 50mμ particles and very long 0.2μ diameter tubes. See Fig 42.
R11	15.8	49	N_2 22	0.5	5	18	38	Agglomerates of 20 to 50 mμ particles and very long 50mu diameter tubes. See Fig 43.

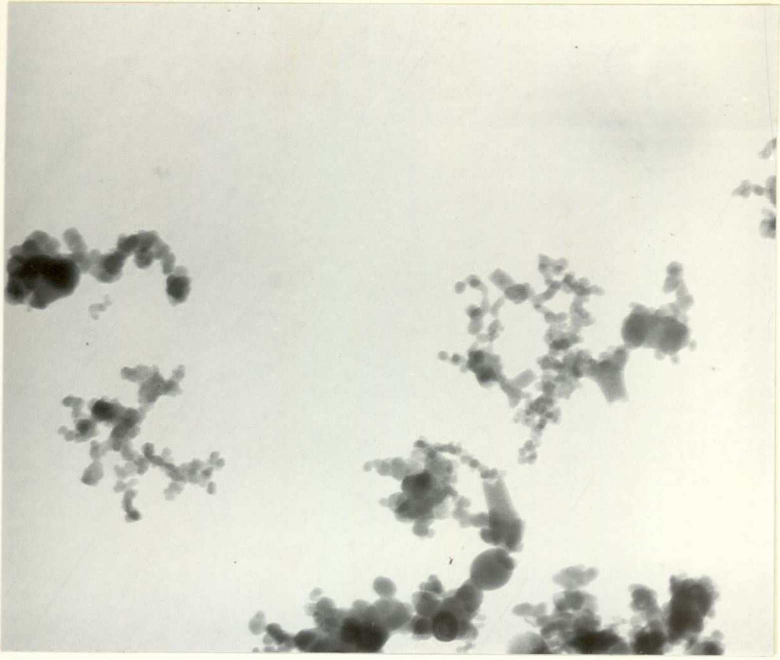


Fig 41. R.9.

Fig 42. R.10.

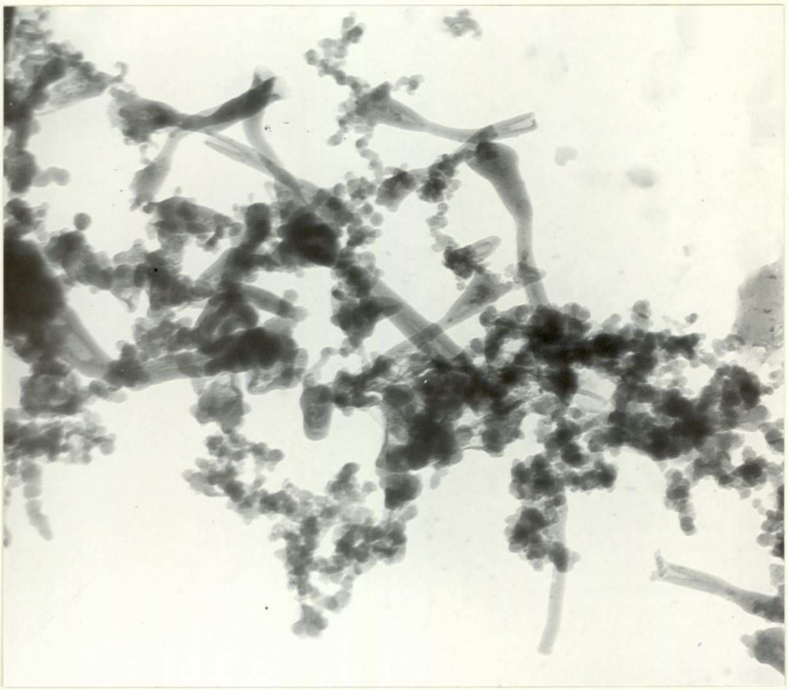


Fig 43 R.11.

0·2μ

An example of a detailed chemical analysis of a particular sample is shown in Table 3 below.

TABLE 3 : Results of Analysis on specimen R9, per cent

Wet Analysis	
Silicon	36.6
Total Nitrogen	20.0
Sol N as NH_4	2.3
Soluble Chloride	11.8
X-ray Fluorescence (for metal radicals)	
Zinc	> 5
Lead	$\simeq 1$
Tin	$\simeq 0.5$
Cadmium	$\simeq 0.5$
Copper	$\simeq 1.0$
Nickel	trace
Iron	trace
Titanium	trace
(plus silicon and chlorine)	

The following deductions may be made from Table 3.

The nitrogen as nitride is 18.2%, giving 45.5% Si_3N_4. There is an amount of un-nitrided silicon of 9.3%. If the soluble nitrogen is as NH_4Cl, there is 7.3% of chlorine unaccounted for. A sample ignited for two hours at 350°C still contained appreciable chloride. The X-ray fluorescence produced ample radicals to account for this, which must be introduced by the action of $SiCl_4$ vapour on various metal components e.g. the injector.

The loss on ignition at 350°C was 15.7%, which if 6.8% was NH_4Cl must have been 8.9% H_2O.

The amount of $SiCl_4$ used was 60.8 gm, which should produce 16.7 gms Si_3N_4. The collector contained 7.0 gms material, giving 3.18 gms Si_3N_4. The collected yield of Si_3N_4 was 19%. The overall yield must have been higher, as some solid accumulates in the reactor.

An analysis of the gas left in the collector bag after the powder had settled, made two points clear.

1) There is no silicon tetrachloride fume in the collected gas products.

2) There is no ammonia in the collected gas products.

2.6.2. Determination of the reaction scheme

The reaction scheme which is consistent with these results is as follows (ignoring balance).

In the injector,

$$SiCl_4 + NH_3 \longrightarrow Si(NH)_2 + SiCl_4 + NH_4Cl + NH_3$$

In the reactor,

$$Si(NH)_2 \longrightarrow Si_3N_4 + NH_3$$

$$SiCl_4 \longrightarrow Si + 2Cl_2$$

$$2NH_3 \longrightarrow N_2 + 3H_2$$

$$2NH_4Cl \longrightarrow 2HCl + N_2 + 3H_2$$

$$H_2 + Cl_2 \longrightarrow 2HCl$$

If the fraction of $SiCl_4$ which is converted to Si_3N_4 is x, which is calculated from the weighed products and measured consumption, then the overall reaction including balance is;

$$
\begin{aligned}
3SiCl_4 + 18NH_3 \longrightarrow\ & x\,Si_3N_4 + 12xHCl + 7xN_2 + 21xH_2 \\
& + 3(1-x)Si + 12(1-x)HCl + 9(1-x)N_2 \\
& + 21(1-x)H_2
\end{aligned}
$$

which reduces to,

$$3SiCl_4 + 18NH_3 \longrightarrow x\,Si_3N_4 + 3(1-x)\,Si + 12HCl + (9-2x)N_2 + 21H_2 \qquad .....2.6.$$

This is the equation which is used to calculate the heat of formation of the reaction, taking into account the yield of silicon nitride.

An examination of eqn (2.6.1.) suggests a method of calculating the yield of Si_3N_4, assuming that a representative sample has been taken for analysis.

The molar ratio of Si_3N_4: Si is as $x : 3(1-x)$

So the ratio by weight is $\dfrac{Si_3N_4}{Si} = \dfrac{140x}{84(1-x)}$

i.e. $R = \dfrac{5x}{3(1-x)}$

Rearranging, $x = \dfrac{3R}{5 + 3R}$

Applying this to sample R9 (Table 3),

$$R = \frac{45.5}{9.3} = 4.89$$

and $x = 0.745$

which gives a yield figure of 74.5%. Applying this analysis to R10 and R11 (Table 2), gives

TABLE 4. COMPARISON OF EXPERIMENTAL AND CALCULATED YIELD

Sample	Yield calculated by collection	Yield calculated from analysis
R9	19 %	74.5%
R10	11 %	51.3%
R11	18 %	80.4%

These differences in yield are to be expected if, as inspection of the reactor verified, products are collected on the inner surface of the reactor.

The low yield of run R10 was associated with hydrogen in the plasma gas, and a high silicon content in the specimen. This suggests that some Si_3N_4 may have been dissociated by overheating.

Interpretation of the reaction thermodynamics into FORTRAN

At $1500^\circ K$, the heats of formation ΔH°_f of the reactants and products as given in the JANAF thermochemical data tables give an overall value for the reaction as,

$$\Sigma \Delta H^\circ_f \text{ at } 1500^\circ K = 444.4 - (179.5\ x) \text{ kcal/mole of } Si_3N_4 \qquad \text{........2.6.2.}$$

and the heat required to raise the reactants to this temperature is,

$$\Sigma (H^\circ_{1500} - H^\circ_{298})_{\text{REACTANTS}} = 619.2 \text{ k cal/mole of } Si_3N_4 \qquad \text{........2.6.3.}$$

In order to include these quantities in a FORTRAN program, the variable names assigned to them are SIGHF and RENTH. The sum of these quantities is the total amount of heat energy required to perform the reaction at $1500^\circ K$, and is designated HEAT. The variable x is designated UFI.

$$\begin{aligned} \therefore \text{HEAT} &= \text{SIGHF} + \text{RENTH} \\ &= +444.4-(179.5 \times \text{UFI}) + 619.2 \text{ k cal/mole} \\ &= (\text{SIGHF} + 619.2) \times 29.9 \text{ kJ/Kg of } Si_3N_4 \qquad \text{........2.6.4.} \end{aligned}$$

This equation is used in section 5.2.2.

2.6.3. Determination of the reaction scheme for TiN

Time did not permit experimental evaluation of the yield of TiN, but a visual comparison between the polythene sack in which a sample was collected and the result of a silicon nitride experiment, indicated that the amounts of material collected were similar. A yield figure of 20% is assumed for the purposes of the cost calculations.

The experiments described in section (2.5.2.) concerning the rates of reaction of $TiCl_4$ vapour and HN_3 gas, showed a high degree of similarity between this reaction and the $SiCl_4/NH_3$ reaction. No reference to a formula for titanium imides has been found in the literature; in fact the only reference to the existence of 'titanimides' is by HARNISCH, HEYMER and SCHALLUS (section 2.4.2.).

ROSENHEIM and SCHUTTE observed that $TiCl_4$ and NH_3 react in the ratio 1 to 6. They claimed that the reaction was;

$$TiCl_4 + 6NH_3 \longrightarrow TiCl_4 \cdot 6NH_3 \qquad \text{...........2.6.5.}$$

The product was an amorphous yellow powder, called titanium tetrachloride hexamine. If this were so, it is likely that heating would cause the ammonia molecules to be detached, rather than form TiN. The state of present knowledge on the chemistry of $TiCl_4$ reactions with ammonia is similar to the situation pertaining to $SiCl_4$ and ammonia before the work of BILLY. The experimental work described in (2.5.2.) has shown the formation of TiN.

Therefore, it is suggested that the reaction scheme is analogous to that of $SiCl_4$, taking place in two parts. In the first part the intermediate Titanium-diimide is formed;

$$TiCl_4 + 6NH_3 \longrightarrow Ti(NH)_2 + 4NH_4Cl \qquad \text{..........2.6.6.}$$

which on heating the reactor yields titanium nitride, hydrogen and nitrogen, (ammonia being unstable at the reaction temperature).

$$2Ti(NH)_2 \longrightarrow 2TiN + N_2 + 2H_2 \qquad \text{..........2.6.7.}$$

The overall reaction, including the dissociation of the NH_4C_1 and a yield factor x, is.

$$TiCl_4 + 6NH_3 \longrightarrow xTiN + 4HCl + (1-x)Ti + \frac{(6-x)}{2} N_2 + 7H_2 \qquad \text{....2.6.8.}$$

2.6.4. Interpretation of reaction thermodynamics into FORTRAN

The value of $\sum \Delta G^o_f$ for this reaction, with x = 1, was calculated and is shown in Fig 44. TiN melts at 3250 K, so to avoid the formation of molten droplets, the injection temperature T_1 is chosen as 3000 K. The reaction should proceed favourably at 1000 K, so this is taken as T_2. T_3 is assumed to be the same as for the Si_3N_4 experiments, giving a value for HNT3 of 322 KJ/mole of nitrogen.

The energy required to bring the reactants to 1000 K is RENTH in the cost model, and is $\sum(H_{1000} - H_{298})$ for $(TiCl_4 + 6NH_3)$, which from the JANAF tables is,

RENTH = +17.4 + (6 x 7.54) = 62.64 KJ/mole of TiN

The energy required to perform the reaction (SIGHF) is $\sum \Delta H^o_f$ at 1000 K, which from equation (2.6.8) is:

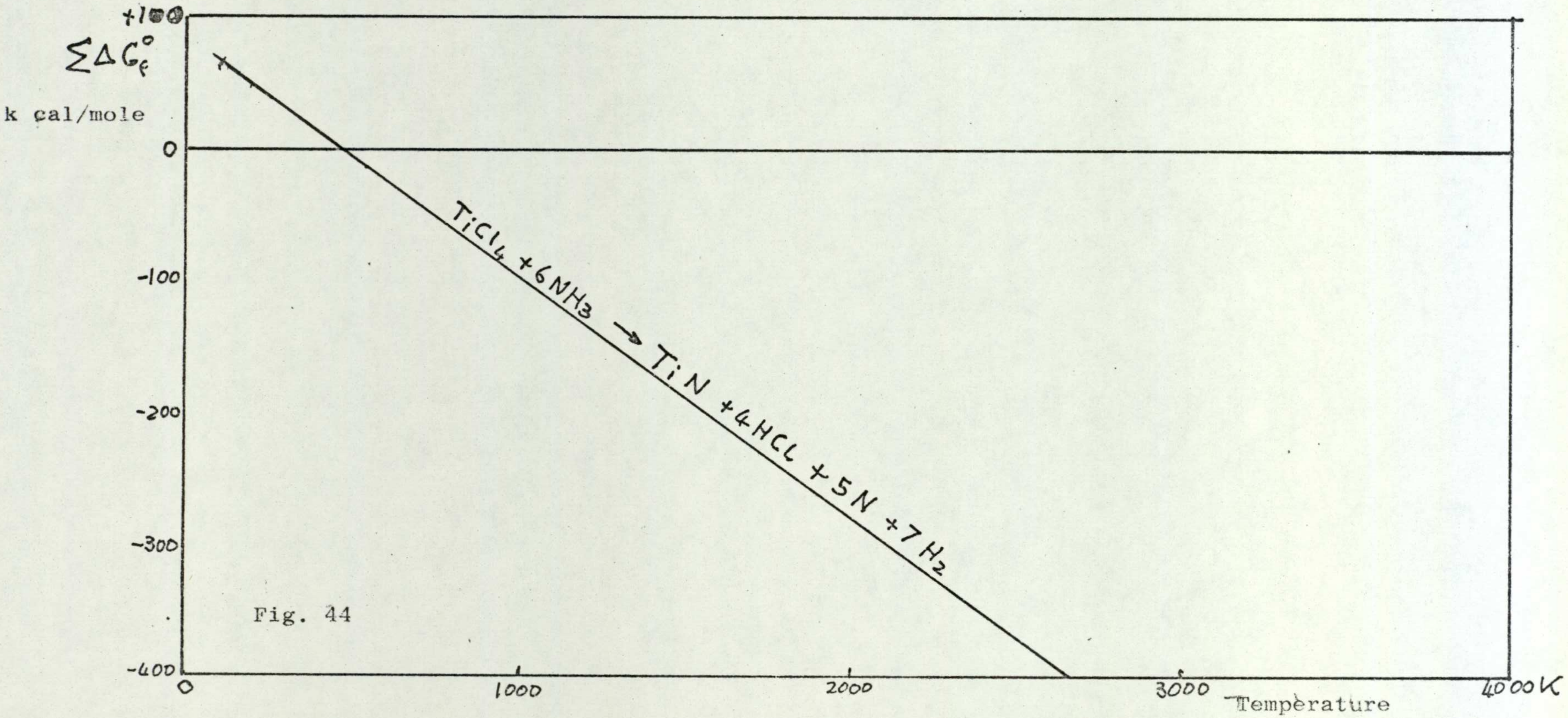

$\sum \Delta G_f^o$
k cal/mole
+100
0
-100
-200
-300
-400
0
1000
2000
3000
4000 K
Temperature
$TiCl_4 + 6NH_3 \rightarrow TiN + 4HCl + 5N + 7H_2$

Fig. 44

$$TiCl_4 + 6NH_3 \longrightarrow xTiN + 4HCl + \text{products in standard states}$$

Substituting: $-182 - (6 \times 13.5) \longrightarrow 79.8x - (4 \times 22.6)$

$\therefore$ SIGHF = + 172.6 - (79.8 x UF1)

where x = UF1

$\therefore$ HEAT = (SIGHF + 62.64) kJ/mole TiN

= (SIGHF + 62.64) x 67.6 kJ/kg TiN

This equation is used in section 5.2.2.

PART TWO

THE CONTRIBUTION OF FINE PARTICLES TO THE PRODUCTION OF MATERIALS

CHAPTER 3

Dispersion strengthened materials - production and properties

3.1. Introduction and Definitions

3.1.1. Cermets

The production of a material combining the properties of ceramics and metals has long been one of the aims of materials scientists. There is little difficulty in defining the class of materials known as metals but the definition of the work 'ceramic' has provided some problems. The United States Government Terminology Committee of the National Institute of Ceramic Engineers once defined the word 'ceramic' as a generic term encompassing those products which are composed of inorganic non-metallic mineral materials prepared and fabricated in any of a variety of methods and usually subjected to high temperatures during manufacture.'

The development of jet engines after World War 2 called for new high temperature materials. The United States Air Force consequently sponsored a research programme and insisted that the term 'cermet' be used by its research contractors. Several attempts have been made to define cermets. Task Group B on Cermets of ASTM Committee C21 suggested the following definition - ' a heterogeneous combination of metal(s) or alloy(s) with one or more ceramic phases'. This statement was accepted subject to reservations concerning the definition of ceramics. However, the ASTM Study Committee on cermets defined cermets as - 'a heterogeneous combination of metal(s) or alloy(s) with one or more ceramic phases in which the latter constitutes approximately 15-85% by volume and in which there is relatively little solubility between metallic and ceramic phases at the preparation temperature'.

3.1.2. D.S. materials

The ASTM definition of cermets automatically eliminates dispersion strengthened materials, which generally contain less than 15% by volume, of the hard or ceramic phase. A definition of dispersion strengthening anything like as precise as the A.S.T.M. definition of cermets has not been found. A general definition as suggested by LENEL and ANSELL is unlikely to be objected to:- 'A material consisting of a finely divided second phase within a metallic matrix'. There is, however, some confusion evident in the literature as to whether 'precipitation hardening' is a sub-set of 'dispersion strengthening' or vice-versa. GRANT and PRESTON consider that D.S. materials do not constitute a new class in themselves, but are rather metallic materials modified in a particular way. In this thesis, the following classifications are used:

1 A dispersion strengthened (D.S.) material is a metal which has been modified by the presence of a discontinuous second phase, which is harder than the matrix metal.

2 D.S. materials are classified according to the method by which the dispersion of the second phase in the matrix is achieved.

The only reason for the presence of the subject of dispersion strengthening in this thesis, is as an application for ultrafine particles. For this reason, no mention is made of precipitation hardened materials except in the sections on the history and theory of D.S. materials. Also, precipitation hardening is usually caused by the presence of an intermetallic second phase, and such powders are not readily made in the size range required of a dispersant. If they were, they would be very reactive and difficult to handle. The detailed survey of D.S. materials presented in section 3.6. and 3.7. is restricted to materials whose dispersant could be produced as a fine powder by known methods, and preferably by condensation from a vapour phase. In this way a comparison of the various methods of introducing a dispersant can be made, and those materials identified which can best (or cheapest) be produced by the introduction of a ready made dispersant.

3.1.3. Production of cermets

As cermets are not naturally occurring materials a suitable method of bringing the constituents together has to be found. A thorough mix may be achieved in the liquid phase by producing a colloidal suspension, or in the solid phase by ball-milling or some other mechanical mixing method. Once this mix has been densified and hardened a cermet material has been produced. One process which does not require mixing is infiltration. A porous skeleton of the ceramic material is prepared and the matrix metal is then melted and allowed to infiltrate the skeleton whilst still in the liquid state. As a continuous ceramic phase is required for this process it is obviously not applicable to dispersion strengthened materials.

A colloidal suspension of a cermet material may be used to produce an intricate shape by the slip casting method. The suspension or slip is cast into a plaster mould where the suspending liquid is allowed to soak through the plaster thus depositing any desired thickness of the suspended powder onto the sides of the mould. The cast specimen is allowed to dry and harden when it is removed from the mould and fired or sintered in a furnace. This is the technique that was used to produce the famous Dresden figurines in Meissen, Germany. Whilst this technique is useful for producing holloware it is not suitable for producing materials in bulk.

Production of cermet materials by dry powder methods relies heavily on powder metallurgical techniques. The simplest and most direct way of producing a fully dense material is to produce a thorough mix of the required ceramic and metal and then to hot-press it. Hot pressing is the compaction of a powdered material under the simultaneous application of heat and pressure. The density effects of sintering and compacting are thus combined into one operation and experience has shown that the final density is greater than that achieved by cold compaction followed by sintering at an elevated temperature. Unfortunately, this direct approach is rarely obtainable in practice. First, the required ceramic and metal powders may not be available in the form required and secondly, hot pressing is not yet, by any means, a well established technique. The various ways of producing the required mixtures in powder form will be described in section (3.6.).

3.2. A review of Methods of Compaction and Densification

A state of the art discussion is given by the IRON and STEEL INSTITUTE (1958).

3.2.1. Uniaxial Pressing

The conventional method of cold compaction of a powder is uniaxial pressing. Some powder is poured into a die and is then forced to take up the internal shape of the die by the action of a ram. It is a feature of this method that the powder has to move relative to the walls of the die. The frictional force exerted on the die walls by the powder during this movement can cause severe wear, and if the height to diameter ratio of the die is large, i.e. greater than 1, density gradients may be produced in the compact. These gradients are likely to remain even after sintering, causing uneven properties in the material. This problem is usually overcome by the addition to the powder of a suitable lubricant such as paraffin wax. The wax then has to be removed before sintering as it will probably interfere with this process. If the powder being compacted is very fine i.e. in the range of 1 micron, the compaction ratio is likely to be very large (compaction ratio = the volume before compaction divided by the volume after compaction). Thus the ram may have to travel a considerable distance whilst compacting the powder and problems may be experienced in forcing the powder into the more inaccessible parts of the die. Also, if the powder is at all flaky it is likely to line-up during this compacting process, resulting in a laminated com pact. The ultimate pressure which can be applied is likely to be limited by the strength of the die which will burst under too severe a load. The combined requirements of strength shape and dimensional tolerance mean that die sets are costly items.

3.2.2. Cold Isostatic Pressing

An alternative method of compaction is isostatic pressing, so called because a uniform pressure is applied to the powder from all directions. The powder to be pressed is sealed into a bag or mould of a material which will deform without fracture, and put into a pressure vessel. Pressure is then applied to the compact by some fluid medium, either gas, or more commonly water. Water is preferred to gas because its lower compressibility means that a given pressure is reached with a shorter pumping time. Also the stored energy at any given pressure is lower in water, thus reducing the severity of an explosion in the event of a failure of the pressure vessel. As there is very little movement of the powder relative to the walls of the enclosing mould, wear on the walls of the mould is governed by the coarseness of the powder particles. Also the lack of relative movement between the powder and the die walls eliminates the need for a lubricant.

The major advantages of isostatic over conventional pressing are higher compact densities and more uniform mechanical properties. The only limit to the size of an isostatic pressing is the size of the pressure vessel. Components with undercuts or re-entrant angles can readily be pressed. The simplicity of an isostatic press with its lack of requirements of expensive die sets make it attractive as a research tool. A comprehensive review of isostatic pressing has been given by SELLORS.

3.2.3. High energy rate forming

High energy rate and explosive compacting has been reviewed by DAVIES. The principles of high energy rate forming is to store energy in the form of a compressed gas, usually nitrogen, and then suddenly to release the pressure and accelerate a ram to a high speed. High speed forming of metals developed substantially in the USA with the introduction of Dynapack machines in the 1950's. These machines were originally developed for hot forging and have maximum impact speeds of the order of 60ft/sec. They have been particularly useful for the production of large parts at a high density. A more recent development is the Petroforge machine which uses an internal combustion cycle to accelerate the ram to speed. A range of machines has been developed with impact energy from 5-50,000 ft/lbs/force. The latest design has a platen speed of 50 ft/sec, a nominal stroke of 9 ins, with a piston diameter of 8 ins.

The cycle time is 1 sec. Compacts have been produced from Swedish sponge iron powder and sintered in a tube furnace in cracked ammonia. Presintered densities of over 90% of theoretical have been achieved with iron powder. The advantages of Petroforge machines are claimed as " a high cycling rate, economical running costs, availability in a wide range of energy capacities and small physical size in relation to energy output".

Explosive charges have been used in various ways to compact powders. Montgomery and Thomas placed the charge in direct contact with the p owder and Wanbold combined explosive forming with the isostatic technique using a surplus railroad gun which was embedded in concrete with a breach exposed for loading. Titanium carbide powder was packed into rubber bags, placed in the breach that was filled with fluid, and sealed in together with a powder charge. On ignition of the charge the powder was compacted by a combination of shock waves and high pressures. More recent work has used the explosive charge to fire a piston at high speeds. Stein, et. al, working with iron powder report densities of over 99% theoretical using such a method. A small press fired by a .22 cartridge has been developed for the production of small compacts and a subsequent examination by electron microscopy.

3.2.4. Hot isostatic pressing

Hot isostatic pressing, otherwise known as gas pressure bonding, has been reviewed by SANDS HERBERT and MORGAN. They distinguish between three basic designs: an externally heated hot wall container, an internally heated hot wall container and a cold wall autoclave. The first two designs suffer from a common basic problem, viz that the vessel which has to withstand the high pressure, in this case 10-15,000 psi, has also to withstand the high temperatures. Such a combination is liable to lead to some hazardous apparatus. The third design does not have this drawback and consequently can be used at higher temperatures. The technique has been mainly confined to the consolidation of refractory substances which would otherwise need very high sintering temperatures such as tungsten, rhenium or tantalum, and for bonding an encapsulating material to a core. The powders treated in this way have to be encapsulated in a material which is plastic at the pressing temperature.

3.2.5. Rolling

A sheet of material may be produced direct from the powdered state by passing it into a specially designed rolling mill. This process is not truly continuous as the sheet produced is very fragile and needs sintering before it can be handled. Pressures of 690 MN/m^2 (100,000 psi) are readily achieved in conventional mills used for rolling sheet. The density of the sheet is dependent upon the maximum pressure experienced by the powder as it passes through the rolls rather than the time for which it experiences this pressure. A small diameter roll should produce the same effect as a large diameter roll. This is indeed the case and commercial practice is to use clusters of rollers with very fine working rollers being supported by larger idling rollers.

TUNDERMANN and SINGER rolled iron, nickel, copper and steel powders in a vertical feed, 3.35" diameter mill, The maximum density obtained was 91%, - if the roll gap was reduced further cracks developed in the edge of the strip.

3.2.6. Hot forging

The hot forging process is an attempt to achieve the excellent properties of materials fabricated by hot pressing, but at a much higher production rate. The drawback to hot pressing is a fundamental one, in that the material is heated within the press, thus tying up an expensive piece of equipment for an inconveniently long time. Alternatively, the 'green' pressing may be heated externally, transferred to a die set and struck a blow, after which pressure is sustained for a few seconds. This method is a cross between high energy rate forming, hot pressing and sintering, as sintering may occur during the heating process.

The process and its advantages over wrought forging for the production of metal components have been described by BROWN and JONES. Advantages include fewer stages of production, improved detail and surface finish, less wastage of material, homogeneous properties and high production rate.

3.2.7. Sintering

The sintering process has been the principle densification process in powder metallurgy for many years. Sintering was defined by JONES as increasing the extent of adhesion of a loose mass of powder. If densification is required as well, then the particles must undergo changes in shape to permit further adhesion. Such deformations may be by virtue of internal stresses such as surface tension, or under applied stress.

The mechanisms governing sintering rate and final density are complex, and not well understood. The important parameters are temperature, time, particle size and shape, and atmosphere. At a given temperature, initial density increase is rapid, the rate falling off until a steady value is reached. If the temperature is increased, the process is repeated, as shown in Fig 45.

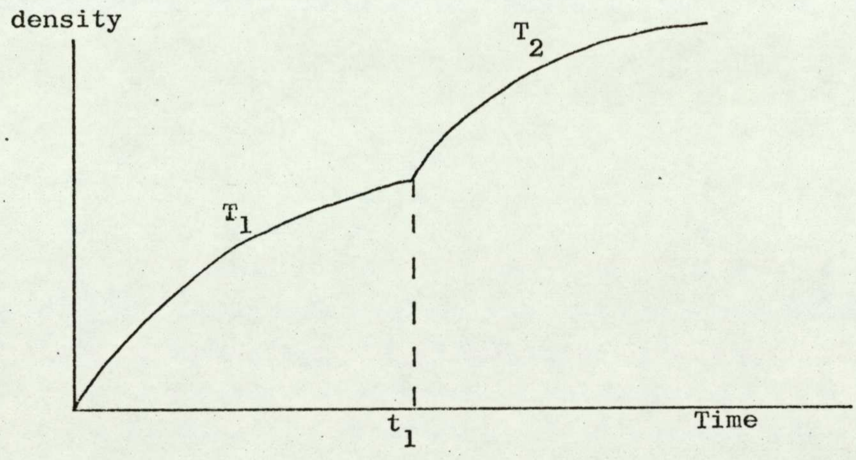


Fig. 45.

The presence of inclusions, such as a dispersant, affect both the sintering rate and final density. JONES has observed that pores shrink only as long as they are connected to grain boundaries, but the higher the sintering temperature the greater the tendency to grain growth, leaving fewer boundaries. Pores trapped inside grains cannot be filled. Inclusions pin grain boundaries, assisting the removal of pores. KUCZYNSKI studied the effect of oxide particles on the sintering of metallic compacts, and concluded that exaggerated grain growth occured at a higher temperature when such particles were present. In a pore matrix, this temperature is about 0.7 Tm.

MOZZHUKHIN studied the stability of dispersed refractory particles and fibres. He noted a tendency for the inclusions to coagulate at elevated temperature:- sintering an Al_2O_3/Fe system above 1250 °C for 4 hours caused coagulation and a decrease of strength in the sample. SINGH and HOUSEMAN also sintered iron + 1$^{W/O}$ alumina compacts, and found by studying the carbon extraction - replica electron-micrographs that 5 to 30mμ alumina agglomerated to 100mμ after 300 hours at 1000°C, and to 200 and 600mμ after 2 hours at 1200°C and 1300°C respectively. They concluded that the increased density which they had obtained at temperatures over 1400°C was partly explained by this agglomeration. It would appear that the aim is to ensure a good dispersion of the powders initially, then sinter for as short a time as possible close to the melting point of the matrix in a suitable atmosphere. This has been proved in the experimental work described in section (4.5.2).

3.2.8. Extrusion

In the extrusion process, which may be carried out hot or cold depending on the material, a cylindrical slug of the material (radius R) is placed in a strong chamber and forced through a small axial hole or die (radius r) under pressure. The operation is very similar to that of a hand operated grease gun. The ratio $R^2:r^2$ is known as the extrusion ratio, and may be as high as 30:1.

The material undergoes severe deformation, and is commonly used to produce non-circular sections in soft materials like aluminium and copper. It is specially favoured in the production of D.S. materials because the deformation promotes mixing, the reduction of grain size, and densification. The dies are expensive, and the process may be slow, as in the case of S.A.P. (see section 3.7.1.).

3.3. COSTING OF COMPACTION AND DENSIFICATION METHODS

The general form of the cost equation used is described in Appendix 4. The cost of the material being processed is omitted, so that each process can be fitted into an overall production route as described in section (4.1). Unless the material being pressed is specified, it is impossible to express the processing costs in terms of weight of material produced. However, the compaction methods described work at constant volume input, so the cost is expressed in terms of volume of material produced , which can be converted to a cost of production in £/kg for a specific material by substituting its density into the appropriate equation. The equivalent volume is the volume which the produced material would have if it were at full density.

3.3.1. Uniaxial pressing

The cost components are as follows:

Variable costs - Materials - Electrical power.
Consumables - Die set.
Fixed costs - Capital and maintenance
Labour and overheads.

Let, Maintenance costs = £0.1 C_D p.a.
Electric power charge = £E per hour
Equivalent volume perpressing = V per piece
Life of die set = x pieces

Then, with the notation set out in appendix 4,

$$P.C. = \frac{1}{V} \left[\frac{E}{S} + \frac{D}{x} + \frac{1}{\bar{S}H\eta} \left(C_{dm} + C_{LOH} \right) \right] \quad £m^{-3}$$

If the die set is height h cm, radius r cm, and the powder has a compaction ratio c and the green pressing a fractional density d,

Then,

$$V = \frac{\Pi r^2 hd}{C} \times 10^{-6} m^3$$

3.3.2. Cold Isostatic Pressing

The cost components are:

Variable Costs - materials - electric power
- consumables - oil as lubricant
- pressing sacs
Fixed costs - capital and maintenance
- labour and overheads

The cost equation is as for uniaxial pressing, except that,

D = cost of pressing sac (£ each)
f = cost of lubricating oil (£ per hour)

$$\therefore P.C. = \frac{1}{V} \left[\frac{E + f}{\bar{S}} + \frac{D}{x} + \frac{1}{\bar{S}H\eta} \left(C_{DM} + C_{LOH} \right) \right] \quad £m^{-3}$$

Let, $C = £7000$

Then $C_{DM} = \dfrac{7000 \times 1.1}{7}$ £ p.a.

For one man operation, $C_{LOH} = £3000$

with, $H = 2000$

and, $\eta = 0.7$

Let $f = £0.2$ per hours

and $E = £0.1$ per hour

$D = 5p$ each

and $x = 5$ pressings

The press capacity is 4 sacs where

$h = 60$ cm

$r = 2.5$ cm

Now the equivalent volume per pressing,

$$V = \frac{\pi r^2 hd}{C}$$

$$= 1180\frac{d}{C} \text{ cm}^3$$

The cycle time is 15 mins

$$\therefore \bar{S} = 16 \text{ per hour.}$$

Substituting, P.C.
$$= \frac{c10^6}{d \times 1180}\left[\frac{0.1 + 0.2}{16} + \frac{0.05}{5} + \frac{(1.1 \times 1000) + 3000}{16 \times 2000 \times 0.7}\right] £m$$

$$=$$

$$= 179 \times \frac{c}{d} \quad £m^{-3}$$

For sub-micron iron powder, experiments have shown values of

$C = 8$

and $d = 0.8$

so with $\rho = 7870$ kg m^{-3}

$$. \text{ P.C.} = \frac{179 \times 8}{7870 \times 0.8} \quad £kg^{-1}$$

$$= 0.23 \text{ kg}^{-1} \text{ for sub-micron iron.}$$

3.3.3. Hot isostatic pressing

The cost components are

Variable costs - Material - Heating power, usually electrical
Pressing power
controlled atmosphere

- Consumables - Cans

Fixed costs - Capital and Maintenance
Labour and overheads

It is usual practice to prepare the charge by cold isostatic pressing, so as to minimise the compaction ratio and make best use of the slower, more expensive process of hot pressing. The green pressing is pre-heated and put into the vessel, which is pressurised with argon. The final density is assumed to be 100%, and the original density 80%.

The general form of the cost equation is as for cold isostatic pressing:

$$C.P. = \frac{10^6}{V}\left[\frac{f + E}{\bar{S}} + b + \frac{(C_{DM} + C_{LOH})}{\bar{S}\,H\,\eta}\right] \qquad £m^{-3}$$

(with V in cm^3)

The following figures are approximate, being based on discussion with GTC personnel.

Let, Capital Costs = £300,000
Plant life = 7 years
$\therefore\ C_D = \frac{3 \times 10^5}{7}$ p.a.

Let, $C_m = 0.3\ C_D$
then, $C_{DM} = 1.3\left(\frac{3.10^5}{7}\right)$ p.a.

Working two shifts, with two men on each,
$H = 4000$ hrs
and C_{LOH} = £12,000 p.a.
Electrical Power = 20 kW
$\therefore$ at 1p per unit, E = £0.2

Machine efficiency $\eta = 0.5$
Cycle time = 4 hours
$\therefore\ \bar{S} = 0.25$
Canning cost b = £5
Argon cost f = zero if the gas is recycled.

The equivalent volume per pressing, is

$$
\begin{aligned}
V &= \frac{\Pi r^2 hd}{C} \\
&= \frac{\Pi \times (0.15)^2 \times 2 \times 1}{1.25} \quad m^3 \\
&= \underline{\underline{0.113\ m^3}}
\end{aligned}
$$

$$
\begin{aligned}
\therefore\ P.C. &= \frac{1}{0.113}\left[\frac{0.2}{0.25} + 5 + \frac{1}{0.25 \times 4000 \times .5}\left(\frac{1.3 \times 3 \times 10^5}{7} + 12000\right)\right] \\
&= \frac{1}{0.113}\left[0.8 + \pounds + \frac{10^4}{500}\ (5.57 + 1.2)\right] \\
&= \frac{1}{0.113}\ (5.8 + 135) = \pounds 1250\ m^{-3}
\end{aligned}
$$

It can be seen that the high capital costs and low cycle time dominate the total costs, so if more accurate figures are required, those are the important factors to be investigated.

For iron at 7870 kg m^{-3}, the cost per kg would be,

P.C. = £0.16 per kg.

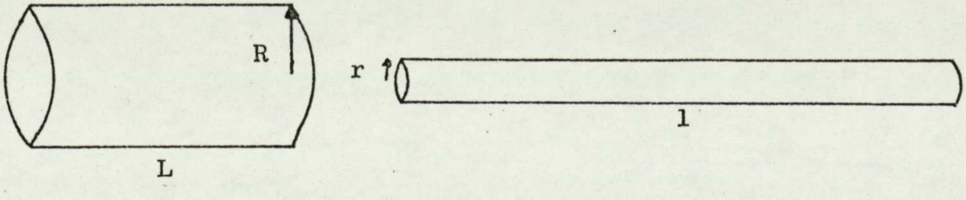
3.3.4. Extrusion

The cost components are:

Variable costs - Materials - Electric power
- Consumables - Die Sets

Fixed Costs - Capital and Maintenance
- Labour and overheads.

The production of cylindrical shape is taken as the most simple example. A short slug is extruded at a ram velocity v, and reduced from radius R to r;



Let Electrical costs = £E pa

Die costs = £D each

Die life = x shots

Capital plus maintenance = $\frac{£1.3C \text{ pa}}{7}$

η = 0.7

Annual production = n pieces

Mass of one piece, m = $\pi r^2 l \rho$

where ρ = material density.

$$\text{Then, P.C.} = \frac{1}{mn}\left[E + \frac{Dn}{x} + \frac{1.3C}{7} + C_{LOH}\right] \quad £/\text{kg}$$

The following cost figures are approximate, based on discussions with G.T.C. personnel.

BOVARNICK and FLOOD extruded iron/alumina compacts at 1075°C, 19:1 and a pressure of 60 T.S.I.

Let the required product be a 1" diameter rod, 10ft long.

Rod area = $\pi(\frac{1}{2})^2 = \frac{\pi}{4}$ sq. ins.

Total force required = $(\frac{\pi}{4} \times 19 \times 60)$ tons

$\approx$ 900 tons force.

The cost of such a press will be in the region of £100,000, and two men will be required to run it.

Let the total cycle time = 2.5 mins

Die replacement time = 5 mins

If x = 10

Then $\bar{S}$ = 20 pieces per hour

If H = 4000 hrs per year

then n = $\eta H \bar{S}$

= 2800 x 20

= 56,000 per year

$$m = \frac{\Pi\ 120\ 16.4.\ 7.8}{4 \quad \times 1000}\ \text{kg}$$

$$= 12.05\ \text{kg}$$

.˙. A furnace has to heat 240 kg per hour (approx 0.25 tons). Assume it is 50 kW. The cost of a belt furnace could be £20,000, and require one man to run it.

Let, D = £50

E = £1 per hour (including the press)

= £2800 p.a.

$$\text{Then P.C.} = \frac{1}{12.05 \times 56{,}000}\left[1800 + \frac{50\text{x}56{,}00}{10} + \frac{1.3\text{x}120{,}000}{7} + 9000\right]$$

$$= \text{£}0.42\ \text{kg}$$

3.3.5. Summary of methods of compaction and densification of fine powders

The very low bulk density of ultrafine powders is a major disadvantage when forming them into fully dense bodies. For this reason, most of the processes just described are not suitable for primary compaction. Uniaxial pressing is liable to produce inhomogeneous density, and binding waxes are required. Cold isostatic pressing has been used successfully, and the results are described in section (4.4.2.). High energy rate forming has not been studied in relation to ultrafine powder, but it is likely to produce inhomogeneous density as the pressure is uniaxial. Hot isostatic pressing and extrusion require that the powder be canned, and it is difficult to see what will prevent the can from collapsing or pinching, especially in the case of extrusion. Rolling of ultrafine powders has not been reported, and again the high compaction ratio and resistance to flow would be a severe problem. Loose powder sintering does not usually produce dense materials, and sintering is better suited to pressed bodies. Some experimental results are given in section (4.5). Hot forging also requires a pre-pressed compact, and results are described in section (4.5.3).

If the loose powder were hot forged, it would need to be canned, and the can would almost certainly collapse on forging.

Cost equations have been developed for methods where sufficient information was available, and data put into the equations for cold and hot isostatic pressing. Cold isostatic pressing can produce an 80% dense compact (with no wax) from an iron powder with a compaction ratio of eight, for £0.23 kg. That compact can then be hot isostatically pressed to full density, for a further £0.16 kg.

3.4. DISPERSION STRENGTHENED MATERIALS

3.4.1. Introduction

Dispersion strengthening was defined in section (3.1) as the strengthening of a metal matrix by a finely divided second phase. A historical account of 'the role of powder metallurgy in the development of dispersion-hardened materials' is given by MARTIN. The earliest known example of dispersion strengthening is the precipitation of fine carbide particles in quenched and tempered steel - a process as old as the art of the smith. HUNSICKER and STUMPF, in a paper entitled 'History of precipitation hardening' give a similarly antique example, in the use of copper-silver alloys for Roman coins. These alloys possess extensive precipitation hardening capability but there is little evidence of this capability being recognised or used. The first patents, on palladium-copper-silver alloys, appeared in 1886, the alloys being used for hair springs, balance wheels and similar watch components, but the swiss inventor, Paillard, was ignorant of the metallurgical processes involved. The earliest discussion of the process of suppressed decomposition of a super-saturated solid solution and the subsequent hardening resulting from precipitation after ageing, is attributed to Merica, Walterburg and Scott in 1919. They studied the copper-aluminium system, which is responsible for the alloy known as Duralumin, and had previously been discovered (but not understood) by Wilm in 1906.

The development of powder metallurgy was originally closely associated with the production of tungsten metal filaments made by extruding a paste of fine powder plus binder through a die. Jeffries, in the period 1916 to 1927, produced a series of papers on the effect of finely dispersed thoria in tungsten. (The thoria was added to increase the thermoelectric emission of electrons). He observed that the thoria particles restrained the grain growth of tungsten up to 1400°C, above which temperature the particles agglomerated and grain growth proceeded. In 1921, Jeffries and Archer laid the foundations for a scientific study of dispersion hardening by proposing the phenomenon of "slip interference", in which the dispersed phase pins or keys the slip planes of the matrix material. They also discussed the order of magnitude of particle size required to effect a "critical dispersion", which they said was about 1mμ. This is smaller than the generally accepted size at present - a cube of 1mμ side and 1Å. lattice parameter contains only about 10^3 atoms, and it is doubtful whether such a group of atoms can be discussed in the accepted terms as a crystalline solid phase. So in 1921, the criteria of particle stability and size, and the effect of "slip interference", were firmly established as fundamental to a dispersion strengthened material.

3.4.2. Present and Potential applications for D.S. materials

The Table in Appendix five gives a fair representation of the dispersion strengthened materials which have been produced to date. Three D.S. materials have, to the author's knowledge, been offered for sale.

Sintered aluminium product - S.A.P.

The story of S.A.P., in the U.K. at least, is a sad one. It is one of those materials that appeared to everyone in the aluminium industry to have a bright future, but which failed to materialise. In fact there has been no backing from any of the big companies for commercial exploitation of this material, and it is now available only from ALCOA in the U.S.A. with relatively poor properties.

S.A.P. was made in this country by High Duty Alloys Ltd, for Anglo Swiss Aluminium Ltd in extruded bar stock at 6½, 10 and 13% oxide levels. There is still a small stock for component replacement purposes. The extrusion process was very slow: about 1m per minute for 5cm diameter bar. The market in the U.K. was in the high temperature components of aircraft engines, but it was very effectively superseded by the introduction of titanium alloys. A market price was never found - it was sold at about £2 kg but never in economic quantities.

Thoria dispersed nickel - D.S. Nickel

This material is available from Sheritt Gordon Mines Ltd, in sheet or powder form. The sheet is up to 61cm wide by 183cm long, either 1.1mm or 1.2mm thick, and costs £28kg, or approximately £740 per sheet.

The powder is available for £7/kg in tonne quantities, and before fabrication should be heated in dry hydrogen at 760°C for 30 mins. The material is unlikely to find applications outside the aero-space industry with a price of the order £28,000 per tonne.

Copper dispersed with BeO - Cube-Alloy

Cube-Alloy is manufactured by Handy and Harman in 1.25 cm diameter rod. Its properties are superior to beryllium copper and zirconium copper and it has 85% I.A.C.S. conductivity. It has properties which made it suitable for high temperature conductors. No prices have been supplied.

Dispersion strengthened lead is believed to be in use, but no commercial literature has been found.

The material most widely processed by the GKN group is steel, so dispersion strengthened iron is likely to be of most immediate interest. Iron matrix dispersions have been made by ball milling followed by compaction and sintering, milling followed by compaction and extrusion and reduction of iron oxide/stable oxide mixtures followed by isostatic pressing and sintering processes of varying degrees of complexity. In addition mixed nitrates have been decomposed, reduced in hydrogen, compacted, extruded in sealed cans and swaged. The dispersants used have included alumina, magnesia, silica, titania, thoria, zirconia and calcium oxide with alumina apparently the most favoured. Increases in the yield stress have been achieved both at room temperature and in the region of 500°C. (10 vol % Al_2O_3 increase in Y.S. from 173 to 717 MN/m^2). No useful applications have been claimed. This is hardly surprising since equal improvements at r oom temperatures can be obtained more cheaply by addition of carbon to produce precipitated carbide phases using conventional steelmaking and heat treatment techniques. To obtain any usable improvement, dispersion hardening techniques such as described in this table will have to be applied to already highly alloyed steel powders with the object of producing properties that cannot be made by conventional steel making techniques. The situation could change if the price of steel powder or the price of processing it dropped dramatically. The most likely area of applications is where improved high temperature creep properties are desirable.

3.5. THEORY OF THE DISPERSION STRENGTHENING (D.S.) EFFECT

3.5.1. Dislocation theory

A critical review of both dislocation and internal stress theories is given by LENEL and ANSELL. They propose a dislocation theory based on a development of a model by OROWAN. The yield of a crystalline material under stress is accompanied by the movement of dislocations through the matrix. OROWAN suggested that as a dislocation approaches two dispersed particles it bows out between them (Fig 46), until it reconnects leaving dislocation loops around the particle. The yield stress is that required to bow dislocation loops about the particles, and is therefore inversely proportional to the interparticle spacing $\bar{D}$. Experimental work showed that the value of shear stress predicted was exceeded by a large class of D.S. materials, and the dependence on $\bar{D}$ was not as predicted.

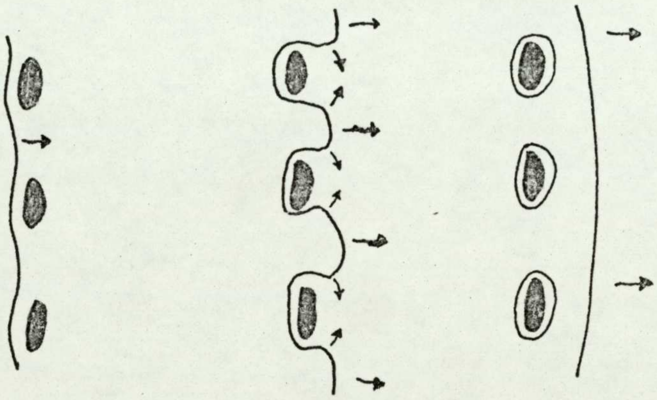


Fig. 46.

LENEL and ANSELL develop the model by postulating that yield does not follow from the mechanism described by OROWAN, but that the stress field caused by the residual loops causes 'back stress' on the dislocation source so that fewer dislocations are nucleated. Also the stress fields around the particles decrease the stress on the lead dislocation, so that it is more easily blocked. If the dispersion is sufficiently fine and distributed, yield does not proceed until the dispersed particles fracture.

Assuming that the dispersed particles present a straight barrier to piled up dislocation of large radius of curvature, i.e. straight, then the stress (r) on a particle due to an array of dislocations is given by:

$$r = n\sigma \quad ....(\text{eqn } 3.5.1.)$$

where n = no. dislocation loops at a particle

σ = applied stress.

and $$n = \frac{2D\sigma}{\mu b} \qquad \text{................(eqn 3.5.2.)}$$

where μ = shear modulus of matrix

b = Burgers vector

$$\therefore \quad \tau = \frac{2\bar{D}\sigma^2}{\mu b} \qquad \text{................(eqn 3.5.3.)}$$

The limiting stress that can fracture a particle is,

$$F = \frac{\mu^*}{C} \qquad \text{................(eqn 3.5.4.)}$$

C = a constant of proportionality, shown theoretically by COTTRELL to be approximately 30.

μ^* = shear modulus of the particles.

$\therefore$ Rearranging eqn (3.5.3) and putting $\tau = F$, the yield stress of the alloy is

$$\text{Y.S.} = \left(\frac{\mu b \ \mu^*}{2\bar{D}C}\right)^{\frac{1}{2}} \qquad \text{................(eqn 3.5.5)}$$

When the piled up dislocation have a small radius, the approach used by FISHER HART and PRY is applicable in which case the stress on the dispersed particles due to residual dislocation loops is,

$$\tau = \frac{n b \mu}{R} \qquad \text{................(eqn 3.5.6.)}$$

R = radius of a spherical dispersed particle.

The minimum radius R(min) is calculated from eqns (3.5.1 and 6);

$$R_{min} = \frac{b\mu}{\sigma}$$

and below this value, the theory does not hold.

The only terms in eqn (3.5.5) which have any appreciable temperature dependence are μ and μ^*, so the variation of Y.S. with temperature should follow,

$$\sigma_T = \sigma_1 \left(\frac{\mu_T \ \mu_T^*}{\mu_1 \ \mu_1^*}\right)^{\frac{1}{2}}$$

where the subscript $(_1)$ refers to room temperature.

3.5.2. Predictions of the dislocation theory, and experimental verification

According to eqn. (3.5.5).

$$Y.S. \propto \frac{1}{\sqrt{\bar{D}}}$$

a relation which agrees well with the plot of Fig 47 taken by LENEL and ANSELL from experimental data on several S.A.P. type alloys.

The performance of any dispersion strengthened material depends on the size, spacing and volume fraction of the dispersed phase. Fig 48 shows the purely geometrical effect of the volume per cent loading of various diameter dispersants (d) on the average interparticle distance ($\bar{D}$) in any homogeneous matrix. Notice that as the dispersants become finer the volume fraction required to maintain a given $\bar{D}$ becomes smaller, and the matrix particle size must match this value of $\bar{D}$ if the dispersion is to be homogeneous. If too much dispersant is added 'overloading' develops, and agglomerates of the dispersant may occur leading to a structural weakness.

Equation (3.5.5.) also predicts that all other things being equal the yield strength should be proportional to $(\mu^*)^{\frac{1}{2}}$. This has been verified by LENEL and ANSELL by comparing aluminium strengthened by alumina, with Al strengthened by copper-aluminium theta phase.

The variation of yield strength with temperature has been verified also by LENEL and ANSELL on data from S.A.P. type alloys within the limits of accuracy of the data available on the high temperature shear modulus of alumina.

3.5.3. Internal stress model : prediction and verifications

It can be seen from the review of D.S. materials in Appendix Five that cold working can increase the tensile strength of such materials (e.g. FRASER and EVANS). The effect is well known in single phase alloys, but is more persistent in a D.S. Material because the dispersant hinders recovery. The relative importance of stored energy (cold work) and the stress required to shear a dispersed particle is shown schematically in Fig 49, by LENEL and ANSELL.

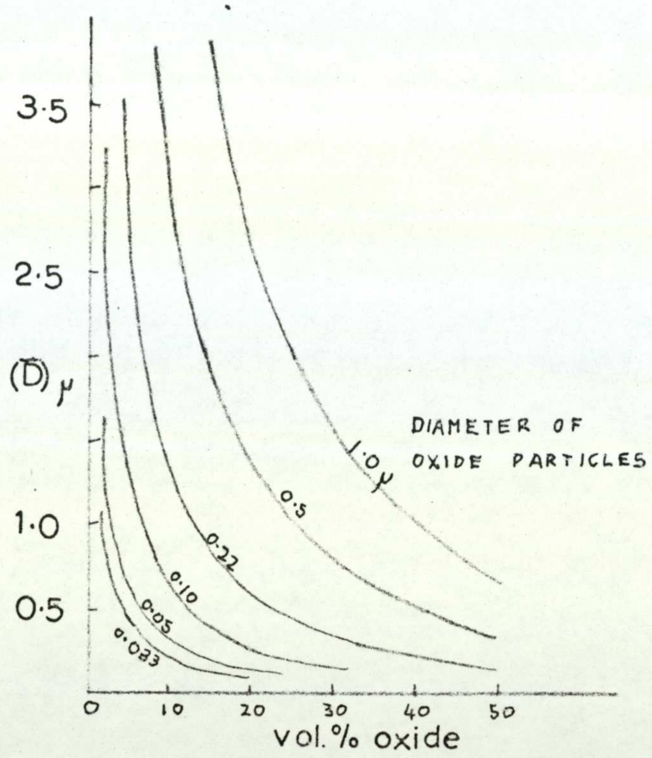

3.5
2.5
(D) μ
1.0
0.5
DIAMETER OF OXIDE PARTICLES
1.0 μ
0.5
0.22
0.10
0.05
0.033
0
10
20
30
40
50
vol.% oxide

FIG. 48.

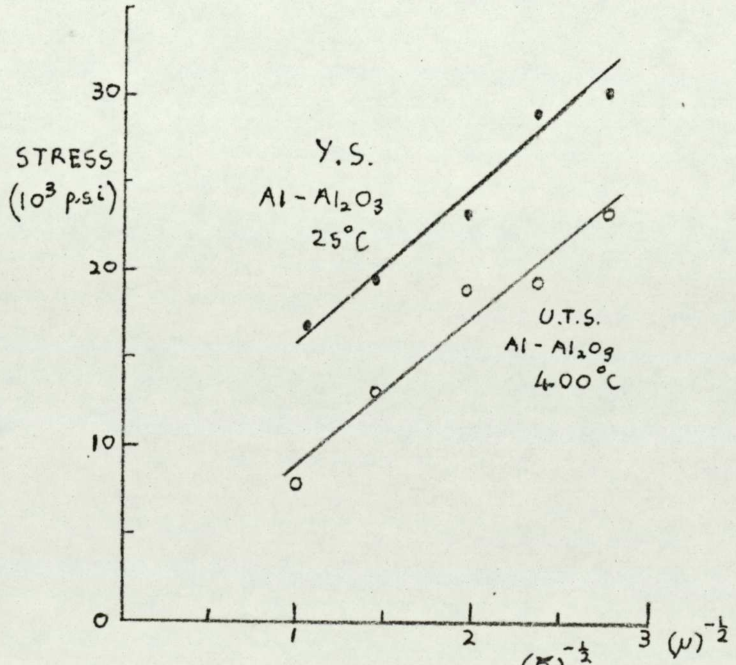

30
20
10
0
STRESS (10³ p.s.i)
Y.S. Al - Al₂O₃ 25°C
U.T.S. Al - Al₂O₃ 400°C
1
2
3
(D)^-½
(μ)^-½

FIG. 47.

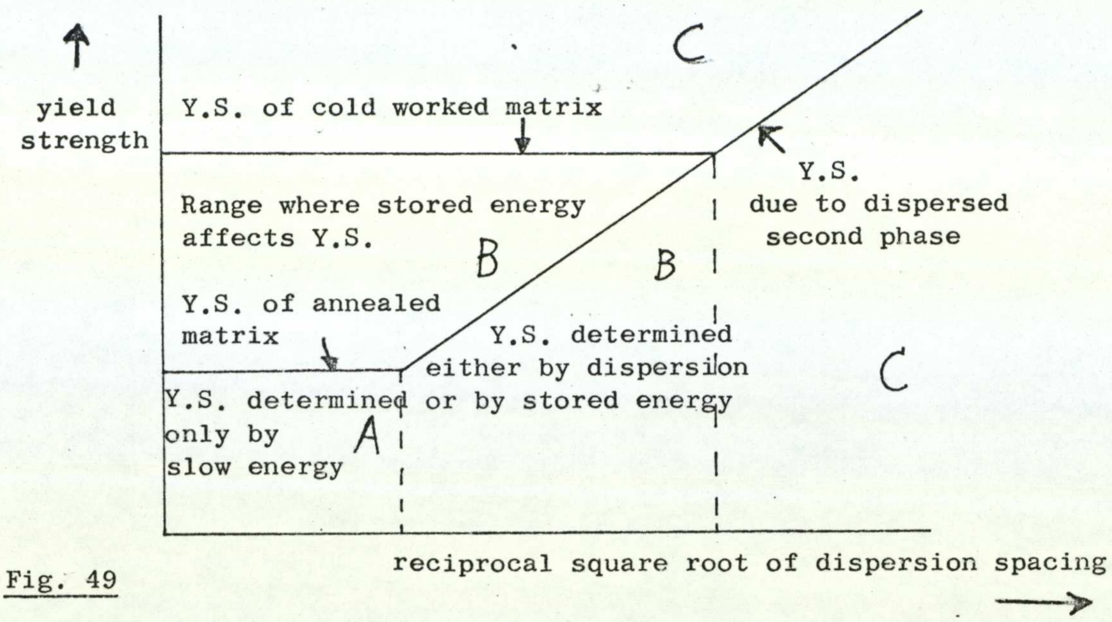


Fig. 49

They explain the scheme as representing a balance between the stress required to nucleate dislocations and the stress required to cause dislocations to fracture the particles. In region A, $\bar{D}$ is very large and the particles ineffective. In region C, the dispersed phase predominates, and region B is intermediate. The upper limit of region B depends on the values of σ and σ^* at the particular temperature.

The dislocation theory assumes that the dispersed particles are effective in pinning the dislocations. The criterion for this to happen is that the interface between the matrix and the particle is capable of transmitting the strain field, from the dislocations in the matrix, into the particle lattice. To accomplish this, the matrix needs to 'wet' the particle, or the interface can act as a matrix crystal boundary, which is an 'infinite sink' for dislocations. The phenomenon of 'wetting', which is concerned with the angle between a liquid drop and a solid surface, is not the true measure of compatability between matrix and dispersant, although it is an indication. The fundamental problem is of coherency between two crystal lattices. If the matrix and particles are not coherent, the D.S. effect is lost.

LIVINGSTON considered the critical particle size from the other end of the scale, that is from 2mμ up to 7mμ, and found that the Y.S. of copper strengthened by precipitated cobalt increased up to 7mμ. Above this value his experimental method, a magnetisation technique, is no longer of use but he applied an extrapolation method to estimate greater particle radii at later ageing times. Above 7mμ particle size, the Y.S. showed a broad maximum with a decrease barely apparent at a particle radius of 18mμ in a 3.2% Co alloy. LIVINGSTON goes on to discuss the work of Geisler (1951) who showed that an aluminium alloy containing a non-coherent precipitate showed no D.S. effect, whereas a similar system containing a coherent precipitate did. Silcock et. al. showed that the optimum hardness of an Al-4% Copper Alloy depended on the presence of the fully coherent GP [2] phase particles. The alloy rapidly lost its hardness when the GP [2] particles were replaced by the partially coherent θ' particles. (A partially coherent particle is matched to the matrix by a set of widely spaced dislocations, whereas a fully coherent particle has no dislocations at its surface). The importance of coherency was further supported by the observations of Nicholson and Nutting also on Al-Cu alloys. They obtained electron transmission micrographs which showed directly the presence of extensive internal stresses in the matrix surrounding GP [2] particles, but a complete absence of similar stresses around θ' particles.

Geisler (1949) suggested that the stress around a coherent particle has a maximum (above which the particle presumably fractures) which increases with particle size until the particle reaches the size at which it loses complete coherence. LIVINGSTON concludes that this is the effect which is responsible for the maximum in Y.S. which he observed in his Cu-Co alloys, and is the major cause of 'overageing' in such systems.

FRASER and EVANS consider that the dislocation theory is inadequate above 0.5 Tm, and for the case of T.D. nickel propose a theory based on a fibrous microstructure which is brought about during the twenty-one cold roll/anneal cycles during production. It is considered that a discussion of this theory belongs properly to the study of fibre composites, which are excluded from this thesis.

3.5.4. The important parameters of a dispersion strengthened material

The theoretical discussions of the previous sections have not included all of the important parameters which have been discovered by experimentalists. One such omission is the difference between the coefficients of thermal expansion of the matrix and the dispersant. The evidence that differential thermal expansion is a significant factor is experimental. WHITE et. al. in a paper on cermets, stated that 'experience has shown that with one system a difference of 10×10^{-6} (per ^{o}C) in coefficients of expansion caused failure, but that in some systems differences of the order 5×10^{-6} could be tolerated.' WHITE was drawing conclusions from experiments made with equal volume compositions which tend to form continuous metal and ceramic phases, and the situation in D.S. Materials is obviously different. YATES, however, in his patent on nitride refractory metal cutting tools, includes in his claims a statement to the effect that the thermal coe-

expansion of t

coefficients of expansion of the various components phases should differ by less than a factor of two. Tools made from such materials were highly resistant to heat cracking. This work bears more closely on D.S. materials, as the materials described rely on a continuous phase of a nitride bonded by a continuous phase of metal which is itself dispersion strengthened by ultrafine nitride particles.

Table 5 shows values of the coefficients of thermal expansion ($\propto$) for the metals and dispersants commonly used in D.S. materials. Where a particular combination of metal and dispersant has shown technical or commercial success, the values of α are placed on the same line, or as close as possible. Whereas the values for the metals are well established and the metals are present as a continuous phase, the values for the dispersants are not so well known and vary with phase changes. The extreme sub-division of the dispersants is another complication, and they may even be amorphous. In such cases the absolute values cannot be relied upon, and specific measurements should be made on the powder before any predictions or conclusions can be drawn about its behaviour as a dispersant in a particular metal.

Of the two really successful high temperature materials, Aluminium-Al_2O_3 (SAP) and Nickel-ThO_2 (D.S. Nickel), the former is well outside either of the limits for differential expansion quoted above, but D.S. Nickel is well within. It is difficult to make comparisons in most cases, as production methods and particle sizes vary too much, but in the rare cases where the only difference between two D.S. materials is the chemical composition of the dispersant, then the material with the closest match of thermal expansions between matrix and dispersant has given better properties, (See GRANT and ZWILSKY, ATOM-E-K, and McCARTHY, SHYNE and SHERBY).

Another point absent from the theory concerns the stability of the dispersant in the matrix. Instability can take several forms, the most obvious being chemical reaction where the dispersant actually loses its molecular structure. This is not likely to occur unexpectedly. A more subtle form is associated with solubility, in which case the dispersed particles become dissolved into the matrix on a molecular scale. This is the fate of precipitation hardened materials at elevated temperatures. The most serious type of instability in practice is caused by mobility of the dispersant at high service temperatures. GATTI (1962) studied this effect in compacts of $10^{w/o}$ alumina (0.2μ diameter) in iron, produced by ball milling, pressing and hot extrusion. The increase in particle size was studied from one to 100 hours at temperatures ranging from $1000^{o}C$ to

TABLE 5 VALUES OF $\propto$, $^{o}C^{-1} \times 10^{-6}$

Metal	(Matrix)	Dispersant		
Aluminium	25.6	Al_2O_3	7.75	
Iron (electrolytic)	11	MgO	14.0	
0 to 700°C	15	CaO	13.6	
Nickel	12.8	ThO_2	9.5	
		TiO_2		
Copper	16.7	BeO	9.5	
Cobalt	12.3	SiC	3.9	(densified)
		TiC	7.4	
Lead	29.1	PbO		
		ZrO_2	5.5	(Stabilised)
		Si_3N_4	2.5 to 3.0	
Chromium	11	ThO_2	9.5	
		SiO_2	0.5	(vitreous)
Silver	18.8	CdO		
Zirconium		Y_2O_3	8.6	
Tungsten 27°C	4.44	ThO_2	9.5	
2027°C	7.26	TiN	8.3	(up to 1450°C

1400°C, and was found to follow a $^1/3$ power law, in agreement with the theory of LIFSHITS and SLEZOV. Gatti found that 'the coalescence of the alumina particles has a disastrous effect on the mechanical properties of the materials studied, with hardness and strength values decreasing rapidly as coarsening occurs.'

The requirements for a successful D.S. material may be summarised:

1) Chemical stability of the dispersant in the matrix.
2) Dispersant particle size in the range 10 to 100mμ.
3) Interparticle spacing of about 0.5 microns, with a uniform distribution.
4) Dispersant particles to have high shear strength, and hardness.
5) A sufficient degree of coherence between the matrix and the particle.
6) Low mobility of the dispersant in the matrix at service temperatures.

The extent to which the experimental materials met these criteria is discussed in section (4.1).

3.6. Methods of production of dispersion strengthened materials relevant to the use of ultrafine particles

Critical reviews of the various methods have been published by SMITH, MOZZHUKHIN, WOLF, and GRANT and PRESTON.

The examples referred to in the following section will all be found in the Table in Appendix 5, which is classified according to the alphabetical order of the matrix material. As has been described in section 3.1, a D.S. material is produced in a number of steps. In general the following sections each describe only part of a production route, which may be completed in a variety of ways. The routes which were considered in the work described in this thesis are discussed in section 4.1.

3.6.1. Mechanical Mixing

Mechanical mixing is the simplest way of achieving the desired powder mix, but there are certain fundamental problems. In order to meet the requirements listed in section 3.5.4. the matrix particles must be submicron size, and it is unlikely that such a powder is readily available in the case of metals. Ball milling has been used by QUATINETZ, SCHAFER and SMEAL, to produce fine nickel. After 96 hours milling in a heptone - 10% ethyl alcohol medium, fine ThO_2 or Al_2O_3 was added and milling continued for a further 48 hours to give a thorough mix. An argon environment ensured that oxidation was inhibited. A similar approach was used by BUFFERD and GRANT for cobalt/chrome alloys with thoria, and these were found to be contaminated by chromic oxide with deleterious effects on the properties of the materials produced.

The advantages of ball-milling are that the powders can be ground down at the same time as they are mixed, and that any powders can be mixed in this way. The disadvantages are contamination from the grinding lubricants and surfactants used (see section 1.1) and also from the balls and liner . Milling times are liable to be of the order of tens of hours and therefore costly.

An alternative to milling is to use a high speed blender, and GRANT and ZWILSKY had considerable success mixing 1µ copper with alumina down to 18mµ, The blender is not described in detail and not identifiable in this country, but is believed to consist of conta-rotating, co-axial spiral ribbons rather like the blades on a conventional lawn mower. The rotation speed is very high (1500 r.p.m.) and considerable shear forces must exist between the blades. ATOMENERGI KOMMISSIONEN describe a high speed blender as the method of mixing of atomised aluminium and thoria or silica, but the effectiveness of the blending cannot be deduced from their results.

Nothing answering to the description of the high speed blender could be found on the U.K. market; the nearest mixer found was a 'dry disperser' which is described in section 4.2.3. Adequate mixing of iron oxide and alumina was achieved with this machine, and one advantage was the heating effect of the mixing blades, which raised the temperature of the mix above 100°C and drove off any water present.

3.6.2. Surface Oxidation

This is the method that proved so successful in the production of S.A.P. The matrix material is prepared in powder form, fine but not pyrophoric, probably in the range 10 to 100µ. The powder is heated in air so that each particle has a thin oxide layer, then compacted. At this stage the material has no remarkable properties - these are obtained as a result of deformation, which breaks the oxide layers up into platelets and particles, allowing the metal to form a continuous matrix. Hot extrusion is usually required to provide the necessary deformation, but McCARTHY, et.al. found that when processing zinc powder in this way, a satisfactory dispersion could not be achieved without cold rolling, followed by further extrusion and rolling. The method is limited to metals which form stable oxides with suitable D.S. properties.

A novel variation was introduced by KELLERER and LOOMAN, who tried to produce an Al-Al_2O_3 material by melting and spraying Al wire with a plasma torch into a drum. The Al_2O_3 was produced as a film by spraying through an oxidising atmosphere.

3.6.3. Internal oxidation

An alloy is prepared whose solvent element has a low affinity for oxygen, but whose solute element readily forms stable oxides. The alloy is heated in an oxidising atmosphere, so that a fine, well dispersed second phase of the oxide of the solute element is formed. These ideal dispersant characteristics are only achieved under certain conditions dictated by diffusion rates - it is important that the oxygen diffusion rate in the alloy is higher than that of the second phase metal. If not, an oxide scale is liable to form on the surface.

It is usual to carry out the oxidation on the material in powder form, to avoid long diffusion paths and so give a rapid and more even oxidation. A.E.I. Ltd prepared copper with an alumina dispersant in this way, but conducted the internal oxidation by annealing in a neutral atmosphere powders which were previously surface oxidised. The oxygen diffused inwards from the surface and produced the desired result.

The method is limited to metals which form suitable alloys. A disadvantage is that during the annealing/oxidation, the dispersant may coagulate - this was the experience of LEWIS, SEEBOHM and MARTIN with copper dispersed with beryllia. The principle advantage is the simplicity with which the dispersion is produced.

3.6.4. Selective reduction

Both the matrix material and the dispersant are mixed in their oxide forms, and then reduced together usually by hydrogen. The dispersant oxide must be stable under conditions which reduce the oxide of the matrix material. The oxide mix may be produced by co-precipitation, as were the copper-alumina and copper-thoria materials made by GRAHAM, EDGE and MOORE. Alternatively the oxides may be mixed mechanically if they are available in suitable forms, as done by GATTI with iron oxide and alumina. GRIMWADE and JACKSON produced a solid solution of Al_2O_3 in Fe_2O_3 by 'doping' the Fe_2O_3 with aluminium nitrate solution, then drying and igniting the mixture at 1250°C for 36 hours. A very high value for 1% proof stress at 20°C was obtained, after considerable hot and cold working.

3.6.5. Co-precipitation (Hydrometallurgy)

An easily reducible metal salt is co-precipitated with a colloidal oxide dispersion using aqueous solutions. After filtering, washing and drying, heat is applied to produce mixed oxides which are then treated by selective reduction as described in the previous section. GRAHAM, EDGE and MOORE reacted cupric nitrate solution with a conc. solution of NH_4OH at a pH of 7.0 in the presence of a colloidal suspension of Al_2O_3 or ThO_2. After heating the dried filter cake at 250°C mixed oxides resulted, and the cupric oxide was reduced in hydrogen leaving copper with an Al_2O_3 or ThO_2 dispersant. The successful material 'D.S. Nickel' is similarly manufactured, as described by FRASER et. al. A basic nickel carbonate slurry is precipitated from a nickel amine ammonium carbonate solution by boiling and driving off NH_3 and CO_2. The slurry is then passed to an autoclave and thoria added, which becomes adsorbed on the suspended carbonate. Reduction is carried out at 130°C and about 20 atmospheres pressure of hydrogen. The powder is chemically pure, containing a little unreduced carbonate, but otherwise consisting of 0.5μ nickel particles with thoria particles studding the surface. Compaction and hot rolling follow to produce a fully dense material, but twenty one cold-roll/anneal cycles are required to optimise the materials properties.

LEVER used a simple method to produce a silver matrix dispersed with cadmium oxide. He precipitated silver and cadmium carbonates from aqueous solution, then decomposed the $AgCO_3$ by heating in air. The material was consolidated by 'powder metallurgy methods.'

The suitability of this method to any particular system will depend on the chemistry involved - whether the precipitates can be produced in a small number of steps, and using reasonable amounts of consumable reagents.

3.6.6. Electrodeposition

The dispersant is suspended in a plating solution and when the current is passed the dispersant is deposited with the metal ions. DUNKERLEY produced nickel dispersed with TiO_2 and Al_2O_3. He obtained dispersions of the oxides which satisfy the optimum inter-particle spacing and dispersed phase loading conditions considered necessary for high temperature strength. The material is stripped from the electrodes, and must be densified by hot and cold working to produce useful properties.

Consistent results can be achieved with a commercial sulfamate-nickel bath, and almost any particle which can be held in suspension without reacting chemically with the electrolyte may be co-deposited. In a liquid free of ions, positive electrostatic charges on the small particles cause inter-repulsion, effectively dispersing them in the liquid. Electrolytes destroy this effect, and the particles tend to agglomerate and settle out, so agglomeration is prevented by mechanical and ultrasonic agitation.

3.6.7. Discussion

Of the six production methods described in the previous section, the surface and internal oxidation methods are the only two which specifically exclude the use of a ready made fine dispersant. The surface oxidation method has proved successful in the production of S.A.P, and attempts have been made to equal its properties using mechanical mixing, with limited success. The production of S.A.P. highlights a point about the choice of manufacturing method for a particular material - it is probable that there is a technical reason which determines the choice, overriding considerations of convenience and economy. Unfortunately there is insufficient knowledge available to enumerate the technical factors in advance, and unless there is a clear economic bar to a particular method, there is no substitute for experiment based on previous experience.

Internal oxidation is probably the method used by HANDY and HARMAN to produce 'Cube Alloy', which is copper dispersed with BeO, but no direct comparison can be made with other work described in the table in Appendix Five.

Among the remaining four methods, which are applicable to the use of ultrafine powders, the only one which is commercially successful at present is coprecipitation, which is the method used to make D.S. Nickel. As there is no chemical reaction between the colloid dispersant and the precipitated metal salt, in principle any inert fine powder could be incorporated using this method. The attraction of this method is that the matrix metal does not have to be comminuted to provide a suitably low interparticle spacing.

Mechanical mixing does involve the comminution of the matrix metal if selective reduction is to be avoided, but oxides, being harder than metals, break down more easily under grinding forces. A decision for any particular material will depend upon a compromise between these two considerations which will require detailed evaluation, and both technical and economic considerations must be included.

Electrodeposition has been shown to give the required dispersion, but no material produced by this method has had its properties evaluated.

3.7. Costing of methods of production of D.S. materials and prices of those commercially available

Introduction

The first section describes form and prices of the commercially available materials.

The cost equation used in the remaining section is of the general form described in Appendix 4. The case of mechanical mixing has been costed in detail, as it is attractive because of simplicity and the ease of scaling up to high production rates, using available equipment and technology. Selective reduction has been studied experimentally and the important technical factors are identified, but plant design is a specialised business so many assumptions have been made in extrapolating laboratory results to produce quantities.

Co-precipitation can be carried out in such a variety of ways depending on the materials, that no analytical approach has been used. Sheritt Gordon Mines, however, offer D.S. Nickel for sale in both powder and sheet forms, so an attempt is made to deduce certain costs from the quoted prices.

3.7.1. Mechanical Mixing

Ball Milling

The cost equation for grinding particles was derived in section (1.1.1), for stainless steel mill with a capacity of 10 tonne of balls.

$$\underset{(\pounds/kg)}{P.C.} = \frac{1}{9000r}\left[S + L + E + \frac{13,800}{x} + \frac{2080}{n}\right] \quad ....(eqn\ 1.1.1)$$

It applies equally to milling a mixture of powders, and the milling time, or number of charges per year (n) can only be determined for a particular application by experiment.

QUATINETZ, SCHAFER and SMEAL milled nickel with ThO_2 or Al_2O_3 in the same apparatus as described in section (1.1.1), with t = 48 hours. The cost per kg would be very close to £0.7 kg.

Jet Milling

The principle and operation of the jet mill was described in section (1.1.2). The mill is intended primarily as a means of grinding particles down, rather than as a mixer, but it can only break powders down if it first breaks up any agglomerates. If a fairly homogeneous mix of two powders is introduced to the grinding chamber, then an intimate mix should result. The experimental results obtained by this method are described in section (4.2.)

The cost equation for operation of a jet mill was derived in section (1.1.2), and evaluated for a particular air driven mill as,

Milling Cost = 0.07 $£kg^{-1}$

Dry Dispersing

The cost components are:

Variable Costs - Materials - Electric power
Consumables - Mixing blades
Fixed Costs - Capital and maintenance
Labour and overheads

Let, number of batches per year = n p.a.
electrical charges per batch =£E per batch
Cost of blades =£b
Production capacity = m kg per batch

The cost equation is:

$$P.C. \quad = \frac{1}{m}\left[E + \frac{b}{x} + \frac{1}{n}\left(\frac{1.1C}{7} + C_{LOH}\right)\right]$$

Tests were conducted as described in section (4.2.) on the following machine:

$C \quad = £2500$

$m \quad = 25$ kg (iron oxide/alumina mix)

$E \quad = 15$p per hour

The operating characteristics were

Mixing time $t \quad = 0.5$ hours

Charging and discharging $t \quad = 0.25$ hours

Let $H \quad = 2000$ hours

$\eta \quad = 0.7$

One operator, gives, $C_{LOH} = £3000$ p.a.

Let $x \quad = \infty$

$$\therefore \quad n = \frac{2000 \times 0.7}{0.75} \text{ p.a.}$$

$$= 1870 \text{ p.a.}$$

Substituting:

$$P.C. \quad = \frac{1}{25}\left[0.075 + \frac{1}{1870}\left(\frac{1.1 \times 2500}{7} + 3000\right)\right] £\text{kg}^{-1}$$

$$= 8.7\text{p kg}^{-1}$$

3.7.2. Selective reduction

The cost components are:

Variable costs - materials - Reducing gas
Heat.
Fixed costs - Capital and Maintenance
Labour and overheads.

The experimental results described in section (4.3.) are not of any quantitative use, but serve to point out the important parameters. These are the efficiency of utilisation of the reducing gases, which may or may not be recirculated, and the amount of wasted heat.

The worst case using recirculation is to assume that no heat is exchanged between the outgoing wet gas and the incoming dry gas. The gas has to be cooled below 100°C during re-cycling to remove the water, unless chemical drying is used.

Let the cost of the stoichiometric amount of
gas to produce one kilogram metal = £g/kg iron

The utilisation factor of the gas = x

The heat lost to the reduction gases per kg of metal produced is a function of x.

The heat required to bring the oxide to temperature and perform the reaction is found from the thermodynamic tables. Let the total heat energy costs per kg metal be (Q).

If the capital costs are £C and the labour one man for a plant of annual capacity M kg, the cost equation is:

$$\text{P.C. } (\pounds/\text{kg}) = Q + g + \frac{1}{M}\left(\frac{1.1C}{7} + 3000\right)$$

The cheapest way of obtaining reducing gases in bulk (other than natural gas) is by transporting liquid ammonia and cracking it using standard commercial equipment.

The case is calculated below for the reduction of Fe_2O_3 by $(N_2 + 3H_2)$ gases for any value of x.

The reduction temperature is $800^{o}C$

From the JANAF tables, assuming the reaction:

$$Fe_2O_3 + 3H_2 \longrightarrow 2Fe + 3H_2O$$

The relevant thermodynamic data is;

ΔH_{298}^{o} for Fe_2O_3 = -196 kcal/mole (U.S. BUREAU OF MINES)
ΔH_{298}^{o} for H_2O = -57.8 " " (JANAF)
$(H^{o}_{1100K} - H^{o}_{298})$ for Fe = 7.2 " " "
" " H_2O = 7.2 " " "
" " N_2 = 5.9 " " "

$$\therefore \Sigma \Delta H_{298}^{o} = 0.5\left[-(3 \times 57.8) + 196\right] = +11.3 \text{ k cal/mole Iron.}$$

and,

$$\Sigma(H_{1100}^{o} - H_{298}^{o}) = +0.5\left[(2 \times 7.2) + \frac{(3 \times 7.2) + 5.9}{x}\right]$$

$$= + 7.2 + \frac{13.75}{x} \text{ k cal/mole Iron}$$

∴ Total energy requirements (Q)

$$= 18.5 + \frac{13.75}{x} \text{ k cal/mole Iron.}$$

$$= \left(18.5 + \frac{13.75}{x}\right)\frac{4.186 \times 10^{3}}{55.8 \times 3600} \text{ kW hr/kg iron}$$

$$= .386 + \frac{.287}{x} \text{ kW hr/kg iron}$$

Let electricity cost = £U per kW hr.

The stoichiometric amount of ammonia required is 1 mole per mole iron produced, i.e. 17 kg per 55.8 kg iron, which at £155 tonne is,

$$\text{Ammonia cost (g)} = \frac{£0.155 \times 17}{55.8}$$

$$= £.047 \text{ kg iron}$$

$$\text{Then, P.C. £/kg} = U\left(0.386 + \frac{0.287}{x}\right) + 0.047 + \frac{1}{M}\left(\frac{1.1C}{7} + 3000\right)$$

If U = £0.004 per kW hr

and x = 0.5

$$\text{Then P.C.} = 0.00384 + .047 + \frac{1}{M}\left(\frac{1.1C}{7} + 3000\right)$$

$$= 0.051 + \frac{1}{M}\left(\frac{1.1C}{7} + 3000\right)$$

3.7.3. Co-precipitation

The methods of co-precipitation vary so widely that there is no value in deriving a general equation.

D.S. Nickel is sold by Sheritt for £9.8 kg in tonne quantities, and considering the research costs at least £2.8 kg of that must be contribution, leaving a cost price of £7 kg. The starting material is nickel amine ammonium carbonate solution, which is derived from Nickel at £1250 tonne. The raw material is, therefore, £1.25 kg, rising to say £1.50 kg by the time it is in the required solution. The processing cost must be at least £5.50 kg to meet the £7 kg cost price, and this includes the hydrometallurgical step and the thoria.

The sheet is sold at £27.8 kg and it is difficult to assess the total contribution. Assuming that the cost price is £20 kg, then the 21 cold roll/anneal cycles must cost £13 kg, or £0.62 kg per cycle.

3.7.4. Summary

The processing costs derived in the previous section are summarised in table 6, below. Each process represents only part of a production route, and the production routes which can be constructed are shown in section 6.

TABLE SIX

Method	Cost £/kg	Comments
Ball milling	0.7	T.D. Nickel powder Cost of mixing only?
Jet milling	0.07	Mixing and some grinding
Dry dispersing	0.08	Mixing only
Selective reduction	0.05	Cost of materials only, using cracked NH_3 Fixed costs to be added.
(Direct reduction)	(0.004)	Iron ore reduced by natural gas.
Co-precipitation	5.5	Deduced from T.D. nickel prices
Extrusion	0.42	Iron compacts at 19:1 and 60 T.S.I.

The question mark on ball-milling is because in the experimental work quoted (section 3.7.1) the nickel was ground first and the thoria added later. The thoria could possibly be present throughout the grinding cycle.

The direct reduction figures are added for comparison purposes. The use of natural gas (methane) may be impossible for a selective reduction process because the presence of carbon may cause unwanted carbide production. Conversely there is the possibility, given suitable thermodynamics, of producing a fine carbide phase at the same time as reducing the metal oxide.

The accuracy of the estimation of the co-precipitation costs depends entirely on the assumption about the contribution percentage in the prices.

CHAPTER FOUR

DISPERSION STRENGTHENED MATERIALS: EXPERIMENTAL WORK AND RESULTS

4.1. Choice of materials and production route

4.1.1. Choice of material

It was recognised that there are two distinct areas of application of D.S. materials; high technology and low technology. High technology includes the aerospace industry where in general cost is no object, and low technology embraces many of the GKN Sub-Groups where cost is a foremost consideration. The matrix material has to be of the order of pence per kg, if plasma produced powders are to be incorporated and the material processed and finished for a cost of £1 kg or less (see 5.1).

The second requirement is that the matrix should be in a powder form, preferably of a particle size order 0.5μ if mechanical mixing is to be used to introduce the dispersant (See section 3.5.4). The only materials which could be found readily available within these specifications were a stainless steel powder used in anti-corrosion paints, and pigment grade iron oxide.

It was intended to use plasma produced powders as dispersants, but in order that experiments on mixing, compaction, densification and metallographic methods could be carried out in parallel with the plasma work a commercially available powder was sought. The powder chosen was a fine alumina, size 30mμ. Although there may be differences in behaviour between different dispersants in the same matrix at sintering temperatures, the purely mechanical processes of mixing and compaction should be independant of the dispersant's chemical properties. The mechanical properties of the densified material will of course vary with different dispersants, as will be seen in Table 9.

The particulars of the powders used are shown in Table 7 (over).

The criteria for a successful D.S. material were discussed in section (3.5.4). The oxide particles should reduce to iron particles of slightly less than 0.5μ, and if the dispersant is thoroughly mixed, this should give the required interparticle spacing. The dispersant particle sizes are all within the preferred range. Alumina is stable in iron up to the

TABLE 7. The powders used in the experimental work

Powder	Size and Shape	Composition	Source	Price per kg
Stainless Steel 316 L	Flakes several μ wide, $<1\mu$ thick.	Cr 16-18% Ni 10-14% Mo 2- 3% Mn $<$ 2. 0% Si 1. 0% C $<$ .03%	Microparticles Ltd, Newbury	£1.50 (small quantities)
Fe_2O_3 HS95	Particles 0.3 to 1μ	SiO_2 .08%	Ashby Morris Ltd.	14p (100kg)
Al_2O_3 (γ)	Particles .03μ $100m^2gm^{-1}$	Al_2O_3 99%	Cabot Corp.	£1.96 (5 kg)
Si_3N_4	15mμ particles	Amorphous	External	-
TiN	15mμ particles	Amorphous	External	-

melting point. Silicon nitride is stable in iron below 750°C, the stability of TiN in iron is not known. Alumina is hard, and Si_3N_4 and TiN are very hard. Si_3N_4 is known to have high shear strength. The coherence between Al_2O_3 and iron is good; between Si_3N_4 and TiN and iron is not known. Al_2O_3 is mobile in iron above 1000°C (see section 3.2.7), and the mobilities of Si_3N_4 and TiN have not been measured.

4.1.2. Choice of production route

It was decided that as the dispersants would be prepared separately from the matrix material, mechanical mixing methods would be explored as a means of producing an intimate dispersion. The production route in general consists of three to five steps:

1 Preparation - i.e. grinding, if necessary

2 Mixing - if necessary

3 Reduction, if necessary

4 Compaction
5 Densification

A major problem is pyrophoricity of the fine matrix particles, or at worst their tendency to oxidise, which hinders densification. The way in which this problem complicates the production route is shown in Figs 50 and 51, and ways of overcoming it are indicated.

The route which was followed in the experiments with a stainless steel matrix is shown in Fig 52, and the route followed in the production of iron-alumina compacts in Fig 53. The jet mill was the only mixing method available at the time, and it was considered advisable to break up the stainless steel flakes. The paraffin wax was necessary as a binder during compaction. The pressing and sintering behaviour is described later. The iron oxide and alumina were mixed in the jet mill until the dry disperser was located, which was used for large volume mixes. Reduction was necessary to produce the iron matrix, which was not pyrophoric but did take up some oxygen from the air. The densification is described later.

4.1.3. Classification code used

A large number of mixes were made, so to avoid confusion a code is used on the compacts produced which enables each mix to be identified, and each compact made from the mix.

The code is as follows:-

Mix number / matrix material and particle size in mμ / volume% of dispersant / dispersant material and particle size in mμ / compact number

Material codes are:
SS 100 : Stainless steel (100mμ thick)
FEO 500 : Iron oxide from H.J. Evans & Co, average particle size 500mμ
FOM 600 : Iron oxide from Ashby Morris & Co, average particle size 600 mμ
AO 30 : Alumina, 30mμ
SN : Silicon nitride

e.g. 1/FOM600/7/AO30/S2

which is the first mix of $7^{v/o}$ alumina in iron oxide, and the second sintered compact.

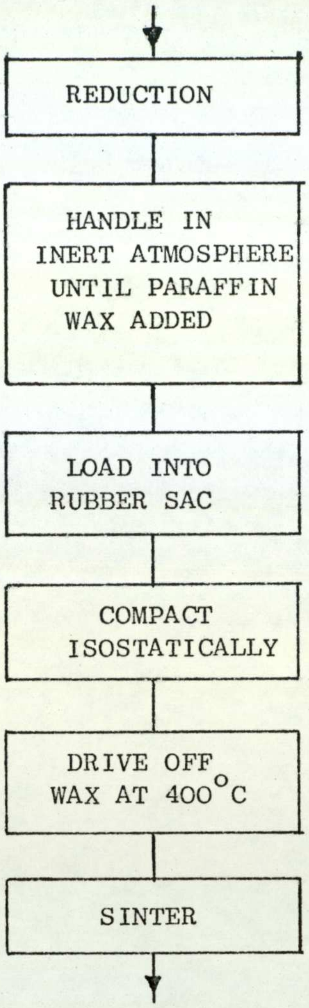


FIG. 50. Handling pyrophoricity using wax.

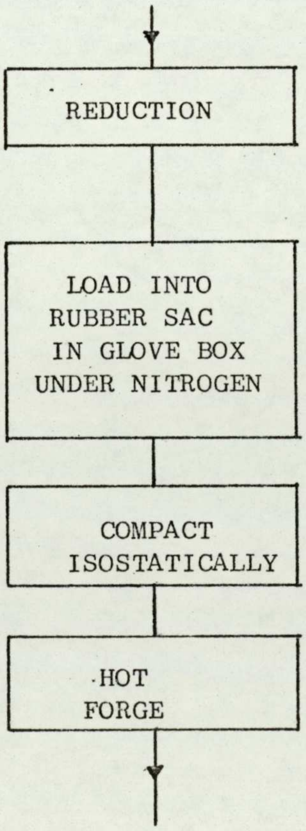


FIG. 51. Avoiding Pyrophoricity without wax: the preferred route.

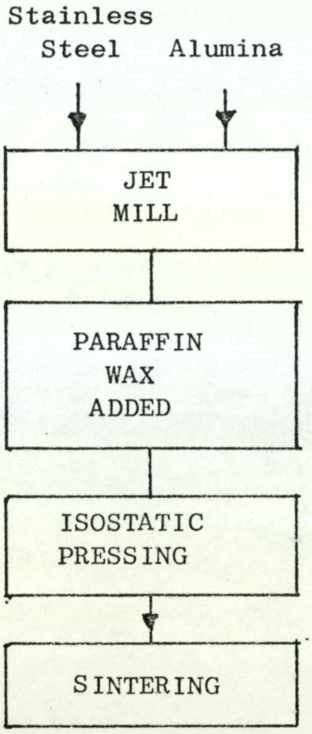


FIG. 52. Route followed with stainless steel/alumina materials.

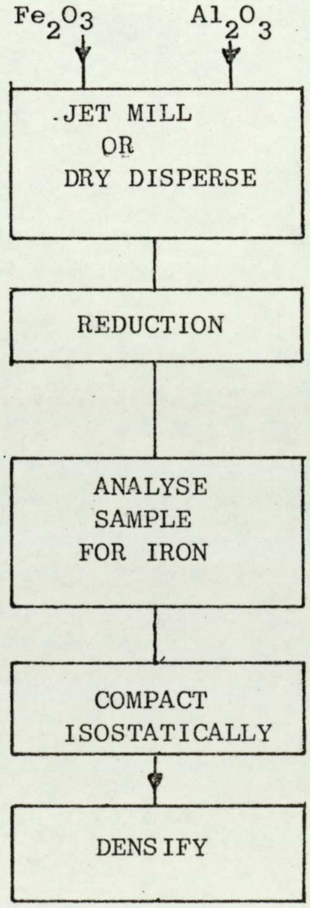


FIG. 53. General route for iron-Alumina compacts.

Each compact has its own record sheet, with the code at the top (see Fig 54.)

4.2. Methods of Mixing

4.2.1. Ball milling

Ball milling was only used on the first three stainless steel mixes. It was discontinued when it was discovered that the stainless steel as received was very flaky, and had poor pressing characteristics, tending to laminate. As the powder had been produced by ball milling, further similar treatment was unlikely to improve its pressing characteristics.

4.2.2. Jet Milling

The jet mill was described in section (1.1.2). One mix of stainless steel and alumina was jet milled, and it appeared to break up the flakes to some extent. The powder was milled once and examined under an optical microscope before and after, and some reduction in powder size is apparent in fig 55.

Most of the iron oxide/alumina mixes were jet milled, as the dry disperser was not on the G.T.C. site, but the powder, instead of falling into the jar, tended to rise up in a vortex and block the filter bag. It could be dislodged by sharp blows on the bag, but then blocked the tube at the entrance to the bag and stopped the mill working. The solution adopted was effectively to turn the mill upside down, so that the powder fell into the bottom of the filter bag, and the plastic jar acted only as a stopper. In this way several hundred grams of oxide could be milled without having to strip the mill down several times to unblock it.

The mill used is only a 4" diameter device, and consequently processing is slow and the feed-in rate needs constant attention or the inlet orifice blocks. Half a kilogram of powder could be milled in about two hours.

The filter bags tend to absorb about 100 gms of powder the first time they are used, so a different bag is used for different material mixes to avoid contamination. Also the felt tends to shed fibres into the powder if it is treated roughly, but these can be removed by hand.

SHEET NO.   Log Book p.   CODE

OBJECT OF EXPERIMENT

	Material	Nom. Size	Weight mixed	Comments
Matrix				
Dispersoid				

METHOD OF MIXING

DATE

REDUCTION

DATE

Atmosphere	Temperature	Time at T max

Pressing lubricant:

Condition: Physical

Chemical

Sieved through mesh No.

PRESSING

DATE

Method	Sack/Die Size	Pressure psi kN/m^2

Green condition: Density   gms cm^{-3}

SINTERING

DATE

Atmosphere	Temperature	Time at T max

Condition:

Density   gms cm^{-3} (Theoretical   gms cm^{-3})

METALLOGRAPHY

No.

Polished	Etched in	Time

PHOTOGRAPHIC RECORDS

Polished	Etched	Replica

CHEMICAL ANALYSIS

TESTS

CONCLUSIONS

Fig. 54. Compact record sheet.

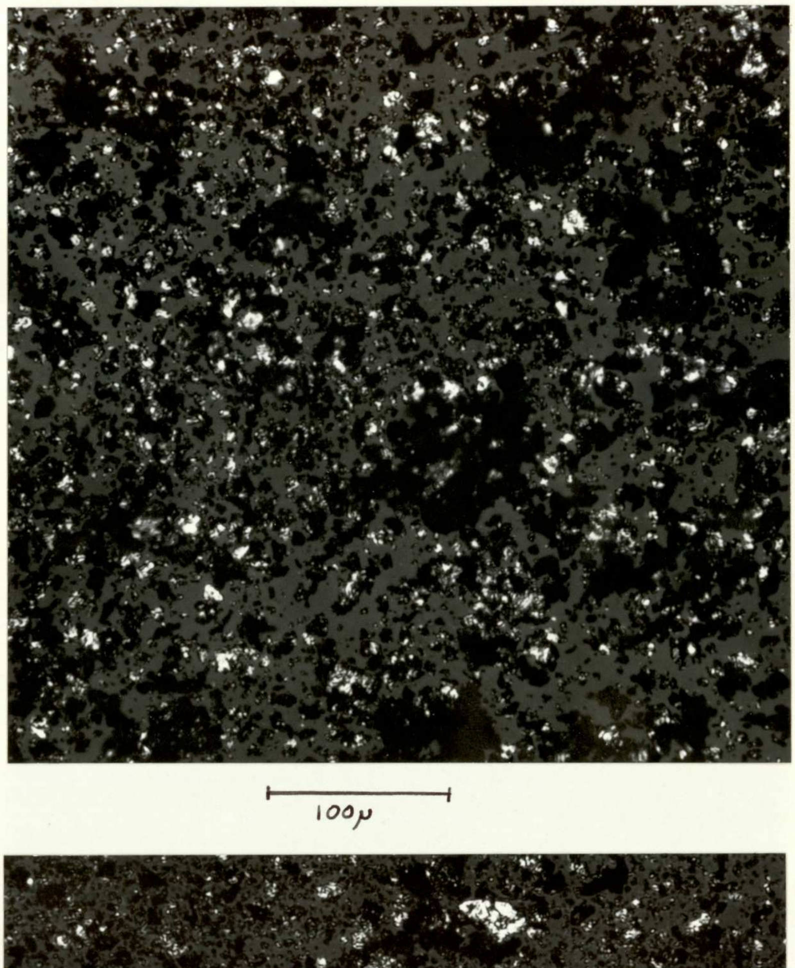


Fig 55. Effect of jet-milling on the stainless steel powder. Above-before
Below-after

4.2.3. Dry disperser

The mixing chamber is shown below and consists of a jacketed, stainless steel tub with a horizontal rotating blade in the bottom. It is charged at the top and discharged from the bottom. The blade causes mixing by shear forces at its surfaces and also causes a circulating motion combined with thrust up the axis of the tub.

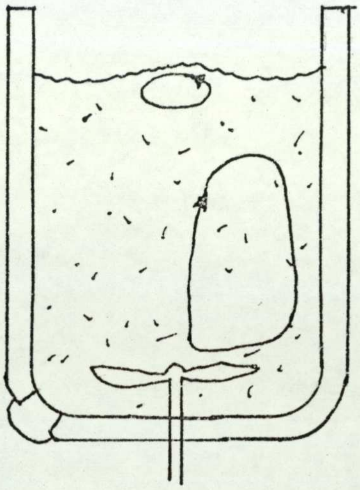


Fig. 56.

A mix of 25 kg of Fe_2O_3 and 600 gm Al_2O_3 was prepared, but had to be put into an oblicone blender first, as the Al_2O_3 is very fluffy and formed an aerosol until it was distributed in the Fe_2O_3 as coarse agglomerates. The coarsely mixed powders were then put into a dry disperser, the quantity being mixed was adjusted so that a smooth circulatory flow developed, With too little powder, it was possible to form a 'bridge' over the blade, whereas too much powder hindered circulation.

Mixing was judged by eye - small specks of alumina were present for 12 mins, during which time the machine was operating at 750 r.p.m. and the powder was heating up from the mechanical work done by the blade. The cover was put on the drum and the machine left to run at 1500 r.p.m. When, 18 mins later, the cover was lifted it was running with condensation. The machine was run for a while with the lid off and the powder encouraged to dry out. The alumina specks began to disappear more rapidly and mixing was ceased after a total of 30 mins.

As with all the mixing methods, the ultimate proof of a thorough dispersion is only obtained from electron-micrographs of a densified compact (see Figs 68 and 69)

4.3. Selective reduction

4.3.1. Furnaces

Three types of furnace were used. The first type was the standard type using a replaceable ceramic tube encased in an electrically heated and insulated box. The disadvantage was the size restriction - the alumina boats used to hold the powder only held a few gms. Coupled with the thermal shock problem, which means that a hot boat cannot come into contact with a cold tube and vice versa, the small size and slow cycling rate meant a very slow production rate. Although useful for producing small samples for pressing and sintering trials this was too slow to produce enough material for mechanical testing.

To overcome these problems, a metal tube furnace was constructed around a nickel alloy tube (Fig 57). The construction was otherwise identical to the standard ceramic tube furnace, but the capacity is an order of magnitude higher and there is no thermal shock problem. One end was sealed by a specially designed aluminium bung through which gases could be passed. As aluminium has a higher thermal coefficient than nickel it was thought that the seal would be effective over the range of operation of the furnace, which was designed to go over 1000°C. In practice no hydrogen leaks were experienced at the bung.

Temperature profile tests were carried out with a Pt-Pt/Rh thermocouple, and the results are shown in Fig 58.

The hot zone was considered flat enough to take a 16 cm long stainless steel boat. The boat is shown below and has a porous stainless steel bottom to encourage good circulation of the reducing gases. The importance of this feature became clear as the porous bottom gradually clogged with use, and powder charges started to show a graduation in colour from metallic at the surface to black at the bottom. Cleaning in warm nitric acid was effective in unblocking the pores and restoring thorough reduction.

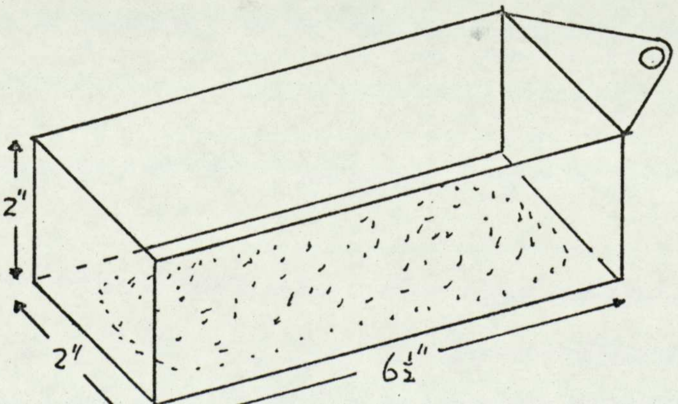


Fig. 59.

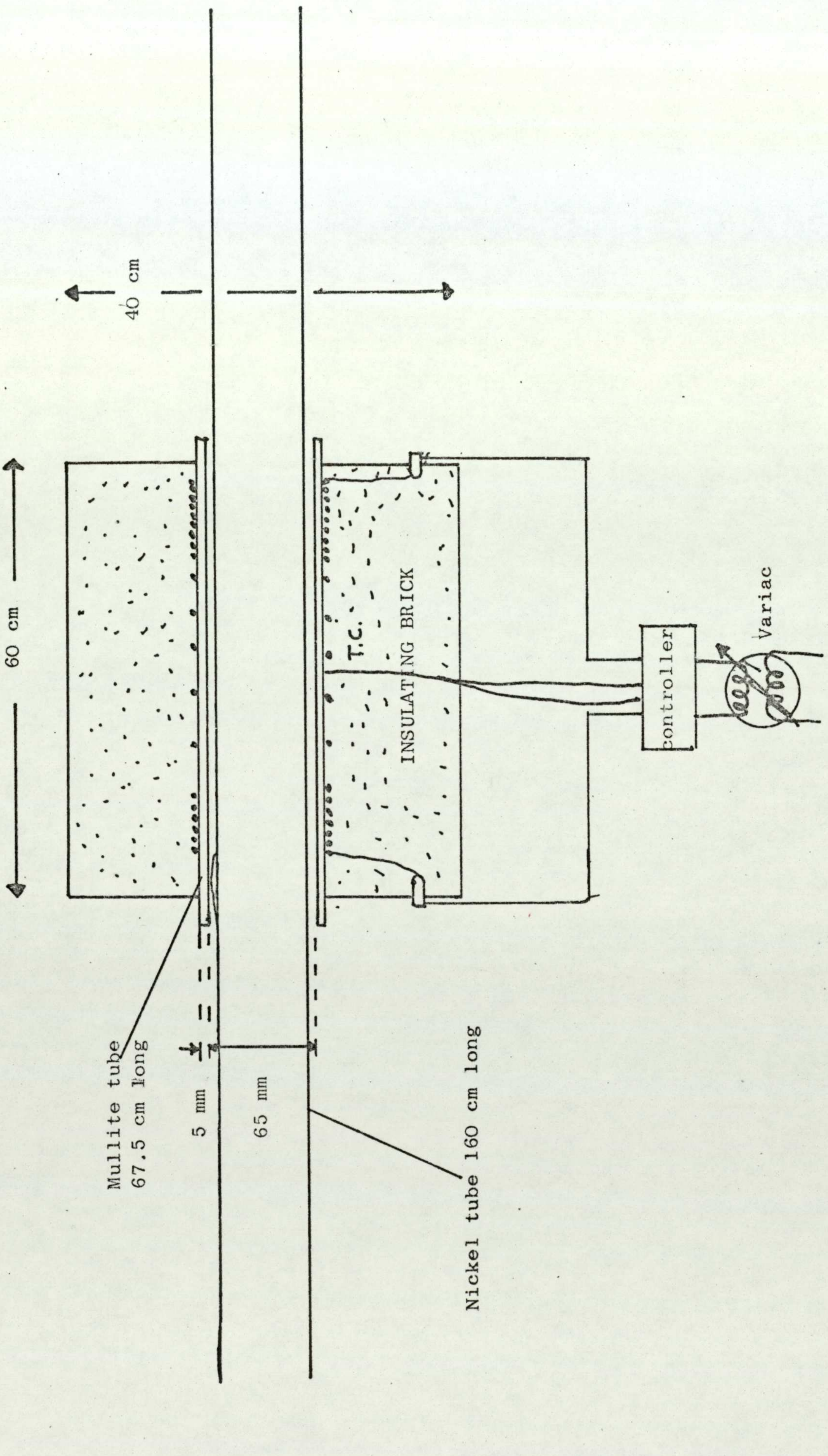


Fig. 57. Tube reduction furnace

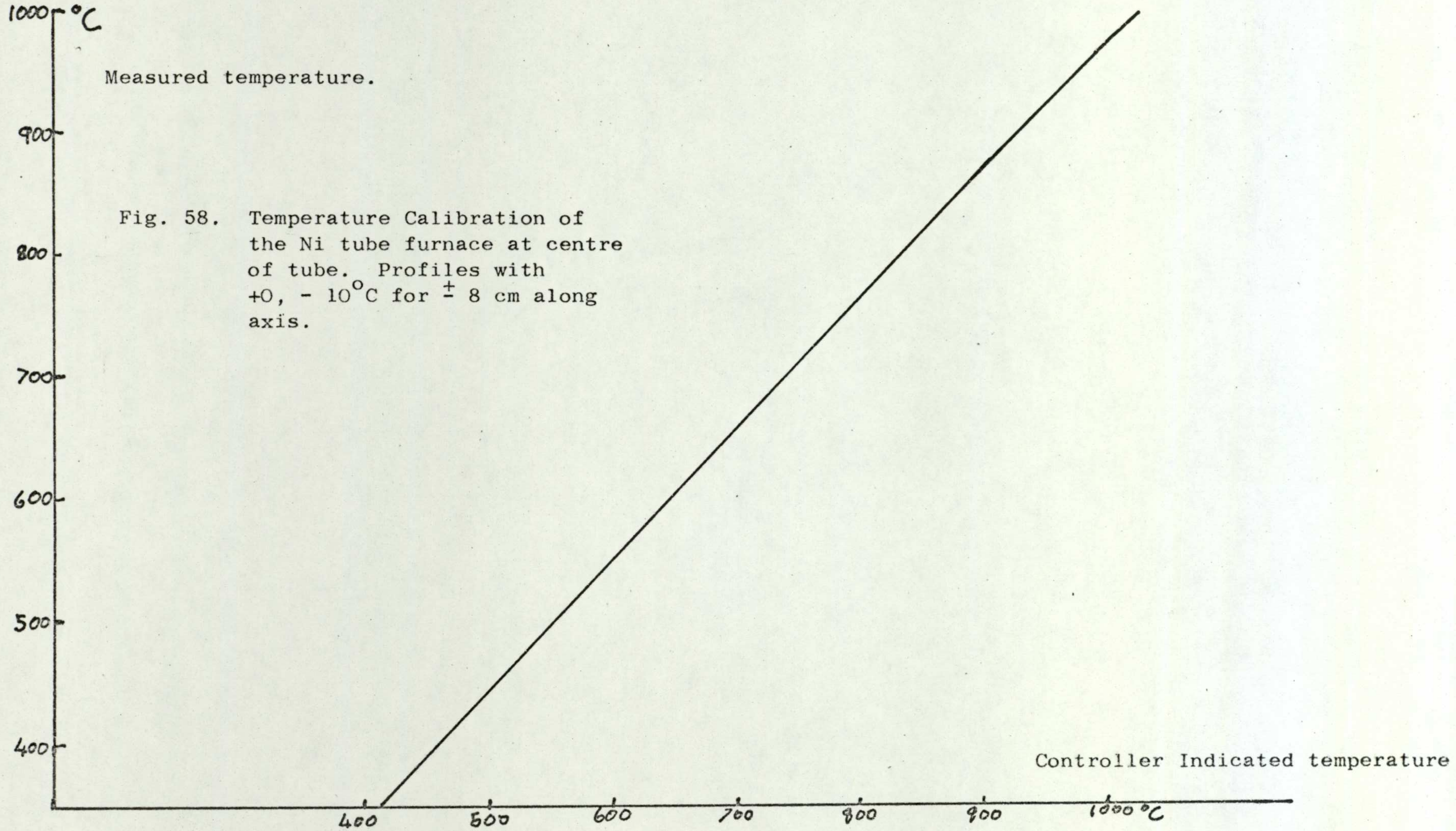


Fig. 58. Temperature Calibration of the Ni tube furnace at centre of tube. Profiles with +0, - 10°C for ± 8 cm along axis.

The operating end of the niçkel tube was sealed with a rubber bung which was protected by a metal heat shield, and pierced by a copper tube to allow passage of a pull-push rod connected to the boat and exit of reducing gases.

A different sort of furnace capable of holding about 1 kg of powder was required to produce larger batches allowing several test pieces to be obtained from the same batch. Previous experience in the laboratory of cleaning up iron powders by hydrogen reduction prior to pressing, has resulted in the use of a rectangular box (with a removable end plate) which was packed with powder and put inside a large electrically heated furnace. The gas was led in through one tube and out through another, the furnace door was let down onto the tubes and the box effectively enclosed in the furnace. After one or two modifications, the arrangement shown in Fig 60 was found to give a satisfactory reduction. The important feature of the design of such a box was found to be the circulation pattern of gases. If one area of the powder receives more clean hydrogen than another the reduction is uneven, and can range from partially sintered to incompletely reduced. It is realised that the final design is still not optimised, but a production plant would be completely different anyway, so no further development is envisaged.

A glove box was required which could be used both with the tube and box furnaces, so the box shown in Fig 61 was designed and built. Connection was made to the tube via a brass clamping flange using a Viton "O" Ring seal, and access to the pull-push rod allowed for via a rubber bung on the opposite side of the box. The glove box was made large enough to contain the box furnace, which was introduced via a removable backing plate held by studs and wing nuts and sealed with a sponge rubber strip. Access was provided by two hand parts on which rubber gloves were fitted. A perspex window in the top gave the required vision. During reduction a connection was made via a tee-piece inside the box, and the gases led out and burnt outside. For purging the connection was removed and Nitrogen passed in via the nickel tube and out by loosening the rubber bung (B). (The plumbing could be improved, but was found adequate).

4.3.2. Degree of reduction

The time and temperature required to give sufficient reduction was only found by experience. A dew-point meter was used with the box furnace, but eventually discarded as its reading, and analysis of the powder,

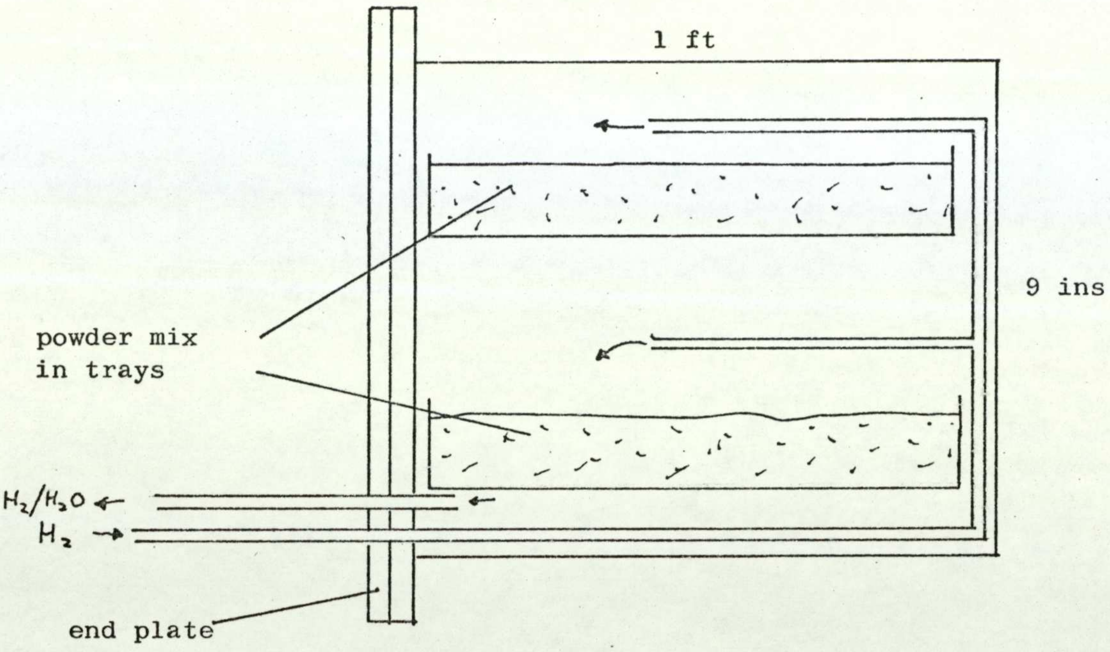


Fig. 60. The 25/20 stainless steel box reduction furnace

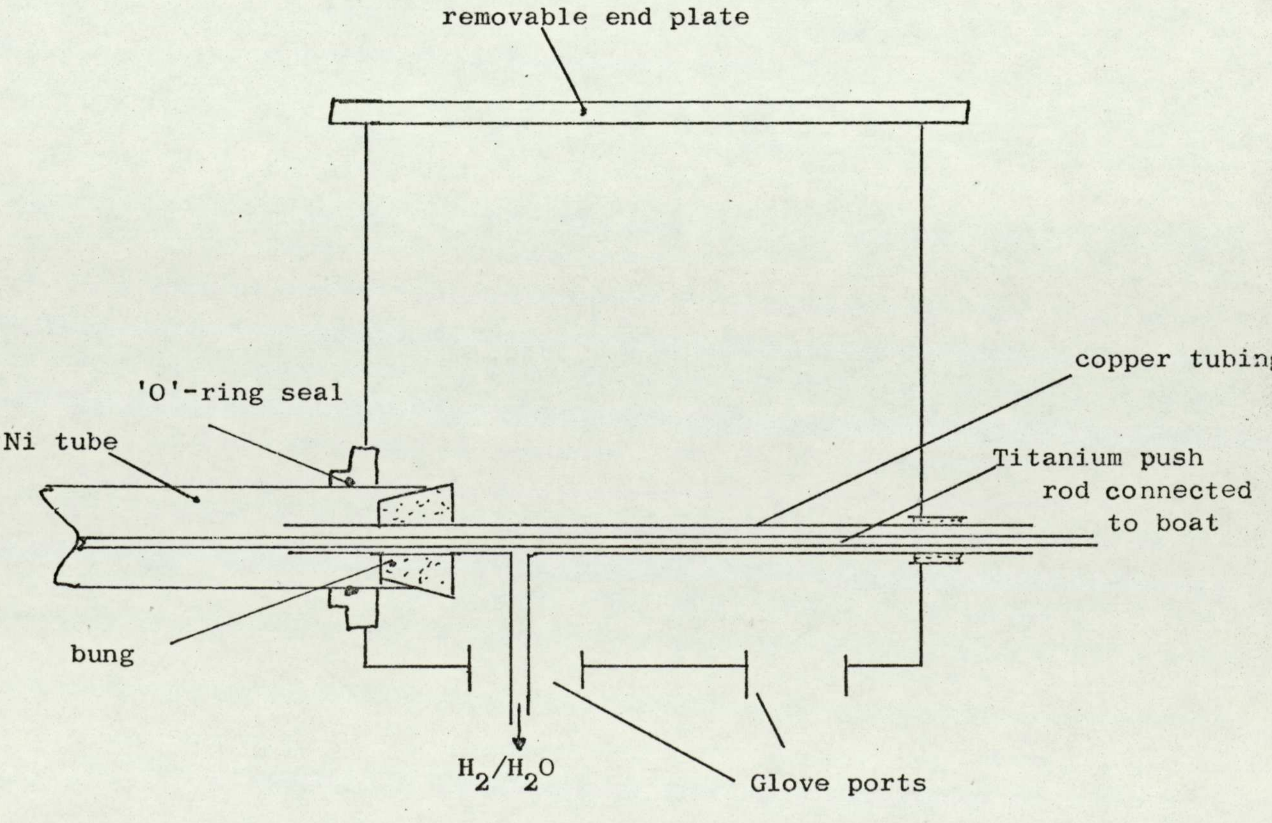


Fig. 61. The glove box for loading pressings sacs.

showed no correlation. The reason is that when the meter is operated the flow of gas is interrupted, and the dynamic equilibrium between the gas flow, temperature and amount of oxide left is destroyed. The water level builds up, and the result is that if a series of readings are taken, they get steadily worse. Also the pumping action used to take a sample can cause a negative pressure in the box and suck air in through any leaks in the asbestos seal.

The percentage reduction of pure hematite (Fe_2O_3) briquets as a function of time and temperature was studied by STRANGWAY and ROSS, and found to increase continuously with both variables. No variation from this behaviour was found in this work. The best pressing condition for the fully reduced powder was found to be similar to that of soft brown sugar, i.e. a soft cake. In this condition it was easy to handle, and did not need heavy grinding in a pestle and mortar before it would pass through a 40 mesh seive. The term 'fully reduced' requires some qualification. If the powder contains no iron oxide at all, it soon aquires some from the air, up to about 2% by weight, when it is stable, If stored in a Kilner jar in air a considerable partial vacuum builds up over night. Although it is possible to grind, sieve and fill a rubber sac all under atmosphere, it is difficult to weigh a sample and do wet analysis without some oxidation taking place. Accordingly 98% iron in a supposedly pure iron powder was considered fully reduced.

The effect of continuing the reduction process after full reduction has taken place is to promote sintering, and modules up to 5 mm diameter have been produced. The effect of reducing at too high a temperature can be to promote sintering on the surface of the powder and trap oxide particles within. The addition of alumina definitely increased the temperature at which Fe_2O_3/Al_2O_3 mixes could be reduced without producing hard grains. In general optimum temperatures were around 700 to 800°C.

4.4. Methods of Compaction

4.4.1. Uni-axial pressing

This technique was used only for the first stainless steel compacts. A rectangular die 2.36 cm x 0.85 cm was used with pressures up to 410 MN/m^2. The stainless steel, being a flaky powder, tended to laminate so severely that the green compacts could be split into slices. The laminations are clearly seen in the sintered specimens in Fig 62. The specimen in Fig 63

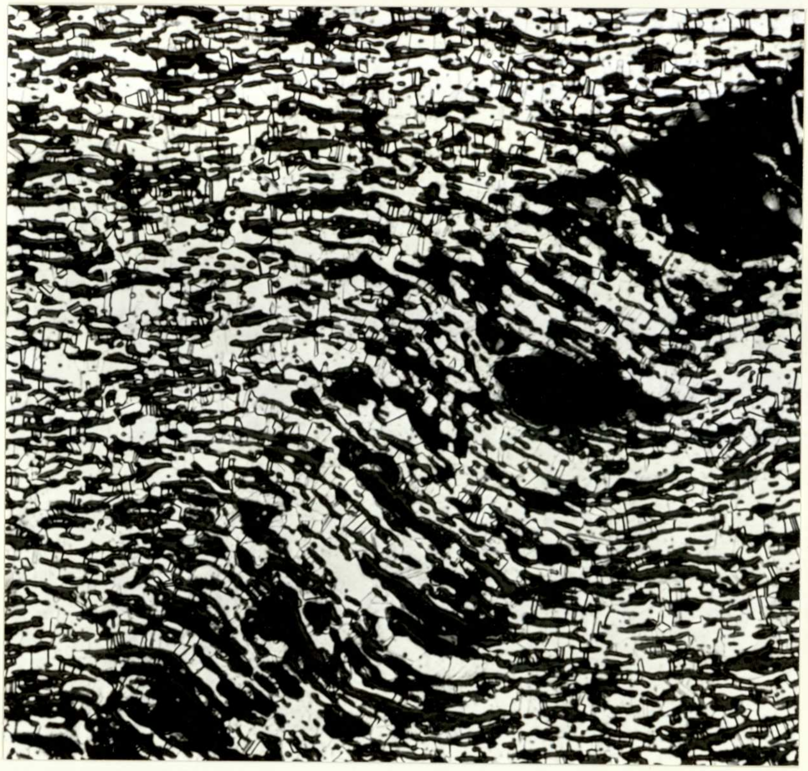


Fig. 62. 1/SS100/20/A030 Uniaxially pressed. Sintered at 1350°C for 2 hours in hydrogen. X 200

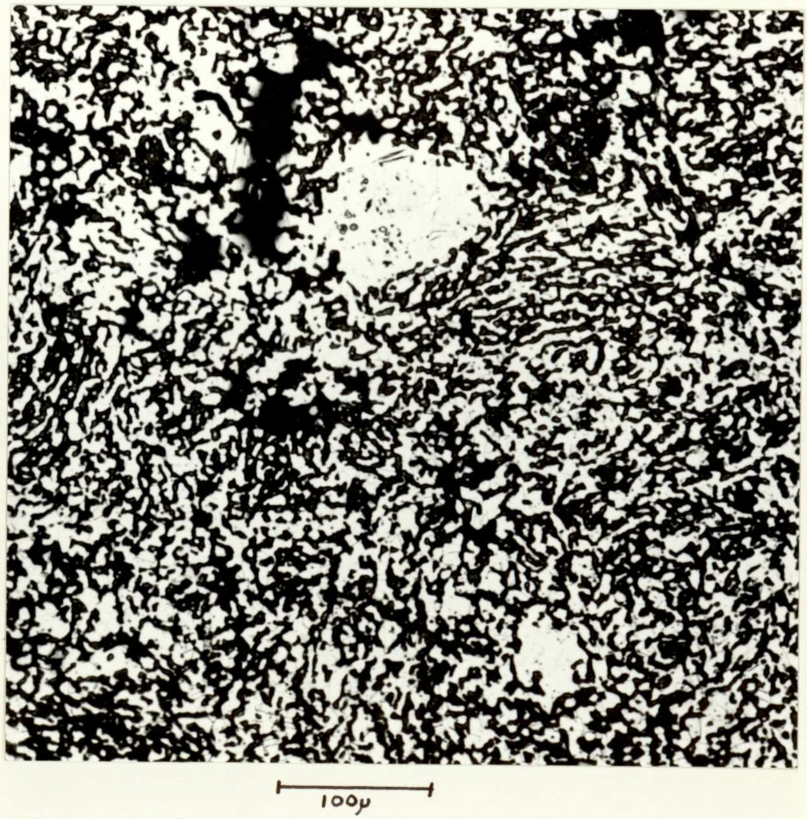


Fig. 63. 2/SS100/20/A030 Isostatically pressed. Sintered at 1360°C for 1 hour under vacuum. x 200

was produced by isostatic pressing. In addition there were no dies available that were suitable for producing tensile specimens, so the method was discontinued.

4.4.2. Isostatic pressing

A National Forge press was used, having internal measurements of 30 cm x 10 cm diameter with the top screwed down. The maximum pressure available was 413 MN/m^2, and this was used in most cases.

Sacs were made by casting silicone rubber into cylindrical moulds, or by slip casting onto a horizontal former rotating at about one rev. every two seconds. The mix was de-gassed under rough vacuum before use, to avoid the formation of bubbles and voids which lead to failure of the mould under pressure. It was found preferable, but not essential, to cure the moulds in a hot oven before use, as this tended to stop the powder charge sticking to the rubber. On a few occasions the sacs were put into the oven after being filled with powder, and the sac stuck to the compact so well that it had to be scraped off.

The thickness of the sac is a compromise between flexibility and strength. The powders being compacted had a large compaction ratio (8), which requires severe deformation from the sac. A thin sac deforms more easily but is also easier to tear, and may either tear on decompression or completely stick to the compact. A thick sac is more liable to tear on compression and, if it does stick to the compact, can pull it apart on decompression. A compromise thickness was found to be about 2mm. No sacs lasted more than three cycles.

The sacs were sealed with a rubber bung, chamfered on the inside edge (Fig 64). Elastic bands held the sac to the bung, and the whole assembly was put either into a large thin sac or a rubber glove. The outer sac was sealed with a clamp or elastic band, to keep water out of the compact should the sac fail.

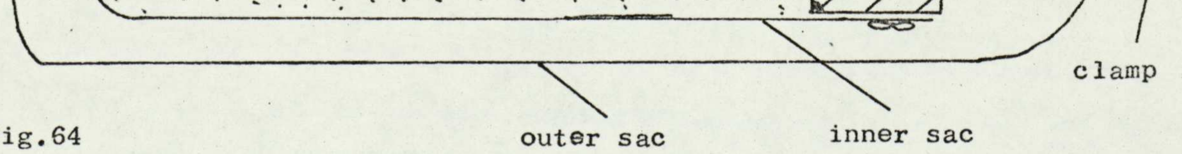


Fig.64

If failure occured on compression, the compact was in damp, half-compressed pieces. Failure on decompression, which was more common, resulted in the compact being contaminated with the water and oil used as pressing medium. Such contamination can interfere with subsequent densification.

The sealed sacs were let down into the pressure vessel, standing in a perforated steel cradle with a wire handle (Fig 65).

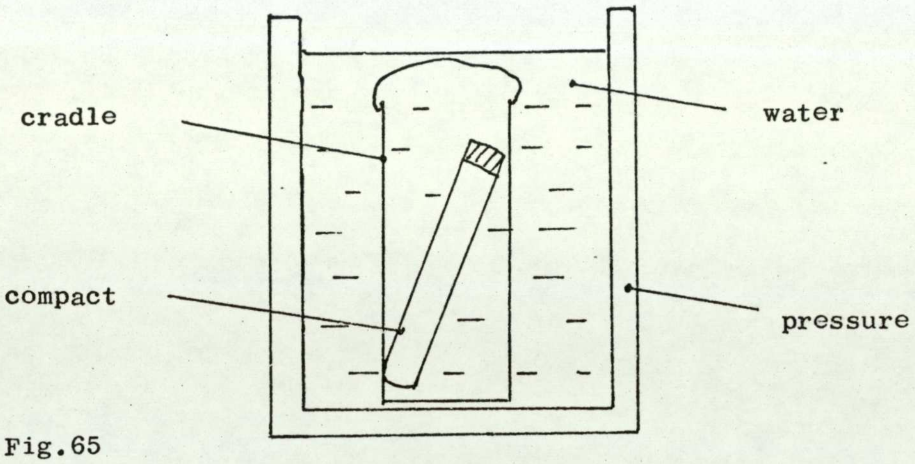


Fig.65

The pressure was increased as rapidly as the pump permitted, held at the maximum for 30 secs, and then slowly reduced, especially over the last few tens of MN/m^2, to allow the rubber to relax and any trapped air to escape without blowing the compact to pieces.

When preparing test pieces, the object was to produce a densified compact a little larger than the blank required, i.e. 2 mm greater in diameter and 0.5 cm longer, to allow for machining. Trial pressings and densifications were necessary to determine the compaction ratio and shrinkage during densification, so that the sac size could be determined. It was essential that once this had been decided upon, powder batches were prepared with consistent properties, particularly density. The density was controlled by the reduction process, and if appreciable sintering of the powder occurred as described in section (4.3), the compaction ratio was reduced, and either too large a compact resulted or there was insufficient powder to fill the sac. The former resulted in waste of material and increased machining time, and the latter usually meant that unless a smaller sac could be found the required blank shape was not produced.

4.5. Densification

4.5.1. Sintering the stainless steel compacts

A 20 $^{v/o}$ mix of alumina in stainless steel was compacted and sintered in vacuo at 1360°C (M.P. 1385°C). for one hour. The density was 89% theoretical. Chemical analysis showed 4.4% of an insoluble chromium compound, which was not present in the green compact. Evidently some reaction was taking place between the matrix and dispersant. No further experiments were performed, partly because of this reaction, and also because it was decided that the flaky nature of the matrix powder was not conducive to obtaining a thorough dispersion. No test pieces were produced.

4.5.2. Sintering the iron compacts

No furnace was available which could sinter compacts in vacuo large enough to make a test specimen, and which was operable at over 1400°C. The only furnace capable of 1500°C was a small ceramic tube 'Gallenkamp' type, which had a hot zone just long enough to produce a blank for machining into the smallest metric Hounsfield tensile specimen. The chief disadvantage was the slow thermal time cycle, which limited production of specimens to one per day (See Fig 66).

At first, the compacts contained $5^{w/o}$ of paraffin wax, both to prevent re-oxidation of the iron and act as a pressing lubricant and binder. It was found that strong green compacts were produced without the wax, and there was some indication that compacts containing wax did not reach as high a density as those with wax.

One compact, whilst sintering at 1400°C melted and dissolved the alumina boat and tube. Subsequent analysis of the green compact from which the piece had been cut showed a large percentage of unreduced oxide, which had formed a slag below the melting point of the iron. All subsequent compacts were analysed for total iron before densifying.

A sintering cycle (Fig 66) consisted of loading the compact into the boat, inserting it into the tube, and then purging the tube with argon. After a few minutes the furnace controller was set at about 100°C above the required temperature, switched on and the argon changed to hydrogen. A thermocouple was inserted into the sheath, as far as it would go, and relied upon to give a true indication of the sintering temperature. This temperature was plotted as the furnace heated up, and as it reached the required level the controller was turned down until the current went off. This was done to decrease the heating up time, as the controller tended to

Fig. 66. A sintering trial time - temperature cycle.

cut in early and slow up the rate of increase of temperature. The furnace was checked periodically during the sintering periods, to keep the temperature level correct, and after the required time the current was switched off. The hydrogen flow was left on until the temperature fell to below 400°C, when it was switched to argon.

The results of sintering a $2^{v/o}$ alumina-compact at various temperatures for a constant time in Hydrogen are shown in Fig 67. It is seen that theoretical density was reached with a sintering temperature of 1450°C.

A furnace was located which had a vertical ceramic tube large enough to sinter three Hounsfield specimens at once. It was capable of 1450°C, but using argon, not hydrogen. Some $7^{v/o}$ pressings were produced and tied together with platinum wire, with which they also suspended from the top of the tube. They were lowered over a period of 10 mins into the middle of the hot tube (1400°C) and then held there. After 5 mins the platinum wire failed and the specimens fell to the bottom of the tube. The tube was removed hot and the compacts tipped out. Their density was found to be 92% theoretical, so a piece was sawn off one compact and further sintered at 1450°C for two hours in hydrogen. The density did not change but the hardness fell. Another compact from the same mix was sintered in H_2 at 1450°C for 5 mins and achieved the same density and hardness as the original argon sintered compacts, but contained large pores.

These experiments suggested that the overiding factor was the sintering temperature, the atmosphere being less important, (but hydrogen preferred), and that the density reached over 90% in only 5 mins at the sintering temperature.

Some compacts were sintered in cracked ammonia at 1100°C for one hour, and no significant deviation was found between the effects of HN_3 and H_2 on the compact. This knowledge is useful for costing purposes, as cracked NH_3 is cheaper than bottled H_2.

The results of the experiments with sintering are shown in Table 8, which gives all the mechanical properties that were measured.

A more detailed study of the effects of time and temperature on the sintered densities was stopped when it was found that the mechanical

SINTERED DENSITY OF IRON 2 VOL.% ALUMINA IN HYDROGEN (H.P.)

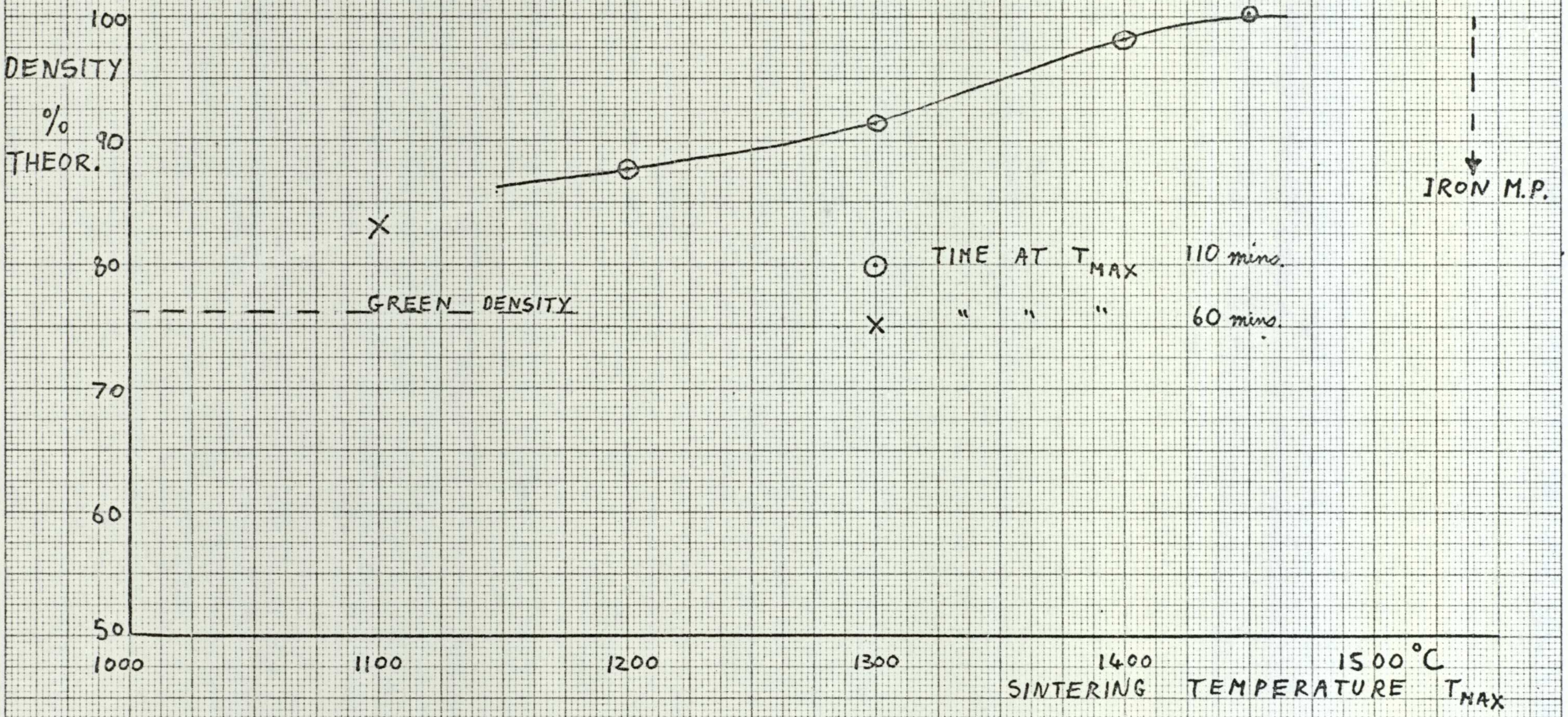


FIG. 67

TABLE 8 PROPERTIES OF SINTERED COMPACTS

Constituent Specification					Sintering Conditions			Properties				
Matrix	Size mμ	Dispersant	Size mμ	Vol %	Atmos	Temp °C	Time hrs	Density (% Theor)	H.V.	U.T.S. MN/m^2	Y.S. MN/m^2	Elongation %
Iron	600	Al_2O_3	30	2	Vac	1400	3	87.8	102.5	187		3
"	600	Al_2O_3	30	2	NH_3	1100	1	86.1	75.8	190	185	2
"	600	Al_2O_3	30	2	H_2	1100	1	83	76.0	220	170	6
"	600	Al_2O_3	30	2	H_2	1450	0.1	76.5		130		0
"	600	Al_2O_3	30	7	A	1400	0.1	93.2	109	275	230	3
"	600	NONE		0	NH_3	1100	1	83.4	74.5	225	125 112	16
"	600	Al_2O_3	30	7	H_2	1450	0.1	87.1	76.4	135		2
"	600	NONE		0	H_2	1450	0.1	94.7	84.8	235		36
"	600	NONE		0	A	1450	0.2	89	71.6	90.0		4

properties of hot forged specimens were considerably superior to those obtained by sintering.

4.5.3. Hot forged specimens

Green compacts were produced that fitted into a 4" x 1" die set using pure iron as the matrix, and alumina, silicon nitride, and titanium nitride, as dispersants. Blocks 4" x 1" were made by pressing in a 2" diameter rubber sac 6" long and squashed roughly into a square shape. This was found to be as good as pressing in an 8" x 2" x 2" rectangular rubber sac specially made for the job.

The compacts were heated up to about 1100^{o}C in an NH_3 atmosphere- a process taking 20 to 25 mins. When hot, they were transferred quickly to the die set, and the ram brought down at a speed of 25 cm sec^{-1}, and an ultimate force of 309 MN/m^{2} which it held for 2 to 3 sec. The specimen was ejected at a temperature of 700 to 800^{o}C and cooled in air.

The densities achieved were 96 to 97%, and the properties measured are shown in Table 9.

4.6. Preparation, examination and testing of specimens

4.6.1. Density measurements

A visual examination of the specimen was made, to ensure that there were no cracks or fissures, and that no melting had taken place. If the specimen was a well shaped cylinder or a rectangular block a simple volume calculation and weighing was used to give quick measurement. Irregular shapes were wrapped tightly in a single layer of thin P.T.F.E. tape and their volume measured approximately by immersion in water in a graduated cylinder. The P.T.F.E. effectively kept the water out of the pores of the compact.

These density measurements, as well as being rapid, were a useful check against a mistake in the standard method, described in A.S.T.M. designation B 328 - 58T. The density is calculated from;

$$D = \frac{A}{B-C} \text{ in gms cm}^{-3}$$

where A = weight in air of the oil-free specimen

B = weight of the oil impregnated specimen in gms.

TABLE 9. PROPERTIES OF HOT FORGED COMPACTS

Constituent Specification					Forging Conditions			Properties				
Matrix	Size mμ	Dispersant	Size mμ	Vol %	Heating up time mins	Forging Pressure MN/m^2	Temp ^{o}C	Density % Theor	HV	UTS MN/m^2	YS MN/m^2	Elongation %
Iron	600	NONE	-	0	25, plus 60 at temperature	309	1100	97	114	325	160 / 143	27
"	600	NONE	-	0	20	309	1160			290	112	22
"	600	Al_2O_3	30	7	25	770	1120	91	196	447		0
"	600	Si_3N_4	15	5	20	309	1100	95		255		0
"	600	TiN	15	5	20	309	1100	93	149	Broke up in furnace		

All compacts heated up in NH_3 atmosphere, and forging pressure held for approximately 2 seconds.

C = weight of the oil impregnated specimen in water in gms.

The theoretical density was calculated at the same time as the amounts of matrix and dispersant required to produce a given volume percent mix were worked out. There is a tacit assumption that the chemical analysis of the compact is as predicted, but if the iron is incompletely reduced the pore-free density will be less than the predicted theoretical density. Strictly speaking every compact should have been analysed, but in the case of e.g. sintering trials where the density rises to theoretical with increasing temperature, it was assumed there was negligible iron oxide present.

4.6.2. Polishing, and hardness measurements

The standard grinding and polishing method was performed on a piece cut from the specimen so as to display the required section, and then mounted in plastic or resin. The surface was ground on a series of automatic rotary grinders, using wet silicon carbide discs. The successive grades were

1) 150 grade
2) 280 "
3) 400 "
4) 600 "

The surfaces were then polished on,

5) 6μ diamond on nylon cloth
6) 1μ " " soft "
7) 0.25μ " " "

The specimens were then either etched and examined, or examined unetched in an optical microscope.

At some stage during the grinding process Vickers hardness measurements were made with a micro hardness tester. The load was 10kg. and the average was taken of four or five readings.

4.6.3. Etching, and preparation of replicas

The stainless steel compacts were etched electrolytically in a solution made by dissolving 10 gms of oxalic acid crystals in 100 ml water. The etching rate was kept low, and the surface was examined under the microscope every two minutes. At the same time as the grain boundaries appeared so did the etch pits, so it was necessary to go slowly to avoid over-etching and spoiling the surface.

The iron compacts were etched in either nital (nitric acid in alcohol) or picral (picric acid in alcohol). Picral was better for low magnification displays, as it had a staining action on the iron oxide particles which made it possible to distinguish these from porosity and grain boundaries. It was found that when preparing a surface for the electron microscope, it was better to use nital. Figures 68 and 69 show two series of replicas taken from the same specimen, the first series etched in picral and the second series in nital. The first of each series of three is what is usually known as a clean up replica, as is the second. The third is the replica which is usually shadowed and coated with carbon, and represents the contour of the surface with all etchant debris and dust removed. The first is an extraction replica, so called because any loose particles which are on (or in) the surface become embedded in the plastic film. It appeared that nital etching produced clearer pictures, with more detail, and that the ordinary replica was deceptive, as any ultrafine particles present in the polished surface were undermined during etching and subsequently removed and thrown away with the clean up replicas.

4.6.4. Tensile strength measurements

Suitably sized densified compacts were machined to Hounsfield metric test piece specification. At first the single shouldered specification was used, but this was changed later to double shouldered, as there was a tendency for the fracture to occur at one end of the gauge length (Fig 70). The double shouldered pieces fractured in the centre of the gauge length.

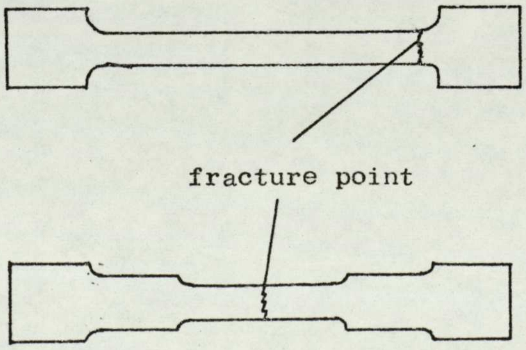
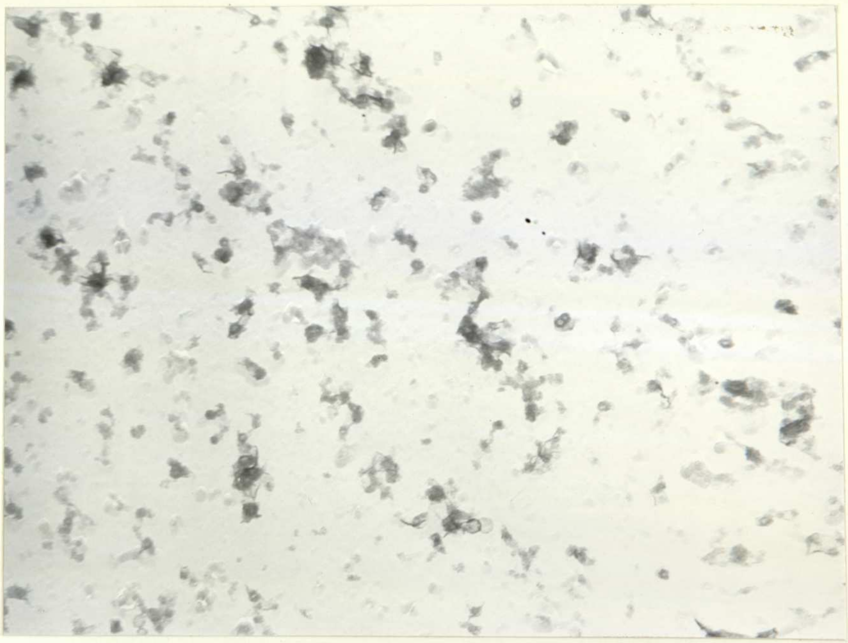
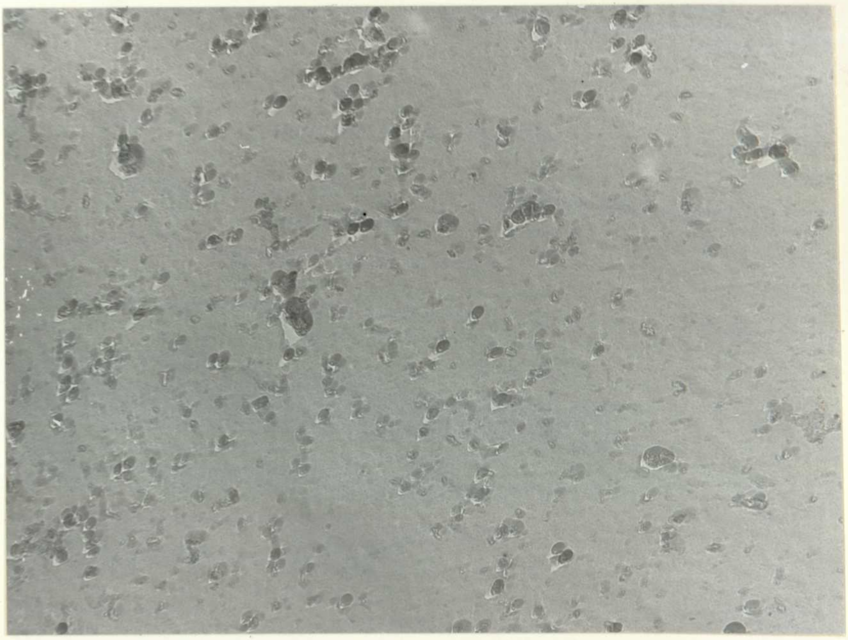


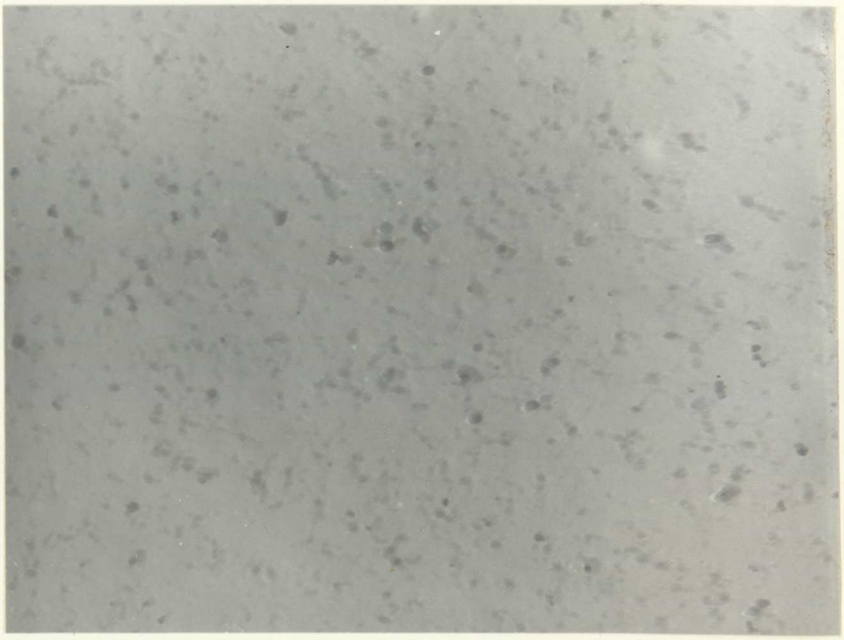
Fig.70



1st replica

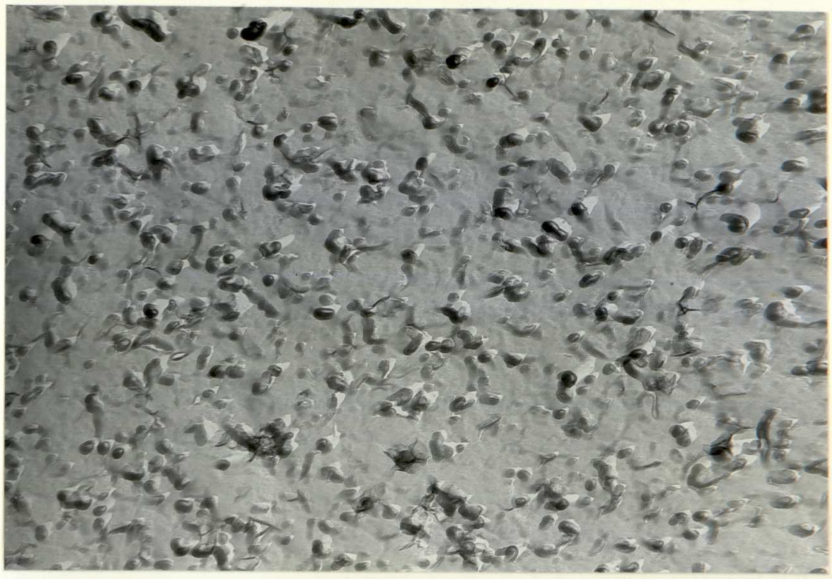


2nd replica

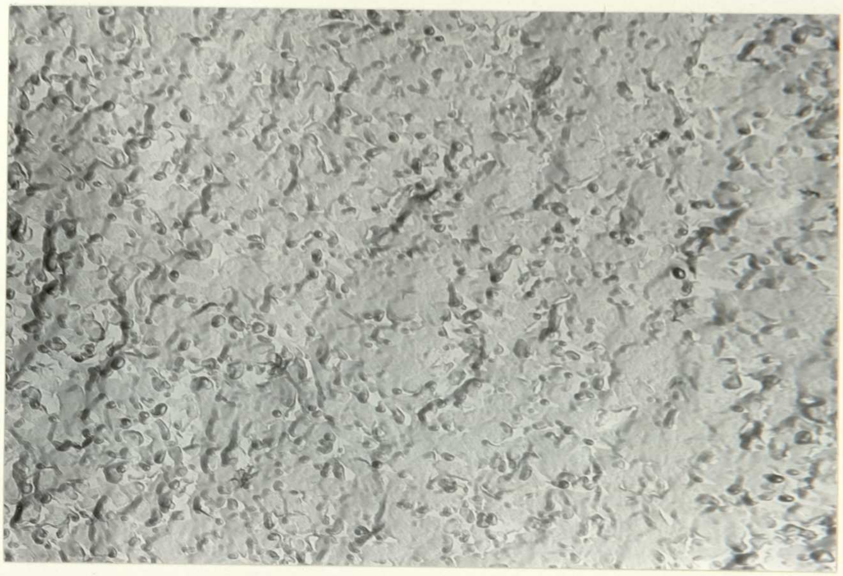


3rd replica

Fig. 68. Electron microscope replicas. Fe + 7^{v}/o Al_2O_3 Etched in picral.



1st. replica



2nd replica

3rd replica

Fig. 69. Electron microscope replicas. Fe + 7$^{v/o}$ Al_2O_3
Etched in nital

The properties measured were yield strength, ultimate tensile strength and elongation. The stress values are quoted in MN/m^2 to conform with S.I. Units. The results are given in table 8, section (4.5.3).

PART THREE

EVALUATIONS AND CONCLUSIONS

CHAPTER FIVE

EVALUATION OF RESULTS OF EXPERIMENTAL WORK AND LITERATURE SURVEYS

Introduction

A manufacturing company is a complex organism. Much of the work of management scientists has been devoted to developing models and approaches which assist managers to understand the nature and behaviour of their company. A simple description of the way in which a company responds to its competitive environment is known as Strengths, Weaknesses, Opportunities and Threats analysis (S.W.O.T.).

The GKN Group's main strength lies in its production capacity, and knowledge in depth of a very broad market which covers nearly the whole of the engineering field and the steel industry. Its main weakness may be that small projects, i.e. less than £100,000 p.a. turnover, however profitable may not readily fit into the organisation unless they are complementary to other activities because of the disproportionate amount of management effort required to run them. This is an ideal situation for small competitors, who can take advantage of the more specialised, lower volume corners of a particular business. Opportunities, for GKN, lie wherever the group can apply its strengths. The problem is to identify future markets which will provide suitable outlets for the sort of large volume production GKN can provide. A similar problem is associated with identifying threats to the groups' business, the most serious source being a sudden change in the material specification for an important line of components.

Research work can be initiated to exploit opportunities or defend threats. It is proposed that if a company's position is considered in this way, two separate strategies for research emerge:these will be termed 'offensive' and 'defensive'. The offensive strategy covers research aimed at improving specific products or processes, or exploiting specific opportunities. The defensive strategy includes activities such as drawing up 'defensive' patents and keeping ahead of competitors.

One of the objectives of this thesis is to assess and evaluate the results of certain research and experimental work. Before this can be done, it is necessary to have a clear idea of the aims of the work, so as to define a basis on which it can be evaluated. In the case of the plasma work, the basis is clearly firstly technical, and secondly costing.

The reason for identifying and costing possible competitors is also clear and was discussed in the introduction to chapter one, but no economic value can be put on it. Review work also, cannot be evaluated in monetary terms. How then can such work be evaluated?

The answer to the question just posed is 'strategically'. It was shown above how the S.W.O.T. analysis defines two strategies for fundamental research. Each strategy can be applied to either process or product research, which in turn is a function of the relation of the research to current activities, and the extent of market knowledge.

The relation of the research to current activities falls into two classes:-

a) Research within a field which is basic to the industry, which already covers a majority of a company's products or processes and which is expected to be central to the company's activities for the foreseeable future.

b) Research in areas related to those already engaged upon by the company, in a search for new products or processes which should fit the existing organisation of the company. (The word 'new' is taken to mean 'new to the company').

In either case, the research may, or may not, be accompanied by market research in existing or new markets, leading to the following scheme in the offensive strategy:-

	Market already well known to the company	New market already identified	New market not yet identified
Research basic to company's main products	I Improvements Possible breakthrough.	II Development of existing products/ processes to well defined objectives	III Development of existing products process (in search of new objectives?)
Research not basic but related to existing company products and processes	IV New products or processes, low risk of failure	V New products or processes, acceptable risk of failure	VI New products or processes. Highly speculative, unknown chance of success

And in the defensive strategy.

	Market already well known to company	New market already identified.	New market not yet identified
Research basic to company's main products or processes.	VII Ensure continuing competitive position.	OBJECTIVES ARE OF	NOT
Research not basic but related to existing products or processes.	VIII Be in positions to take up expected opportunity.	QUESTIONABLE VALIDITY	APPLICABLE

Fig.72 Fundamental research objectives: Defensive strategy

Bearing the previous discussion on evaluation and objectives in mind, this chapter begins by examining the problems of finding markets for the results of fundamental research and describes two possible applications, of interest to GKN, for D.S. materials. The results of the various costing exercises are drawn together, so that the total cost of a particular production route may be obtained. The second section is devoted to a cost model for the plasma chemistry process, and the results of the computer program are given. The final section discusses methods of financial evaluation.

5.1. Application and Markets for Dispersion Strengthened materials

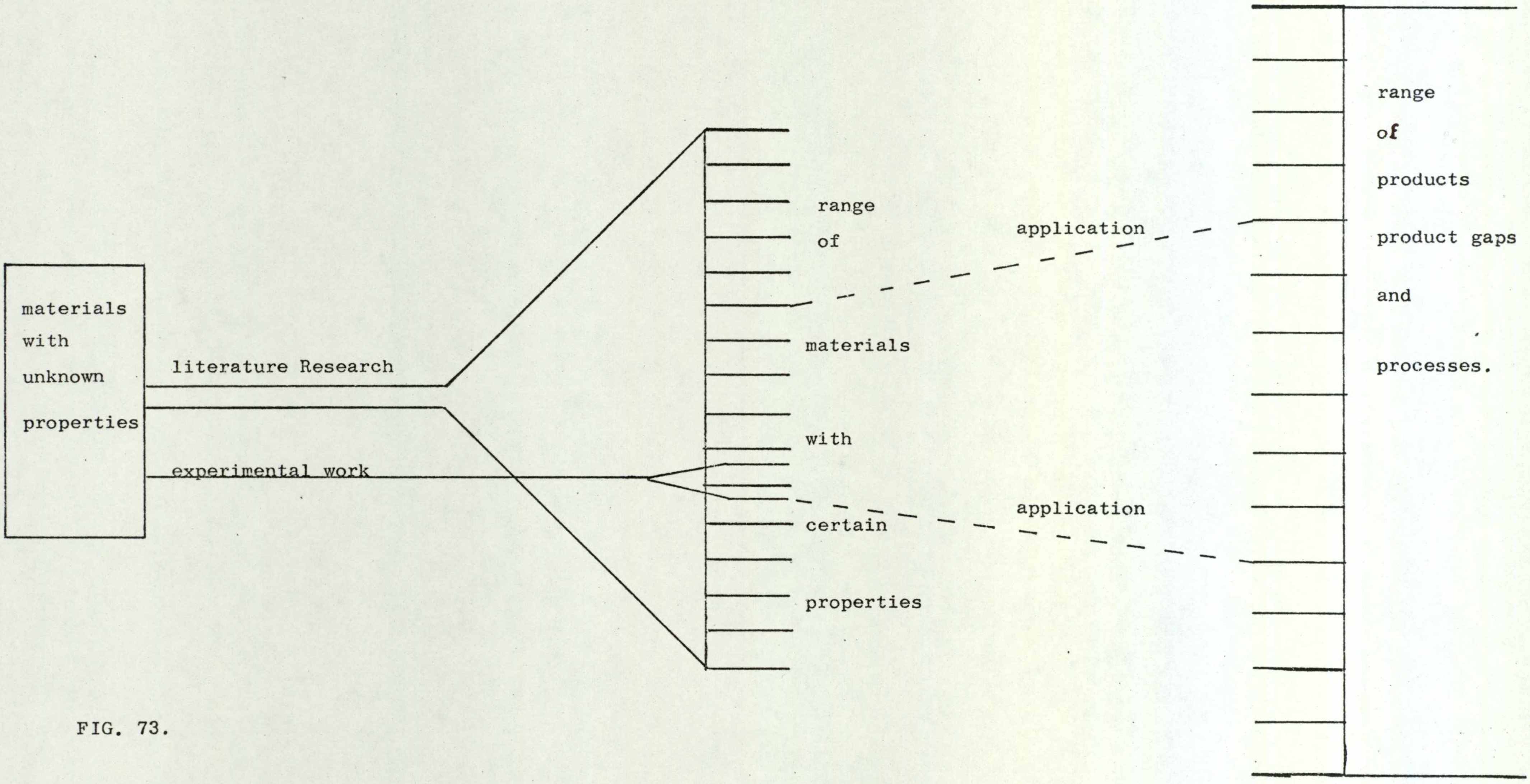
5.1.1. Finding Markets

As the length of the project was subject to a time constraint, the search for applications was begun as early as possible, before any indications had been received of the properties which could be expected from the materials produced in the experimental programme. The contradiction in terms which is inherent in the previous statement was recognised from the start, and presents a problem which is fundamental to the situation. The problem may be formulated by the question : how does one seek applications for a material with unknown properties?

A major implication of the problem is that a search for applications must be in part predictive. The various techniques which have been developed to predict the future behaviour of demands as a function of time and technology are known collectively as Technological Forecasting. These methods were examined. None of the specific techniques were found to be of direct predictive use in this situation, but the approaches used were helpful in formalising certain concepts: Figure 73 shows schematically the question formulated above, and the contributions of the literature research and experimental work in the effort to find an answer. Research into the literature on D.S. materials was initiated to discover their characteristic properties, and the results are set out in the table in Appendix 5.

5.1.2. Two possible markets for the use of D.S. materials

As described in the main Introduction, a large proportion of GKN's business is metal forming. Most conventional metal forming and cutting processes rely on the use of a consumable tool to do the work, which wears away until it is no longer usable. It is then recut or replaced. Tool materials are important in hot and cold forging, upsetting, milling, punching, cutting, and machining. Part of the secret of commercial success depends on making the optimum use of expensive machinery and labour, so a major aim of production engineers is increased productivity. One of the constraints in machining rate when surface cutting is that above a certain rate, temperature of the working surface rises to a level at which wear increases rapidly, reducing tool life. Any tool material which has increased wear resistance at an acceptable cost has a potential market.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and
processes.

FIG. 73.

Hard materials are machined with cemented carbide or ceramic tool pieces. A throw-away tip of the tool material is clamped into a tool holder which acts both as support and heat sink. YATES has shown an improvement over the conventional tungsten or titanium carbides cemented with cobalt. He made materials from nitrides cemented with dispersion strengthened tungsten, and rhenium/molybdenum matrices, in which the dispersant was an ultrafine nitride.

This is an application of ultrafine nitrides used as dispersion strengtheners in a material which could be of use to GKN, as a replacement for conventional cemented tungsten carbides, so it is worth examining the current U.K. market. Figure 74 shows the U.K. production of cemented carbides from 1955 to 1967, taken from the Board of Trade Figures (Census of Production, Business Monitor). The market is of course much larger than that of GKN alone, but if the company were to produce tool materials for its own use, there is also a possibility of sales to the rest of industry. Also on the figure are the index of production and the cost of tungsten powder, which the sales curve follows.

The development of new tool materials is consistent with an offensive strategy. GKN's main strength lies in its production capacity, and knowledge in depth of a very broad market which covers nearly the whole of the engineering field and the steel industry. An improvement in tool materials can lead to immediate savings in tool costs per component, and an increase in production efficiency. This represents an improvement in one of the company's main processes in a well known market, so is consistent with the objectives in Box I in Fig. 71.

2) Heavy duty friction materials

Friction materials are the working surfaces of brake shoes and disc, and clutch plates. They are expected to wear during service, and are replaceable. The application of cermet materials to clutches in earth moving machinery is described by DRISLANE, as an extension of their use in aircraft brakes. The technological aim of research is to improve the performance characteristics of the material, which must be able to maintain its coefficient of friction at several hundred ^{o}C, with low wear rates. The economic aim, as always, is to produce a competitive material at a lower price.

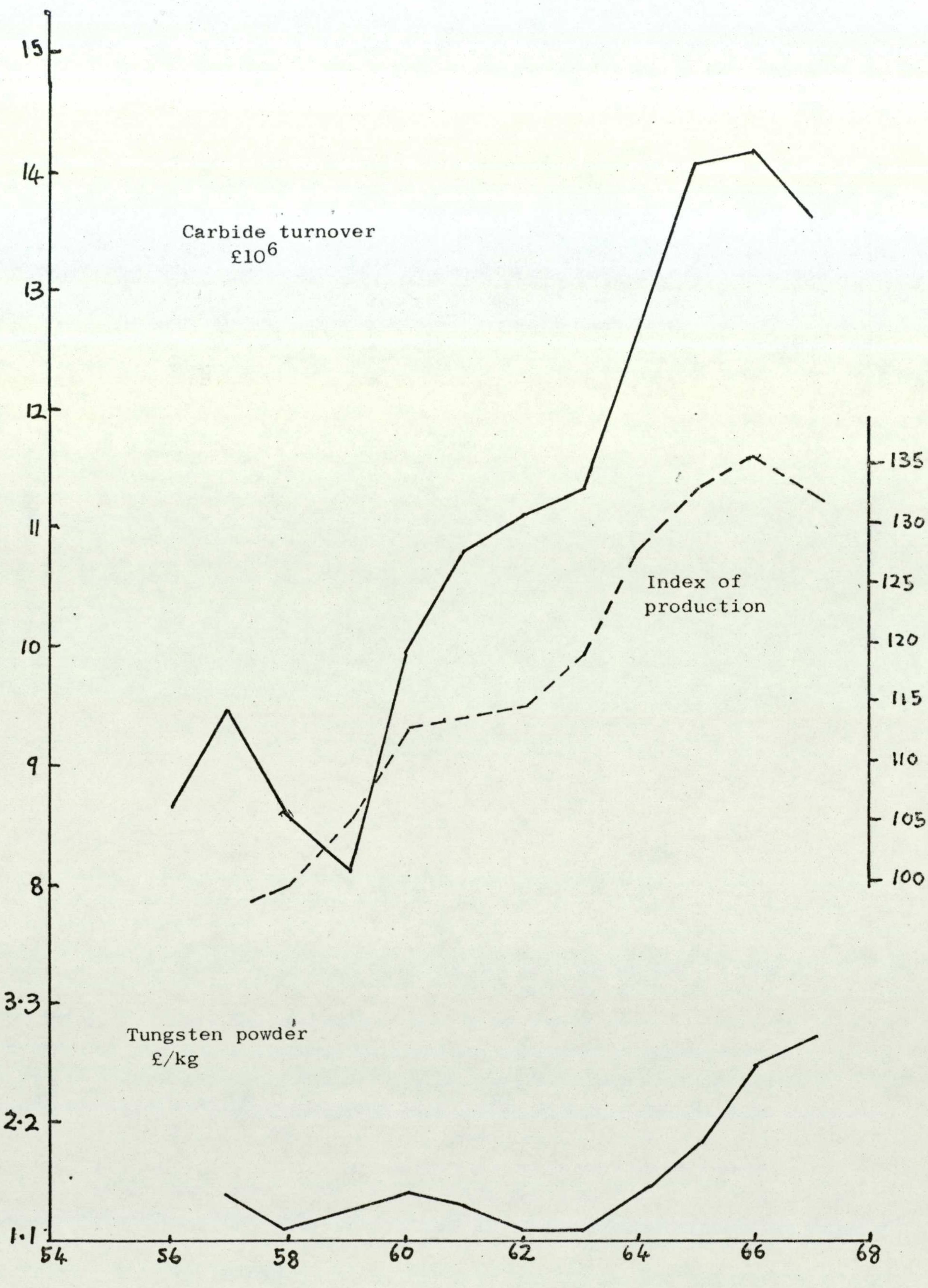


FIG. 74. U.K. production of cemented carbide.

To obtain an idea of the potential market, the Engineering Base of B.E.A., as major customers, were asked for data on their expenditure on brake pads. Their reply is summarised below.

Material	Form	Annual Purchase	Manufacturer
Copper/Ceramic	cupped pad	£110,000	Dunlop Ltd.
Sintered iron	pad on a flat backing plate	£150,000	"

B.E.A. have no data on the composition or performance of the pads.

B.E.A. represent only a small proportion of the world market in aircraft brake linings, which could be in the region of £10m. According to DRISLANE, the cup pad construction of copper/ceramic materials was necessary to confine structurally the high (25%) ceramic content'. Some information on cera-metallix materials is given by BATCHELOR.

Further investigations are needed to determine the composition and cost per kg of these materials before useful data can be put into the cost model.

The manufacture of heavy duty friction materials is also an 'offensive' action, in a market which may be new, but is identified. One of the subgroup's already manufactures transmission units for the automotive industry, so any new products would be related to existing ones. The relevant objectives belong to Box V in Fig. 71.

5.1.3. Summary and comparison of the costs of production of D.S. materials using ultrafine powders

Fig. 75 shows how the various processes of production, mixing, reduction, compaction and densification can be combined to produce a dispersion strengthened material. Where the process has been costed for a particular material, that material is specified.

As an example, the cost of an iron + $5^{w/o}$ plasma silicon nitride material is followed through a production route. The cost of the materials

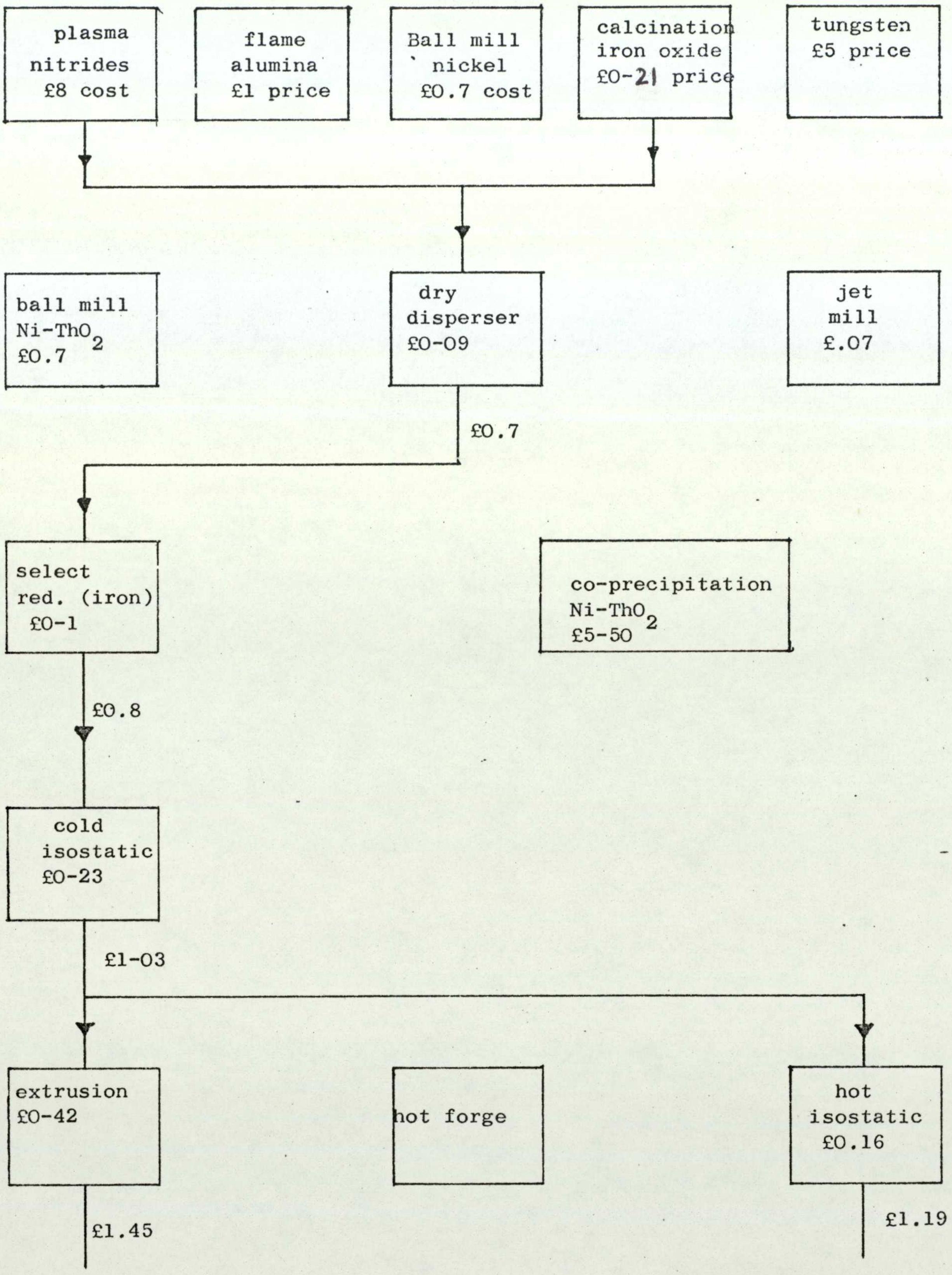


FIG. 75. Summary of process costs for D.S. materials, in £/kg of product.

is included in the powder production step.

The major cost items in the case cited are the dispersant nitrides, and the densification process if extrusion is chosen. The figure for extrusion is heavily dependant on the life and cost of die sets. In the figure quoted, these were taken as £50 each, and ten extrusions per die.

These cost figures are a good basis from which to start a detailed cost analysis of producing D.S. materials, should it be decided that they are of commercial interest to GKN.

5.2. The cost model for the production of materials using a D.C. plasma torch

A cost equation is developed along the standard lines, but the interrelation of components is so complex that a computer program is necessary to evaluate it. The program is described, and the results of a sensitivity analysis on the cost elements are presented.

5.2.1. A simplified cost equation

The cost components of the production of ultrafine powders (or any other product) using a D.C. plasma torch are as follows:

Variable costs - materials -		Reactants
		Plasma Gas
		Electricity
	Consumables -	Torch nozzles
Fixed Costs	Capital and Maintenance	
	Labour and Overheads	
	Maximum Demand.	

Let the annual production = A.P. kg of product
Reactant cost = £R kg of product.
Plasma gas cost = £G/mole
~~z = no. of moles/kg. of product~~
Electricity cost = £E hour
Hourly production rate. = $\frac{AP}{H}$ kg hr^{-1} = M kg hr^{-1}
Plasma gas flow rate = F moles/hr
Annual Max. demand charges = £D yr^{-1}
Nozzle cost = £N
Nozzle life = x hours

∴ The cost equation, using the standard notation, is

$$P.C. = R + \frac{N}{xM} + \frac{E + FG}{M} + \frac{1}{A.P}\left(\frac{C}{Y} + C_{LOH} + D\right) (£/kg)$$

This equation does not appear complex, until the inter-relations of the components and the effects of efficiencies are examined. Thus we have,

Energy requirements per kg of product (Heat) = f (product yield)
Fraction of available thermal energy used (T.L.F.) = f (reaction temperature)
Electrical capacity of the plant (Elcap) = f (M, Heat, T.L.F. Theff)
where Theff= Torch efficiency
Capital costs = f (Elcap)
Labour costs = f (Hours worked per year)
D = f (Elcap) on a sliding scale.
E = f (Elcap, hours worked) "
Cost of plasma gas per kg product = f (Elcap, Theff, M, torch gas enthalpy)
Cost of reactants per kg product = f (product yield)

To make rapid and reliable calculations, it was considered advisable to write a computer program to evaluate this equation.

5.2.2. Program Documentation

Included in the program (Fig 76) are calculations of the cost of producing a fine iron matrix powder, and the cost of a mixture of this and any percentage of the plasma produced powder.

The program is written in FORTRAN IV for an I.C.L. 1900 series machine. Table 10 gives a list of variables used in order of appearance. A simplified flow chart is shown in Fig 77 and the full flow diagram in Fig 78. In order to simplify the reading and presentation of the flow diagram, the chart has been broken at three points, and the detailed chains of IF statements removed and shown in separate figures (78a, 78b and 78c).

The majority of the statements in the program are self explanatory when considered in conjunction with the flow diagrams, but some may need further explanation.

The use of turnover and selling price to define the annual capacity of a production plant is based on the requirement that new projects rise to a turnover of from £10^5 to £10^6 in three operating years. If a selling price is then decided on, AC is defined and may be compared with the total market as a first test to see if further computation is realistic. When the cost price has been calculated, a comparison between SP and CP forms a test and branch step which decides whether to continue with a financial

```
    MASTER SLAVE
    N=0
100 READ(2,50)TURNO,SP,YLIFE,PDISP,TOKET
 50 FORMAT(5F10.0)
    AC=TURNO/SP
    IF(AC-TOKET)3,3,2
  2 WRITE(1,60)AC
    GOTO75
 60 FORMAT(19H THE VALUE OF AC AT,F10.0,26HIS GREATER THAN THE MARKET)
  3 AMAT=AC*(1.0-PDISP)
    ADISP=AC*PDISP
    ZMCAP=0.015*AMAT
    ZMLAB=3000.0
    MDEPR=ZMCAP/YLIFE
    READ(2,51)XMML1,XMML2,XMML3,XMML4,XMML5,YMCS1
 51 FORMAT(6F10.0)
    CMAT=XMML1+XMML2+XMML3+XMML4+XMML5+YMCS1+(ZMLAB+MDEPR*1.1)/AMAT
    READ(2,51)WHRS,UF1,THEFF,HNT1,HNT2,HNT3
    HPROD=ADISP/WHRS
    SIGHF=444.4-(179.5*UF1)
    HEAT=(SIGHF+619.2)*29.9
    TLF=(HNT1-HNT2)/HNT3
    ELCAP=HPROD*HEAT/(TLF*THEFF*3600)
    ZDCAP=55.0*ELCAP
    IF(WHRS-2000.0)5,5,6
  5 ZDLAB=3000.0
    GOTO9
  6 IF(WHRS-4000.0)7,7,8
  7 ZDLAB=6000.0
    GOTO9
  8 ZDLAB=9000.0
  9 DEPRC=ZDCAP/YLIFE
    B=0
    C=0
    D=0
    E=0
    IF(ELCAP.GT.5000.0)GOTO10
    IF(ELCAP.GT.1000.0)GOTO14
    IF(ELCAP.GT.500.0)GOTO15
    IF(ELCAP.GT.200.0)GOTO16
    A=ELCAP*0.9
    GOTO20
 10 E=(ELCAP-5000.0)*0.778
    D=4000.0*0.808
 11 C=500.0*0.84
 12 B=300.0*0.87
 13 A=200.0*0.9
    GOTO20
 14 D=(ELCAP-1000.0)*0.808
    GOTO11
 15 C=(ELCAP-500.0)*0.84
    GOTO12
 16 B=(ELCAP-200.0)*0.87
    GOTO13
 20 ZDDEM=(A+B+C+D+E)*12.0
```

FIG 76. The plasma cost model program.

```
   READ(2,52)XDML1,XDML2,XDML3,XDML5,
52 FORMAT(4F10.0)
   READ(2,53)CNOZ,YLNOZ,CMIX
53 FORMAT(3F10.0)
   AELCOM=ELCAP*WHRS
   S=180.0*ELCAP
   Q=0
   R=0
   IF(AELCOM.GT.2.0*S)GOTO70
   IF(AELCOM.GT.S)GOTO73
   P=AELCOM*0.498
   GOTO74
70 R=(AELCOM-2.0*S)*0.341
   Q=S*0.395
72 P=S*0.498
   GOTO74
73 Q=(AELCOM-S)*0.395
   GOTO72
74 XDML4=(P+Q+R)/(ADISP*100.0)
   YDCS1=CNOZ/(YLNOZ*HPROD)
   XDGAS=ELCAP*THEFF*XDML3*3600.0/(HNT3*HPROD)
   CREAC=(XDML1+XDML2)/UF1
   ZSIDG=(DEPRC*1.1+ZDLAB+ZDDEM)/ADISP
   CDISP=CREAC+XDGAS+XDML4+XDML5+ZSIDG+YDCS1
   CP=PDISP*CDISP+(1.0-PDISP)*CMAT+CMIX
   WRITE(1,61)TURNO,SP,WHRS,UF1,THEFF,ELCAP,CDISP,CMAT,CP,PDISP,CREAC
  1,XDGAS,XDML4,ZSIDG
61 FORMAT(1H0,5(/),4X,8HTURNOVER,6X,2HSP,4X,4HWHRS,3X,3HUF1,1X,5HTHEF
  1F,4X,8HELCAP KW,2X,7HCDISP £,2X,6HCMAT £,4X,4HCP £,1X,5HPDISP,2X,7
  2HCREAC £,2X,7HXDGAS £,2X,7HXDML4 £,2X,7HZS1DG £/4X,8(1H=),6X,2(1H=
  3),4X,4(1H=),3X,3(1H=),1X,5(1H=),4X,8(1H=),2X,7(1H=),2X,6(1H=),4X,4
  4(1H=),1X,5(1H=),2X,7(1H=),2X,7(1H=),2X,7(1H=),2X,7(1H=),5(/),2X,F1
  50.0,2X,F6.2,2X,F6.0,2X,F4.1,1X,F5.2,2X,F10.0,2X,F7.2,2X,F6.2,2X,F6
  6.2,2X,F4.1,2X,F7.2,2X,F7.2,2X,F7.2,2X,F7.2)
75 CONTINUE
   N=N+1
   IF(N-100)100,80,80
80 CONTINUE
   STOP
   END
```

FIG. 76 (cont)

TABLE 10

FORTRAN VARIABLES USED IN COST MODEL

N	Number of data set.
TURNO	Annual turnover in £ required from sale of the material (company constraint).
SP	Selling price of material in £/kg
YLIFE	Life of capital assets in years - company policy
PDISP	Percentage of dispersant in the material.
TOKET	Total market attainable in kg per year.
AC	Annual production of material required.
AMAT	Annual production of matrix material required in kg
ADISP	Annual production of dispersant material required in kg.
ZMCAP	Capital expenditure required for plant to produce AMAT
ZMLAB	Annual labour plus overheads
MDEPR	Annual capital cost.
XMMLI	Cost of Fe_2O_3 per kg iron produced.
XMML2	Processing cost per kg iron
XMML3 XMML5 YMCSI	Unused variables, allowing for a more precise calculation of processing costs if necessary.
CMAT	Cost of matrix material £/kg
WHRS	Number of working hours in the year, for running the plasma plant.
UFI	The utilisation factor for the conversion of $SiCl_4$ to Si_3N_4. Measured experimentarily as 'yield'.
THEFF	Thermal efficiency of the torch.
HNT1	Enthalpy of the plasma gas at injection point before reactants mix (kJ/mole)
HNT2	Enthalpy of the plasma gases after reaching equilibrium with the reactants at the reaction temperature T_2 (kj/mole)
HNT3	Enthalpy of the plasma gases at the torch exit (kj/mole)
HPROD	Hourly production rate of dispersant (kg)
SIGHF	Sum of heats of formation for the reaction (kcal/mole of Si_3N_4)
HEAT	Sum of SIGHF and the heat required to raise the reactants to T_2 (kJ/kg of Si_3N_4)
TLF	Thermal loading factor, or measure of efficiency of utilisation of the available heat.
ELCAP	Electrical capacity of the production plant (kW)

ZDCAP	Capital cost of the production plant (£)
ZDLAB	Annual labour and overheads charge (£)
CDEPR	Annual capital cost (£)
A	Maximum demand charge for the first 200 kVA
B	" " " " " next 300 kVA
C	" " " " " " 500 kVA
D	" " " " " " 400 kVA
E	" " " " " each additional kVA
ZDDEM	Annual maximum demand charge (£)
XDMLI	Cost of $SiCl_4$ per kg Si_3N_4 produced stoichiometrically (£/kg)
XDML2	Cost of HH_3 " " " " "
XDML3	Cost of plasma nitrogen gas, (£/mole)
XDML5	Unused variable, set to zero.
CNOZ	Cost of one plasma torch nozzle.
YLNOZ	Life of nozzle (hours)
CM1X	Cost of mixing matrix and dispersant, per kg of mixed powder (£kg^{-1})
AELCOM	Number of electrical units consumed per year.
S	Range on which the unit electrical charges are based, related to maximum demand (See Tariff No 7)
P	Annual charge for the first S units. (pence per kW)
Q	" " " " next S " "
R	" " " each additional unit "
XDML4	Electrical unit cost (£/kg)
YDCS1	Cost of consumable nozzles (£/kg)
XDGAS	Cost of plasma gas (£/kg)
CREAC	Cost of reactants (£/kg)
ZSIDG	Sum of fixed costs (£/kg)
CDISP	Cost of dispersant (£/kg)
CP	Cost price of mixed matrix and dispersant (£/kg)

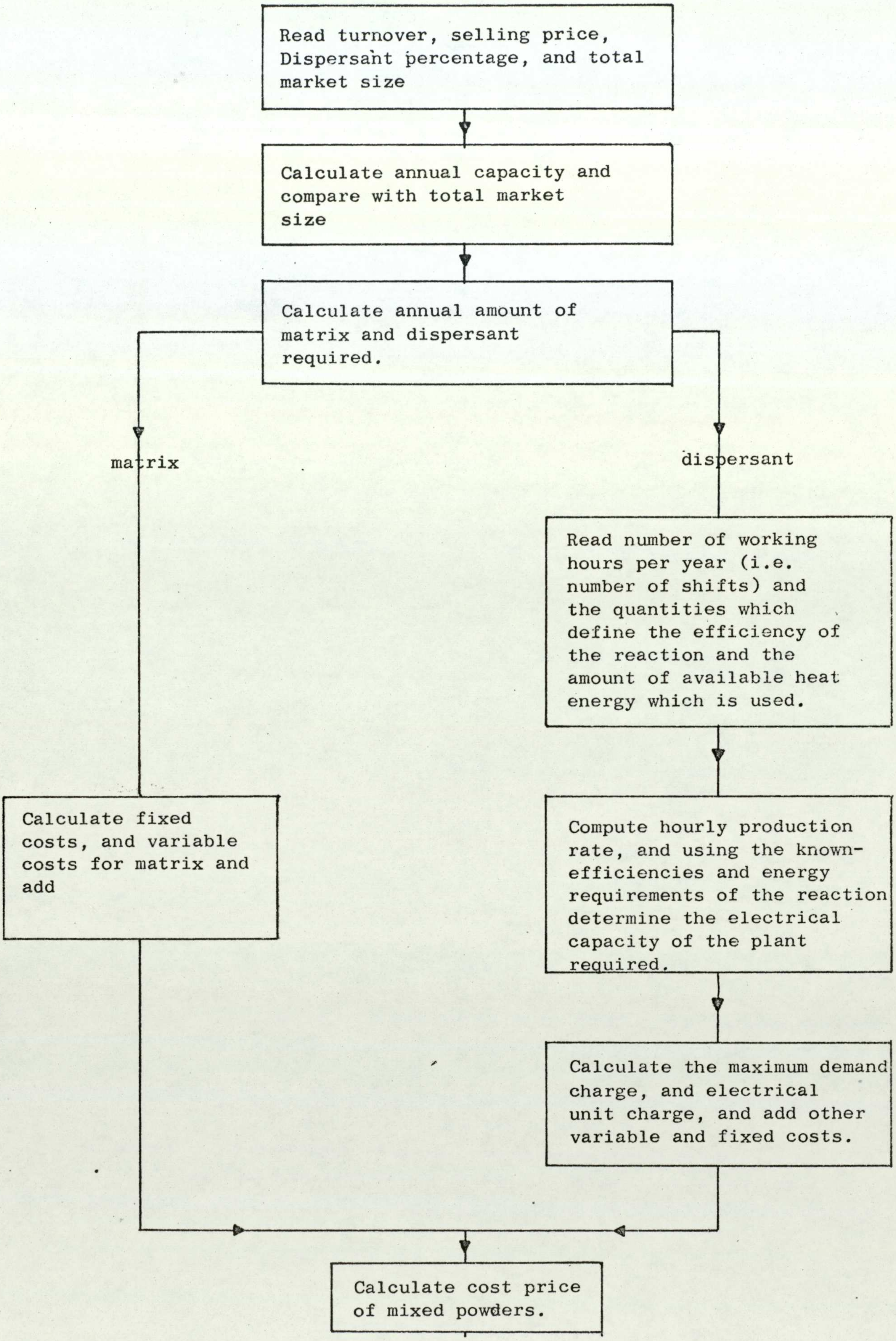

Read turnover, selling price, Dispersant percentage, and total market size
Calculate annual capacity and compare with total market size
Calculate annual amount of matrix and dispersant required.
matrix
dispersant
Read number of working hours per year (i.e. number of shifts) and the quantities which define the efficiency of the reaction and the amount of available heat energy which is used.
Calculate fixed costs, and variable costs for matrix and add
Compute hourly production rate, and using the known-efficiencies and energy requirements of the reaction determine the electrical capacity of the plant required.
Calculate the maximum demand charge, and electrical unit charge, and add other variable and fixed costs.
Calculate cost price of mixed powders.

FIG. 77

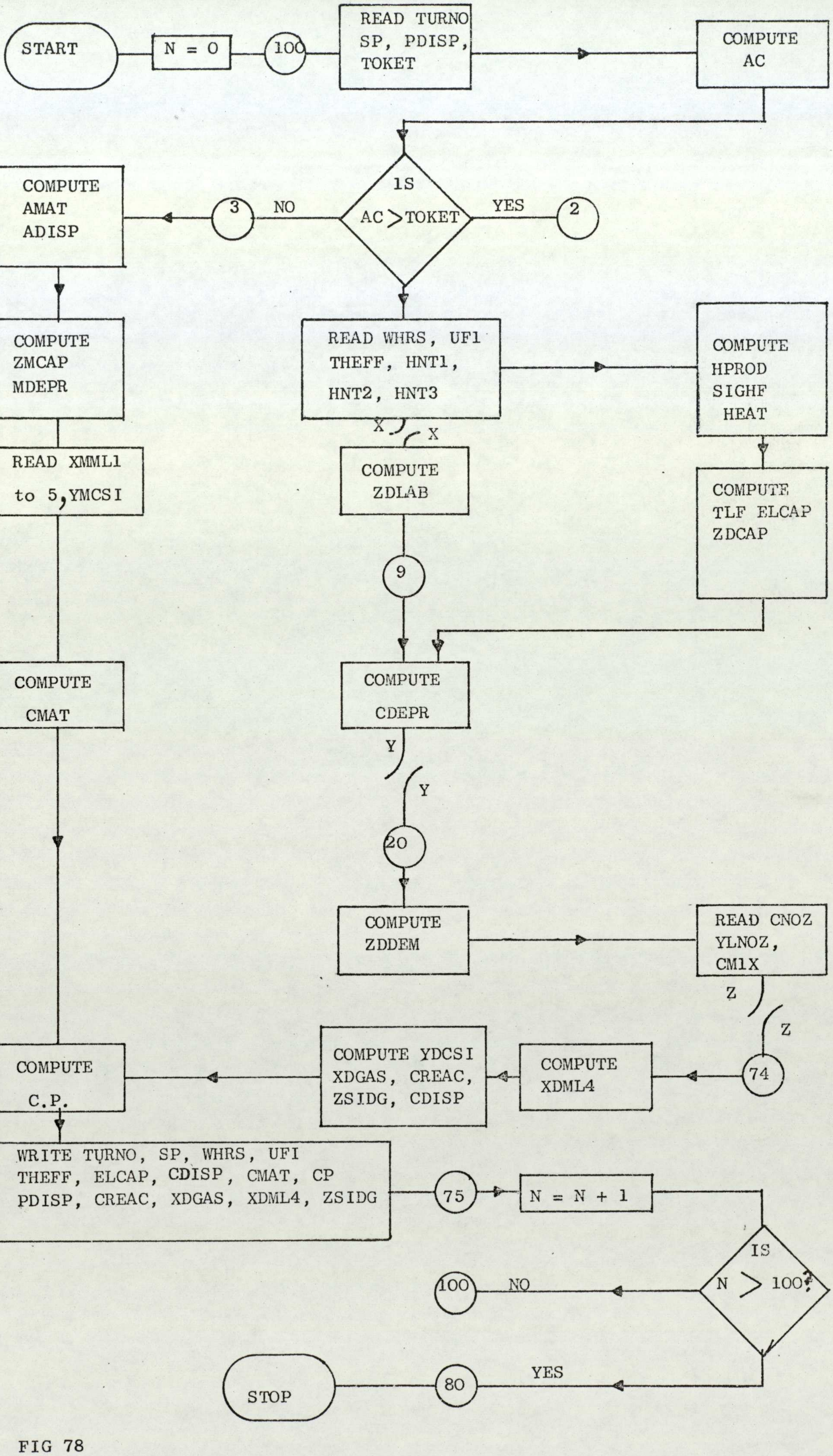

START
N = O
100
READ TURNO SP, PDISP, TOKET
COMPUTE AC
IS AC > TOKET
NO
3
YES
2
COMPUTE AMAT ADISP
COMPUTE ZMCAP MDEPR
READ XMML1 to 5, YMCSI
COMPUTE CMAT
READ WHRS, UF1 THEFF, HNT1, HNT2, HNT3
X
X
COMPUTE ZDLAB
9
COMPUTE HPROD SIGHF HEAT
COMPUTE TLF ELCAP ZDCAP
COMPUTE CDEPR
Y
Y
20
COMPUTE ZDDEM
READ CNOZ YLNOZ, CM1X
Z
Z
74
COMPUTE XDML4
COMPUTE YDCSI XDGAS, CREAC, ZSIDG, CDISP
COMPUTE C.P.
WRITE TURNO, SP, WHRS, UFI THEFF, ELCAP, CDISP, CMAT, CP PDISP, CREAC, XDGAS, XDML4, ZSIDG
75
N = N + 1
IS N > 100?
NO
100
YES
80
STOP

FIG 78

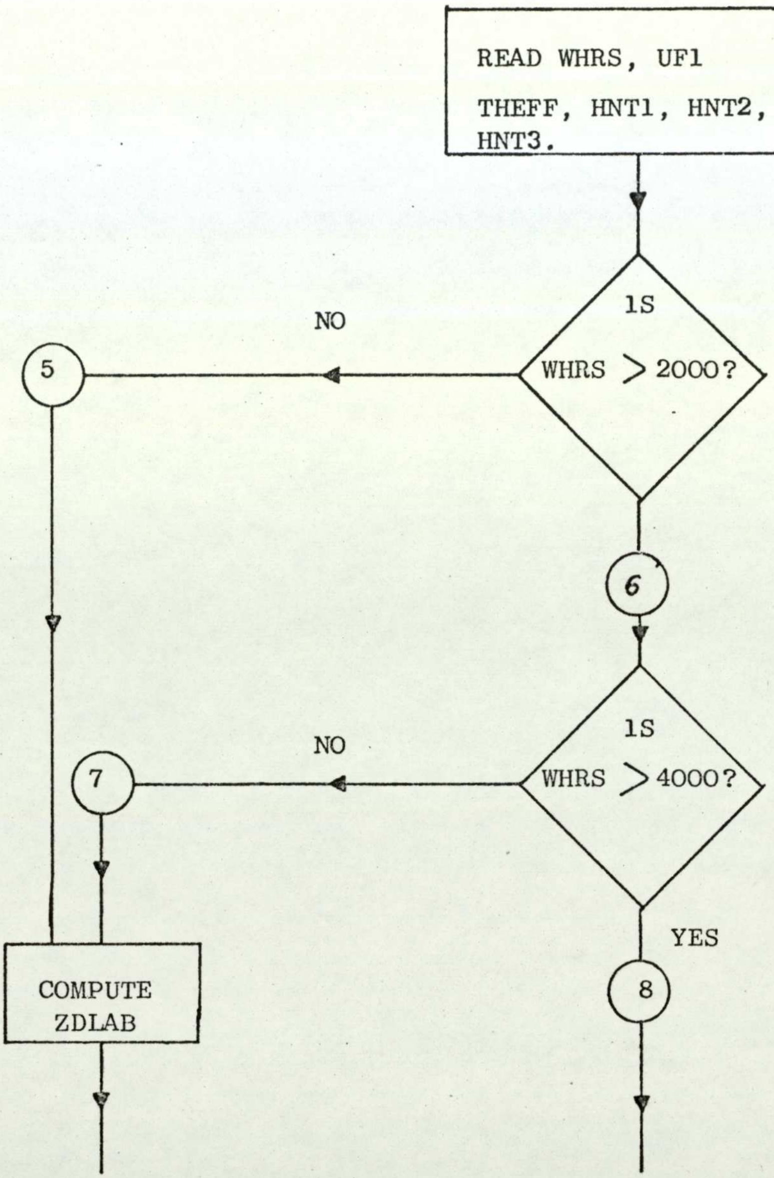


FIG 78a. Section X-X from FIG. 78.

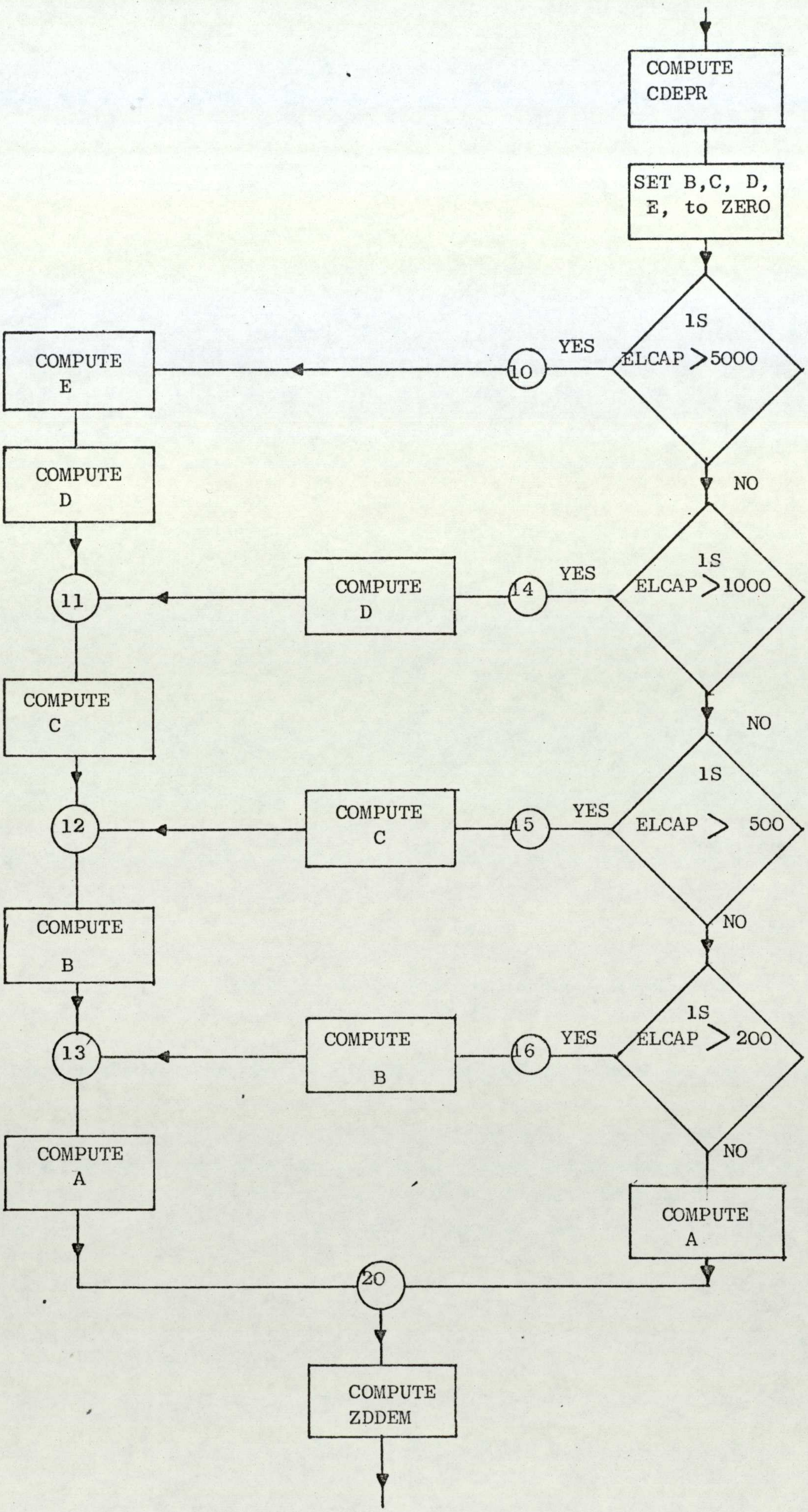


FIG. 78b. Section Y-Y From FIG. 78.

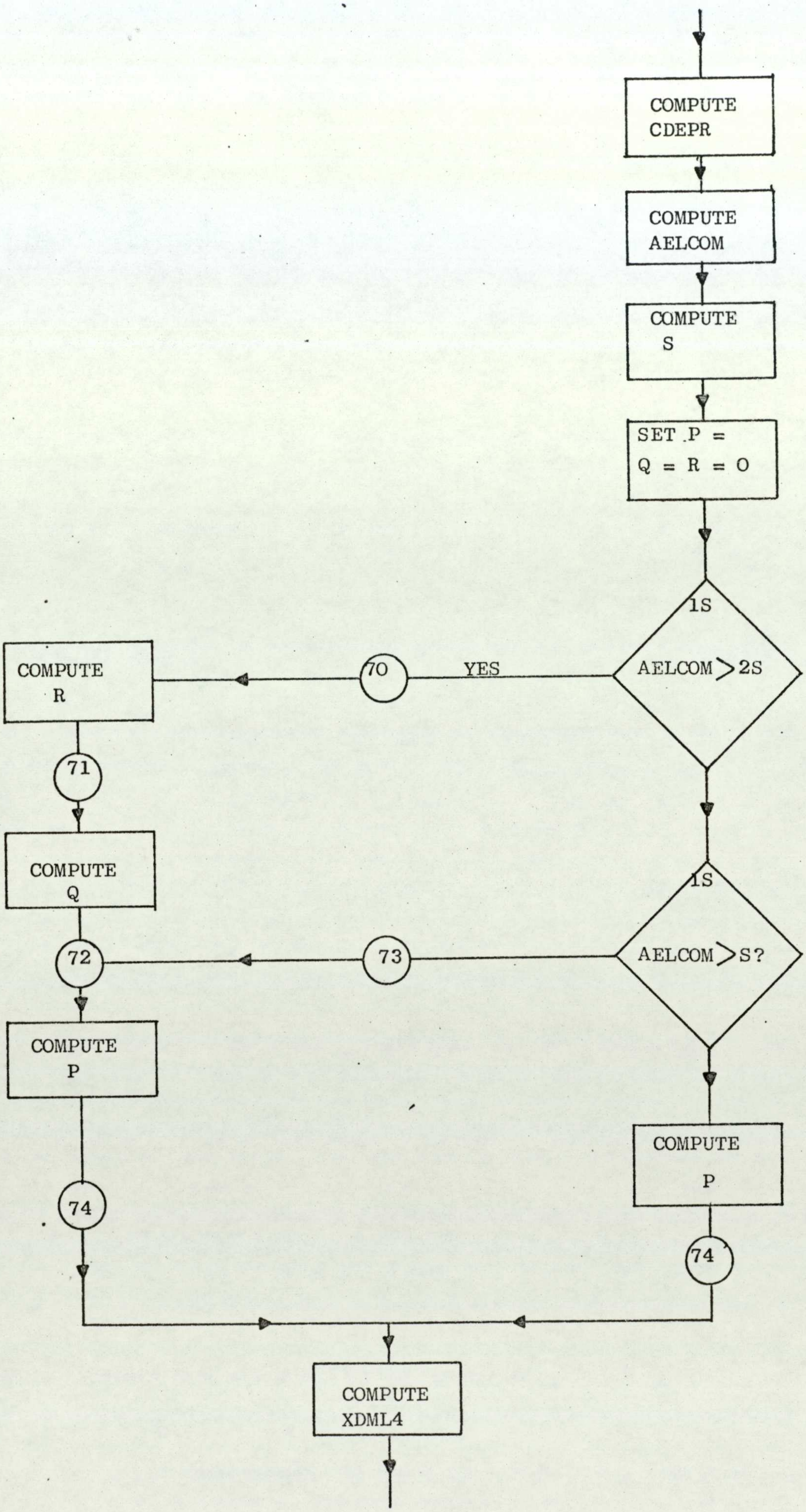


FIG. 78C. Section Z-Z from FIG. 78.

The capital cost of the iron oxide reduction equipment was taken from an article on direct reduction by McMANUS, and is expressed as 0.015£/kg annual capacity of iron. The same article gives figures for processing costs.

The derivation of SIGHF and HEAT was given in section (2.6.2) and the thermal efficiency THEFF in section (2.1.2.).

The electrical capacity of the plasma torch required to give the hourly production rate HPROD, is calculated from,

$$\text{ELCAP} = \frac{\text{HPROD (kg hr}^{-1}\text{) x HEAT (kjkg}^{-1}\text{)}}{\text{TLF (dimensionless) x THEFF (dimensionless) x 3600 (sec hr}^{-1}\text{)}} \qquad \text{........(eqn 5.2.1)}$$

and it can be seen that the units resolve to kJ sec^{-1}, or kW.

The capital cost of the plasma torch equipment (ZDCAP) was taken from a graph of data received as quotations and published figures from various firms, and is expressed as a simple linear relationship between electrical capacity and cost (Fig 79)

The maximum electrical demand charge ranges and the associated prices of electrical units are taken from industrial tariff No7 of the M.E.B. (pamphlet No. 161469) and the charges are those in force from 1st April, 1971. There is an alternative tariff, No 7a, which has higher maximum demand charges and lower electrical unit charges. A comparison showed tariff 7 to be the cheaper by 3% for a 200 kW set and 2000 working hours, and tariff 7a the cheaper by 6% for a 1000 kw set and 6000 working hours. As most calculations have given values of ELCAP of 100 to 600 kw, the tariff No 7 has been used.

The enthalpy of the gas stream at the nozzle exit is given by;

$$\text{HNT3 (kJ mole}^{-1}\text{)} = \frac{\text{ELCAP (kJ Sec}^{-1}\text{) x THEFF}}{\text{Gas flow (mole sec}^{-1}\text{)}} \qquad \text{..........5.2.2.}$$

and the cost of gas per kg of Si_3N_4 is,

$$\text{XDGAS} = \frac{\text{Gas flow (mole sec}^{-1}\text{) x XDML2 (£mole}^{-1}\text{) x 3600 (sec hr}^{-1}\text{)}}{\text{HPROD (kg hr}^{-1}\text{)}} \qquad \text{..........5.2.3.}$$

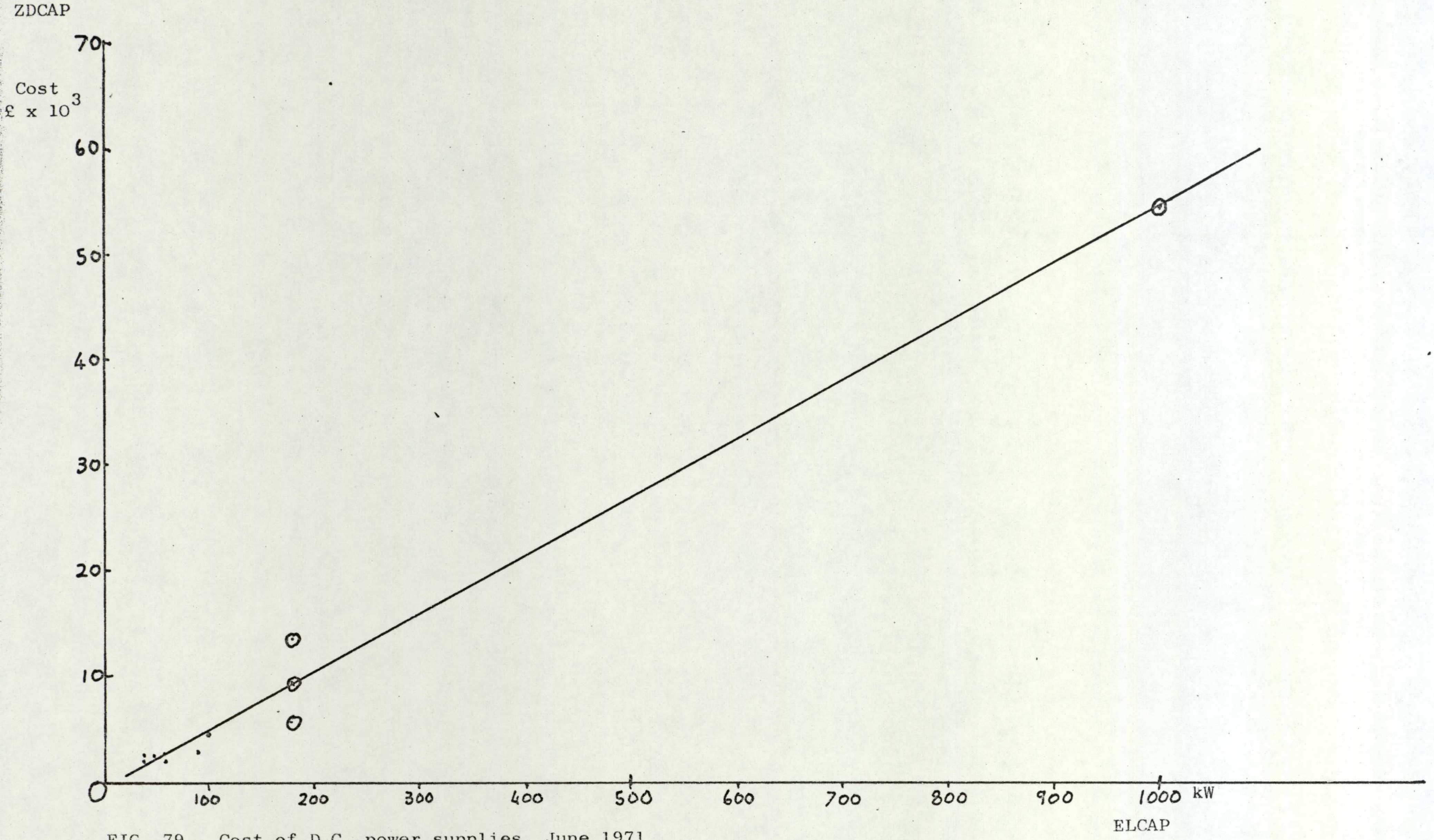


FIG. 79. Cost of D.C. power supplies. June 1971

$\therefore$ substituting for the gas flow from eqn (5.2.2.) into eqn (5.2.3) gives

$$XDGAS = \frac{ELCAP \times THEFF \times XDML3 \times 3600}{HNT3 \times HPROD} \qquad ....5.2.4.$$

The loop which begins at the second line with N=0 and closes on statement 80, allows up to 100 sets of data to be read in during a single program run.

5.2.3. Results obtained from the cost model

Iron with dispersed silicon nitride

In order to see the effect of the various parameters on the cost of the silicon nitride powder and a D.S. iron material in which it may be used, a standard set of data is used. This is as follows:-

Turnover = £100,000 p.a. (minimum company requirement)
Selling Price = £4 kg (less than the £5 kg of cemented carbide tools).
Amortisation period = 7 years (average figure in practice)
Percentage mass of dispersant = 5% (gives approximately 10% by volume in iron)
Total market = £10^6 p.a. (see market analysis 5.1.2.)
Cost of Fe_2O_3 per kg iron produced = £0.2 kg (from McMANUS)
Reduction cost " " " = £.004 kg (" ")
Annual working hours = 2000 p.a. (one shift)
Product yield = 20% (experimental result)
Thermal efficiency of torch = 65% (" ")
Enthalpy of nitrogen at T_1 = 56 kJ mole (see section 2.6.2.)
" " " T_2 = 38.4 kJ/mole (see section 2.6.2)
" " " T_3 = 322.0 kJ/mole (see section 2.6.2.)
Cost of $SiCl_4$ per kg Si_3N_4 = £0.51 kg (based on stoichiometry and £140 tonne)
Cost of NH_3 = £0.358 kg (" " " " £155 tonne)
Cost of plasma nitrogen = £0.00032 mole (private communication from suppliers)
Cost of nozzle = £0.5 each (based on manufacturing experience
Life of nozzle = 16 hrs (experimental experience of 30 kW, - a conservative estimate)

Cost of mixing = £0.07 kg (experimental experience, section 4.2.3)

The results of the program runs are shown in Figs 80 to 87.

The effect of turnover, and the directly related annual production of material, on the cost of the Si_3N_4 dispersant, is shown in Fig 80. The curves level out at £350,000 p.a. below which the rise is seen to be due to the increase in labour component. The largest component is reactant costs, and the effect of yield is shown in Fig 81. The cost rises steeply below about 30% yield, but is relatively insensitive above 50% yield. Fig 82 shows that costs are not very sensitive to torch efficiency above the 50% level.

The effect of the percentage of dispersant on the cost is shown in Fig 83. The high cost of the dispersant at the low production rate required by a low percentage is more than offset in the cost of the dispersed material, by the reduced amount of dispersant required. As would be expected, as the percentage is increased the cost of the dispersant and the 'dispersed' iron approach each other.

Fig 84 shows the effect of reducing the mean enthalpy of the torch gases, which would be achieved by mixing cold nitrogen with the jet before the reactants are introduced. This process is very similar to increasing the by-pass ratio on a jet engine. The cost is not very sensitive to this parameter.

Fig 85 and 86 show how the cost of the Si_3N_4 varies with the number of hours worked per year, for annual turnovers of £10^5 and £10^6 p.a. The cases are quite different. The lower production rate is labour cost controlled, and the advantages which would be expected from reduced plant size and therefore capital expenditure, and reduced maximum demand charges are exceeded by the extra labour cost. The upward steps are at the points where another shift is required, but is barely used. The minima represent maximum utilisation of the labour employed. The higher production rate is no longer labour cost controlled, and the advantages of the lower capital cost and maximum demand charges per kg of product are realised.

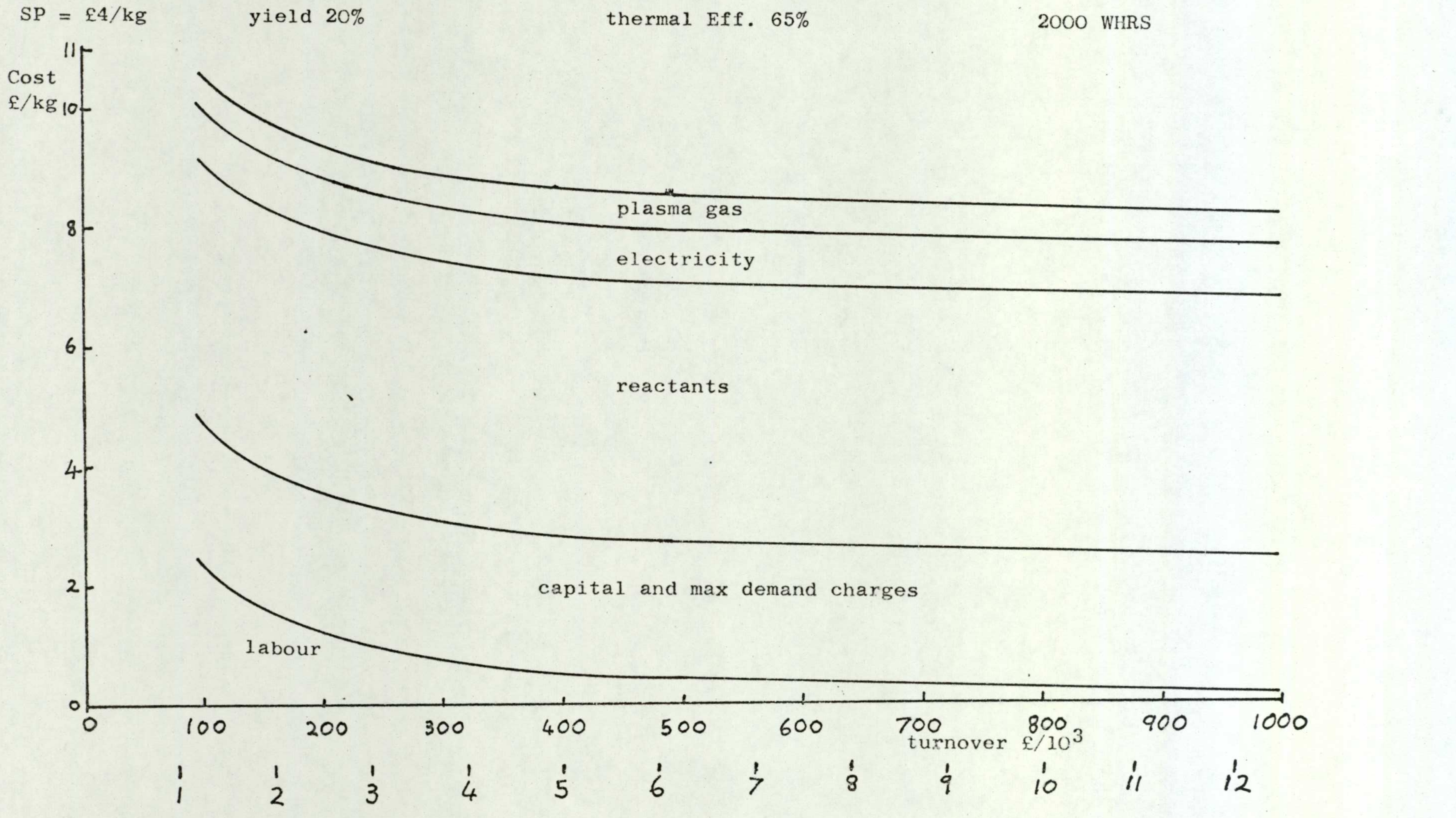


FIG. 80. Iron + Si_3N_4 ($5^{v/o}$)

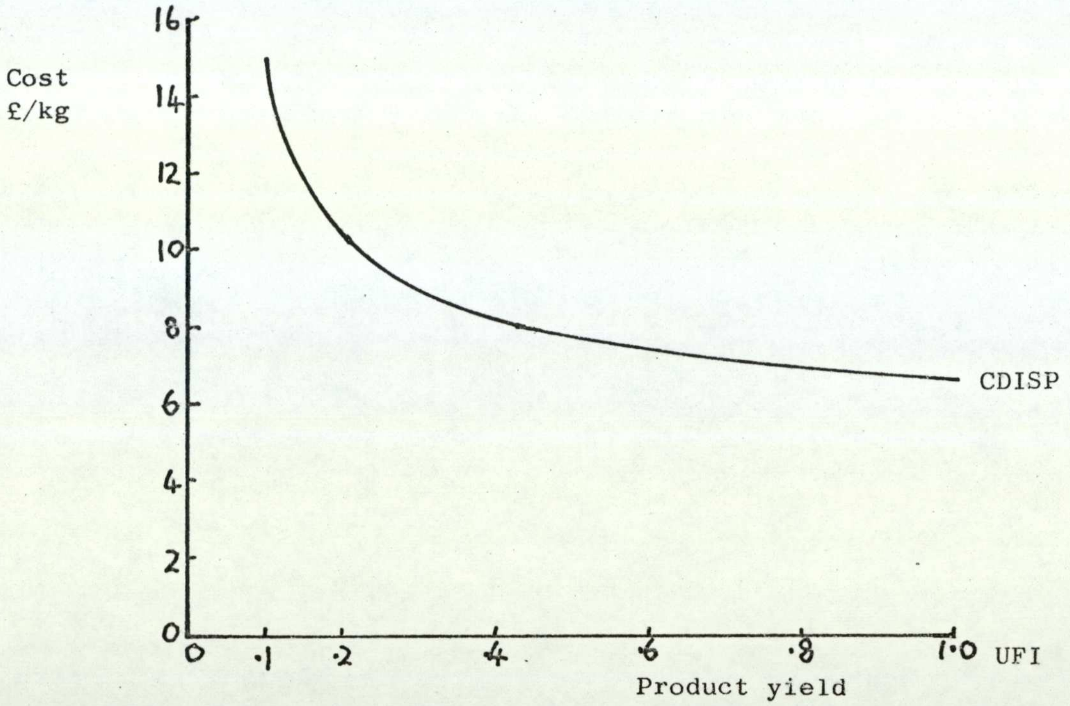


FIG. 81. Cost of Si_3N_4 as f (UFI)

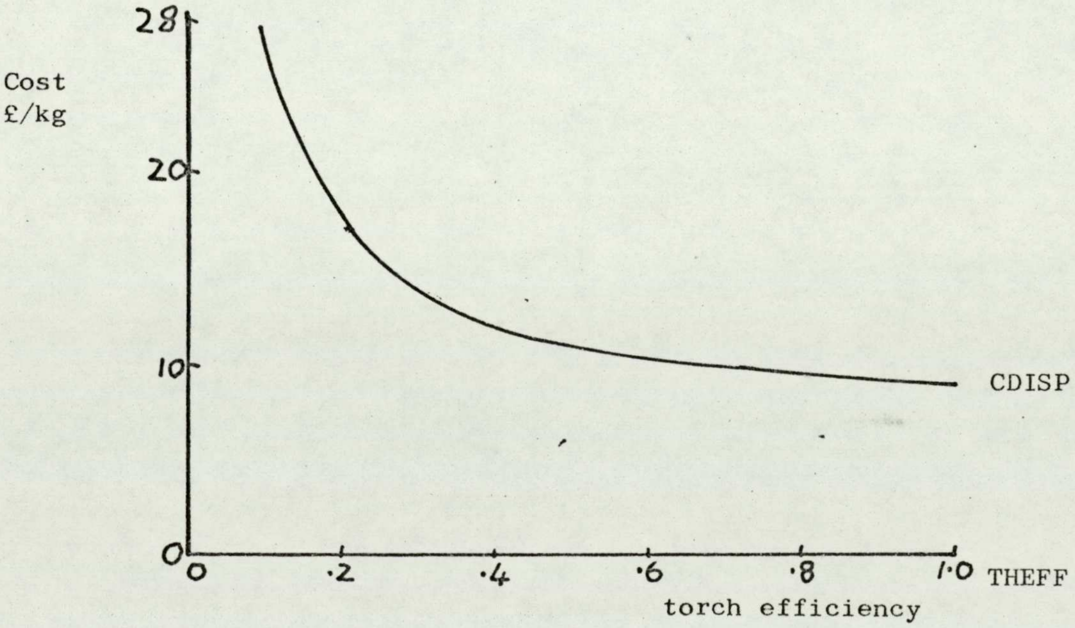


FIG. 82. Cost of Si_3N_4 as f (THEFF)

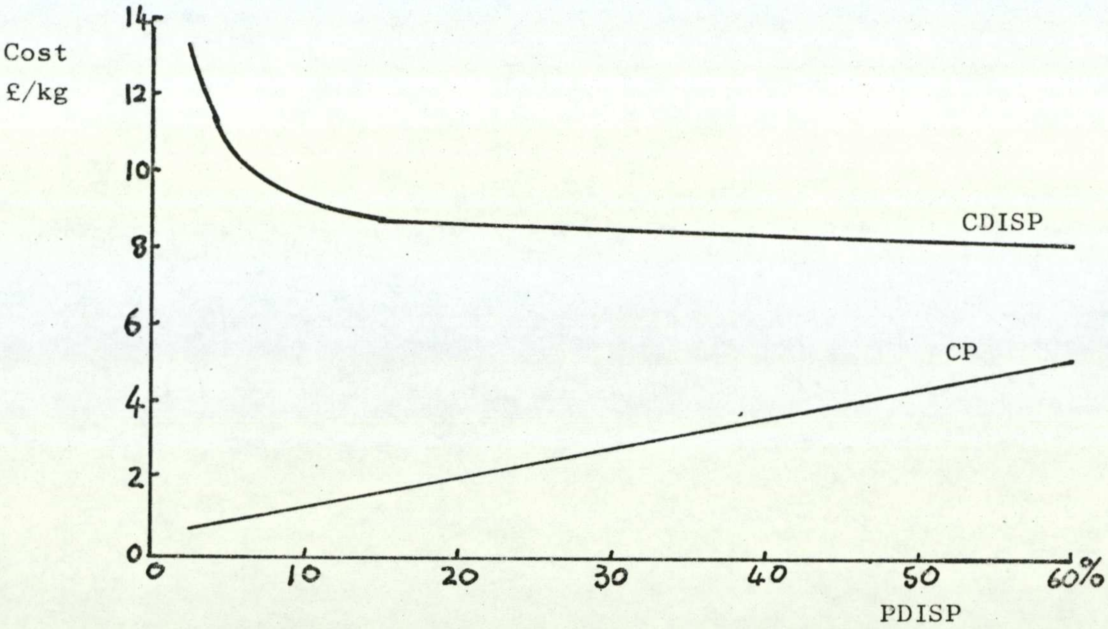


FIG. 83. Cost of Si_3N_4 and D.S. iron as f (PDISP)

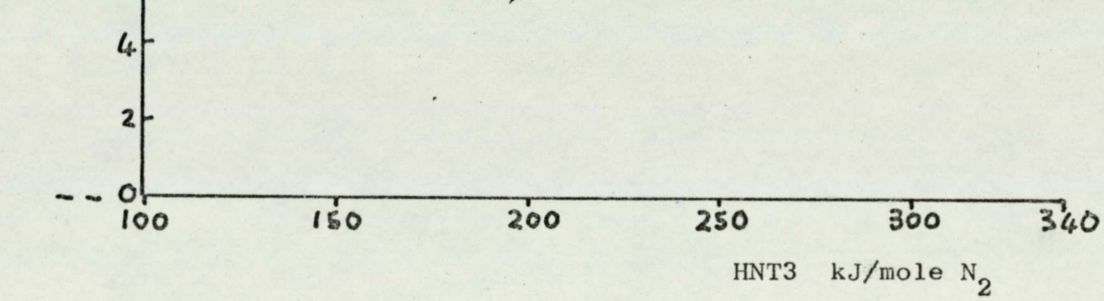


FIG. 84. Cost of Si_3N_4 as f(HNT3)

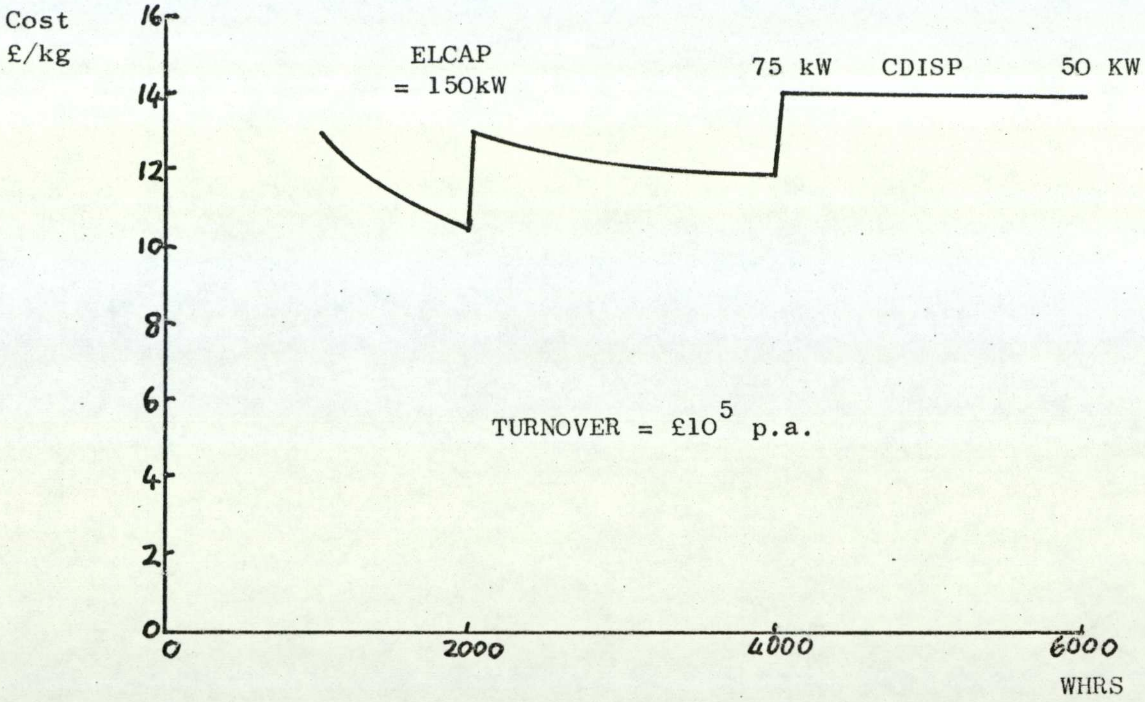


FIG. 85.

FIG's 85 and 86 Effect of yearly hours worked on cost of Si_3N_4

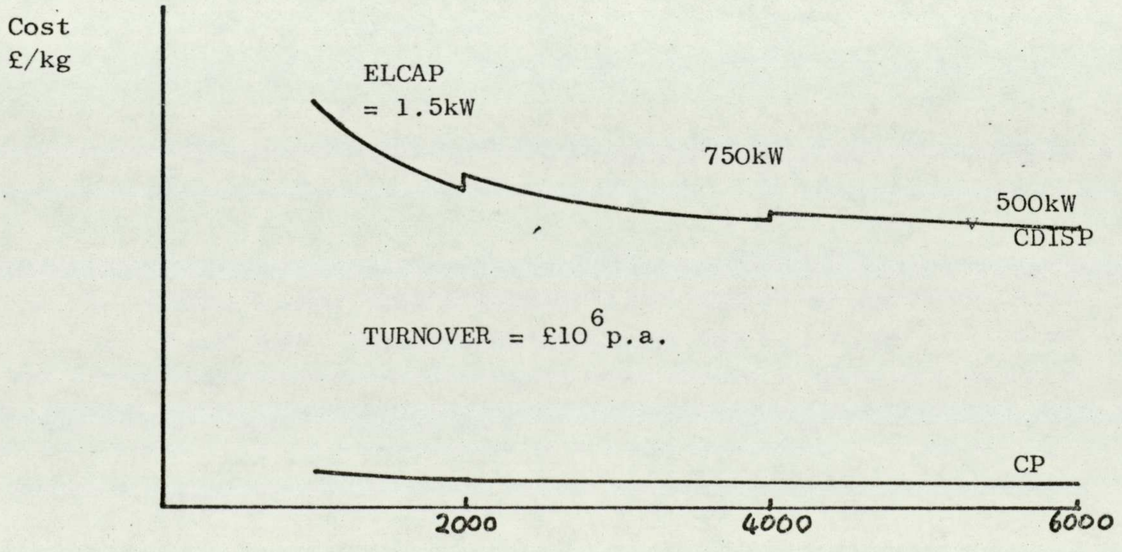


FIG. 86

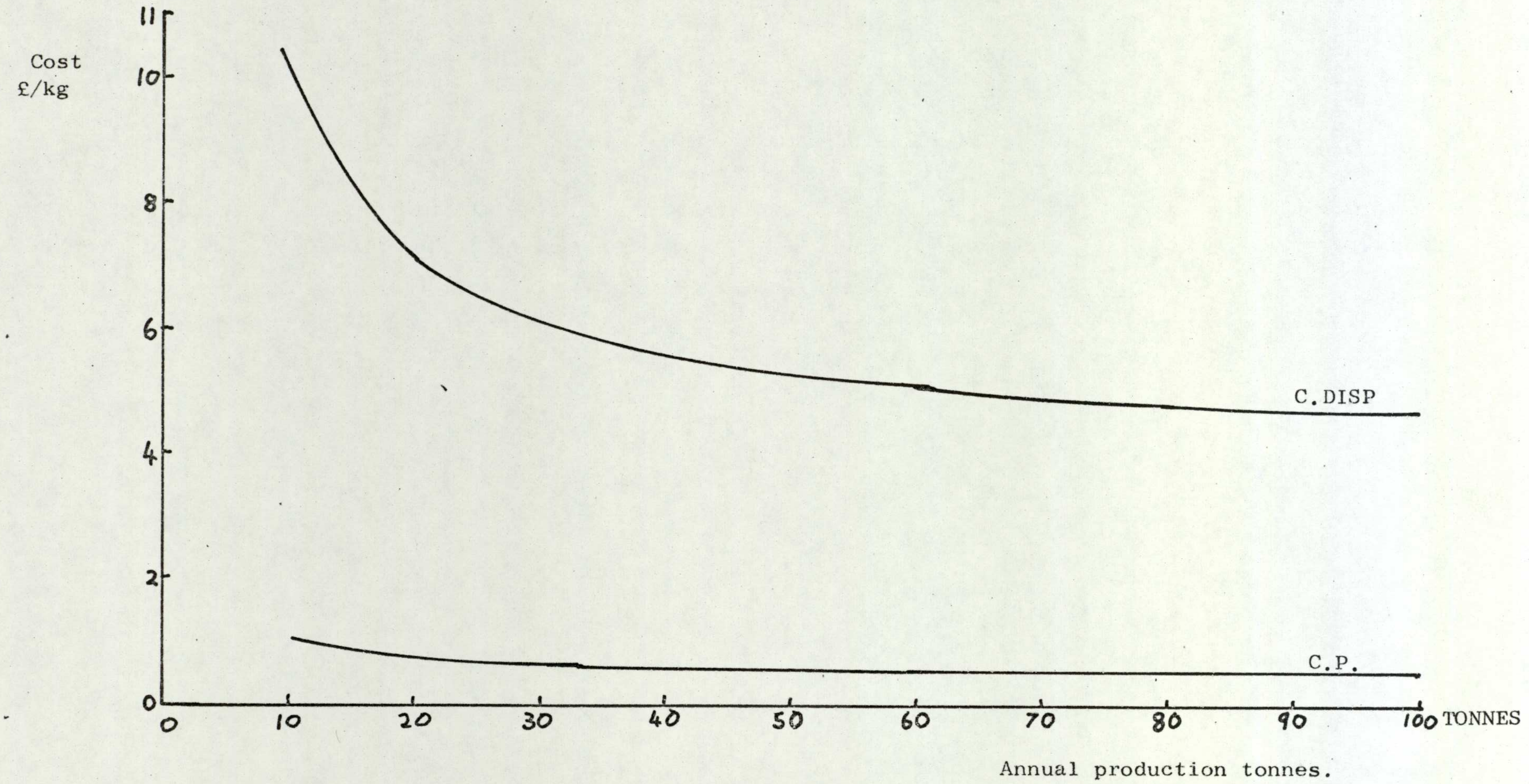


FIG. 87. Iron + TiN ($5^{w/o}$)

Titanium nitride

The standard set of data is the same as with Si_3N_4 with these exceptions.

Selling Price = £1 kg (means that £ turnover = kg annual production)
Enthalpy of nitrogen at T_1 = 67.2 kJ/mole (see section 2.6.4)
" " " " T_2 = 38.0 kJ/mole (" " ")
Cost of $TiCl_4$ per kg TiN = £0.389 (based on stoichiometry and £127 tonne)
" " NH_3 " " " = £0.256 (" " " " £155 ")

Fig 87 shows the cost of TiN as a function of annual turnover. The effect of varying parameters will be the same as for the case of Si_3N_4, as the inter-relation of variables is the same. The only alteration to the program is in the lines that calculate "SIGHF" and "HEAT".

5.3. ECONOMIC EVALUATION

5.3.1. Methods of evaluation

The purpose of economic evaluation in the context of this thesis, is to quantify the contribution that a proposed course of action is likely to make to a company's profitability. It is necessary, but insufficient, to cost the proposal as accurately as possible. As was seen in section (5.2.3) - before a cost model can be used it needs information on volume of production. When a cost price is known, positive cash flows (contributions) cannot be calculated until a selling price is fixed - and this requires some market knowledge.

From the overall company view, for an activity to be successful it must show a sufficient return on investment (R.O.I.). The level of return is a matter of policy, but should allow the company to cover the cost of the capital involved, i.e. pay a competitive dividend to its shareholders and service its loan charges, and still show a profit margin.

The R.O.I. is calculated by an analysis known as Discounted Cash Flow (D.C.F.) generally by determining the 'Internal Rate of Return', which can be defined as the rate of return on the amount of investment remaining in a project. The method is to calculate the net cash flows for each year of the expected life of the project, and find the discount rate which makes the present value of the sum of the cash flows equal to zero. The life depends on the type of project and is usually determined by company accountancy policy.

When the D.C.F. method is referred to in this thesis, it is strictly confined to real cash flows, and not used in the broader sense of cost benefit analysis.

D.C.F. is a thorough method of investment appraisal, and has many well established applications. In GKN, it is used to judge whether a certain capital sum is justified to replace a man, and to evaluate both simple capital expenditure problems and incremental investment proposals. D.C.F. is also appropriate to decide between mutually exclusive projects, e.g. low cost/high maintenance wooden poles versus high cost/low maintenance steel poles. It is important to note that this example is of two genuinely comparable propositions. Propositions which are per se. mutually exclusive, can be validly compared by D.C.F. It is not necessarily true that propositions which have nothing in common except that they belong to a set which are <u>said</u> to be mutually exclusive, can be compared with any useful meaning solely on a D.C.F. basis.

5.3.2. Present Application of D.C.F. to research programmes

It has become necessary for company boards to demand hard facts on the benefit the company is receiving from its research expenditure - and by 'benefit' is usually meant cash. The usual result is that although the costs of past research are clear enough, no attempt has been made to quantify the returns. The situation has to change, so the research manager is asked to estimate the future return that could be expected from the present research programme. When the estimates are in, all the information is available for a D.C.F. analysis of individual projects and the research budget as a whole - except for one factor. Attached to each estimated benefit is an unknown probability, related to both technical and commercial success.

Once the use of D.C.F. on the research budget is established, the next step is to ask the manager to select his projects so as to meet a certain overall rate of return. One approach is known as 'portfolio' management, which although varying in detail with the user, relies on certain principles. Briefly, the present value of the expected benefit from each project is calculated, and multiplied by the considered probability of success, to give the 'expected value'. A set of projects is put together to form a portfolio, and the probability of gaining a particular overall financial objective is calculated from the sums of expenditure, benefit and expected value using a simple probability formula. If the probability is too low, a new portfolio is chosen and the process repeated. A D.C.F. method is being used to calculate the benefits of individual projects which may have nothing in common, but are then compared on this basis.

The major objection to the use of D.C.F. in this way, is in its association with doubt of technical success. D.C.F. is too fine a tool to be used in this context - the cruder 'payback period' would do just as well. The use of variation analysis is different - it is quite reasonable to see how the internal rate of return varies with the degree of commercial success, with say market share or price. This is analogous to putting error bars on physical quantities in order to obtain a measure of the reliability of the final result, which is judged accordingly. To include the possibility of technical failure in the same way, would be like saying that the value of the physical parameter is + 100 ± 10, but might be minus 50!

5.3.3. Suggested application of D.C.F. to research programmes

Before discussing the way to evaluate research work, it is necessary to examine the way in which an 'idea' becomes a money earning activity. Methods like portfolio analysis tacitly assume a certain ideal situation, namely that there are enough projects to choose from. To find out just what the ideal situation is, and how ideas become cash flows, the problem was discussed with research managers and other interested parties both inside and outside the GKN group. Fig 88 is the result of the distillation of these discussions, and the place of D.C.F. analaysis is shown.

It is assumed in Fig 88 that in a hypothetical company which engages itself in research, there is a suitable creative atmosphere and staff to produce a large number of ideas, say one hundred. Preliminary considerations throw out fifty of these, and the remainder are subjected to experimental work, cost analysis and market evaluation in whatever combination and depth is necessary to accumulate enough information for a D.C.F. analysis to be made on each proposal which appears to have earning potential. With luck, there may emerge ten projects which are technically proven, and meet the company's R.O.I. requirements. There is a limited amount of capital available, so a choice has to be made. This choice can only be made on strategic grounds, so a board decision is required to choose say five projects as new activities.

If D.C.F. is used on individual project any earlier in the scheme in Fig 88 , it is used prematurely, and the results are of dubious utility. If it is used as a selection criterial to compare proposals at an earlier stage, say at the preliminary examination stage, when there is a probability of both technical and economic failure, the results are nonsense.

The experimental work described in this thesis is still in need of further technical market evaluation before a D.C.F. analysis can be made. It is sufficient at this stage to state that a sufficient profit margin could exist if a dispersion strengthened iron could be developed as a competitor to cemented carbide tool materials.

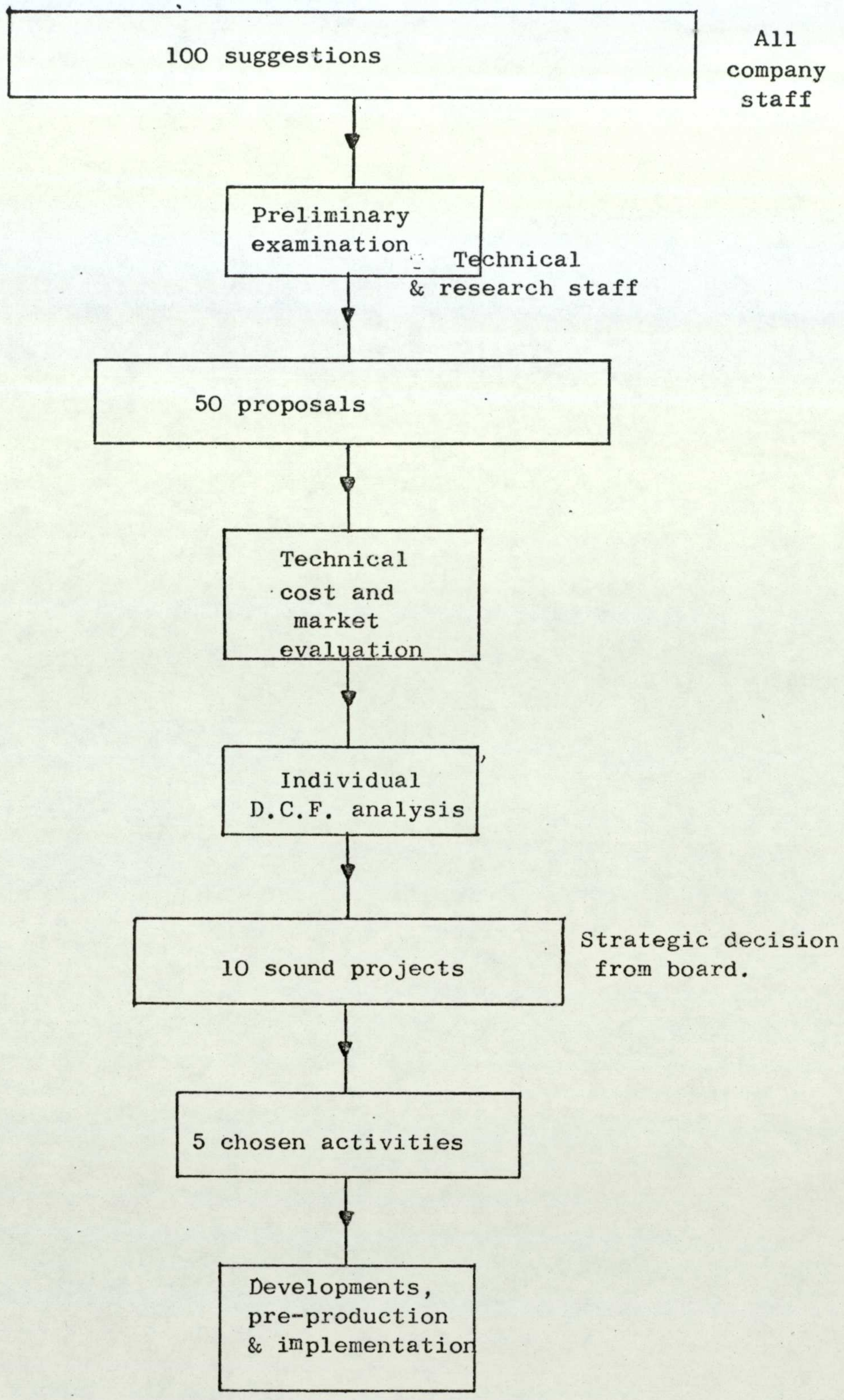

100 suggestions
All company staff
Preliminary examination
Technical & research staff
50 proposals
Technical cost and market evaluation
Individual D.C.F. analysis
10 sound projects
Strategic decision from board.
5 chosen activities
Developments, pre-production & implementation

Fig. 88

CHAPTER SIX

DISCUSSION AND CONCLUSIONS

6.1. Summary of the conclusions reached in the text

The methods and costs of production of powders with average size between 1mμ and 1μ have been reviewed, and discussed from the view-point of producing nitrides in the 10mμ to 100mμ region and metals of about 0.5μ. From this review it is apparent that the only way of producing the nitrides from raw materials is by condensation from the vapour phase in a non-oxidising atmosphere. It is shown that the most convenient way of supplying the atmosphere at the right temperature is by running a D.C. plasma torch on nitrogen into a graphite reactor.

During the course of the experimental work, very thin platelets of silica were produced, and it was found that silicon nitride is not readily prepared by the direct nitridation of $SiCl_4$ vapour. Silicon nitride was prepared in an original way by mixing $SiCl_4$ vapour and NH_3 in a jet of argon, and propelling the di-imide formed into the exhaust of the plasma jet. The silicon nitride so prepared was found to be largely in the form of fine tubes, about 0.1μ diameter, the remainder being particles and agglomerates in the 0.01 to 0.1μ range.

Titanium nitride was prepared in a similar way, from $TiCl_4$, and a previously unreported intermediate compound $Ti(NH)_2$ is proposed. The titanium nitride was in the form of fine particles .01 to 0.1μ size range.

The inter-relation between the thermodynamics of the chemical reaction, the reactant flow rate, and the plasma torch gas flow and power have been examined and explained. This knowledge has been incorporated into a computer program together with cost information, and used to compute the cost of producing a mix of two powders in any percentage. There is no restriction on the form or origin of one powder (matrix) the other is produced using a D.C. plasma torch.

The program was run to calculate the cost of a mixture of iron and silicon nitride, and a sensitivity analysis performed to identify the important cost parameters. The cost of silicon nitride lies between 8 and 11 £/kg, and the cost of titanium nitride between 5 and 10 £/kg, depending on the quantity produced, and yield etc. The sensitivity analysis showed that the largest cost component is reactants, and that costs rise steeply below 30% product yield, but are relatively insensitive above 50%. In a powder mixture, of nitride and iron at a given annual production rate the high cost of the nitride at the low production rate required by a low percentage is more than offset by the reduced amount of nitride required. The cost of the nitride is not very sensitive to the mean enthalpy of the torch gases. The relation between cost and the number of shifts worked for a given required annual production depends on the order of magnitude of the production. For an annual turnover of £10^5 the cost is labour dominated, and it is cheaper to use a more powerful torch for one shift than a less powerful torch for two or three shifts. For a turnover of £10^6, it is cheaper to use the smallest torch possible, and make the best use of time possible.

The cost model is applicable from the kW to the MW torch power level. The only piece of apparatus which would need to be completely different is the collection method. A commercially proven method is agglomerators followed by cyclones and bag filters, which are used to collect fumed alumina and silica.

Sub-micron metal powders can be produced by milling coarse powders. A ball mill can grind 2.5μ nickel down to 0.1μ using the appropriate technology, for £0.72 kg. A jet mill working on air can process powders at a rate of £0.07 kg, but any specific powder should be tested to ensure that the required subdivision is achieved. Liquid phase methods produce oxides, and a half micron Fe_2O_3 powder is obtainable for £0.14 kg. Some oxide powders can readily be reduced to metals, in which case they can then be mixed with ultrafine powders, It is generally preferable to mix the powders before reduction if possible, as some agglomeration is likely during reduction, so a more thorough final dispersion will be achieved.

The theory of nucleation and growth of alumina particles in a flame has been examined, and its predictions considered against the review of previous work in the production of ultrafine powders from plasma torches. The predictions of the theory on the dependance of particle size on reactant concentration are in qualitative agreement with most of the observed phenomena. The theory does not attempt to account for the production of lamellae or fine tubes, which were encountered during the experimental work described herein.

The review of previous work with plasma torches brought out three distinct approaches to fine powder production. The first type was to feed in coarse powder, volatilise it and allow it to recondense in a finer form. This method is not suitable for nitrides, because they are unlikely to be obtainable in powder form. Also, in the case of silicon, it was shown that the direct nitridation of silicon vapour does not proceed at any useful rate. In the second approach reactants are introduced to the hot gas in either powder or vapour form, and a reaction takes place at the high temperature. The vapour is often a halide, because many elements have liquid halides (usually chlorides) which are volatile at room temperature. This method has been shown in this work to be suitable for producing ultrafine nitrides. The third approach is to apply an electric arc to materials stored inside a reaction chamber. Two commercial processes have resulted from this approach - the high intensity arc and the liquid wall furnace. Neither method is suitable for nitride production. No work on the factors which affect the cost of using a D.C. plasma torch to produce fine powders (or any other materials) was found, a statement which was also made by BROWN, EVEREST, LEWIS and WILLIAMS.

Important experience has been gained in the production of materials from ultrafine powders using powder metallurgy methods. It was found that uniaxial pressing gave inhomogeneous density because of the very high compaction ratio (order 10) of sub-micron powders. Isostatic pressing gave firm compacts of 80% density, from fine iron powder. After examining the other densification and compaction processes it was concluded that in the case of ultrafine powders, any method of densification must be preceeded by isostatic pressing. A review of work on dispersion strengthened materials showed that the most commonly used densification processes were hot extrusion, and hot pressing.

The experimental work in this thesis was mostly confined to the selective reduction of iron oxide/7$^{v/o}$ alumina powder mixes for reasons previously given. It was shown that sintering near the melting point of the matrix produced compacts of 100% density, but that the material did not show any improved properties over the pure matrix. Hot forged compacts had densities up to 97%, and the tensile strength improved from a U.T.S. of 325 MN/m^2 for the pure matrix to 447 MN/m^2 with alumina. The ductility decreased from 27% to zero. Both of these results are consistent with the dispersion strengthened effects. Silicon nitride and titanium nitride did not alter the properties of the matrix, in fact the titanium nitride/iron compact broke up in the furnace before it was forged.

The theory of dispersion strengthening was examined, and found to omit the effects of differential thermal expansion on the properties of the material. A review of the work on D.S. materials was found to contain one reference to this problem in a patent on cemented nitride tool materials, to the effect that the values of α should be within a factor of two for any components in a composite material. If this is so, it is not likely that Si_3N_4 with its value of $\alpha = 2.46.10^{-1}\,^{o}C^{-1}$ should be compatible with iron with $\alpha = 11$ to $15 \times 10^{-6}\,^{o}C^{-1}$. (Alumina has $\alpha = 7.75 \times 10^{-6}\,^{o}C^{-1}$)

The methods of production of D.S. materials which could make use of ultrafine particles are co-precipitation, mechanical mixing followed by selective reduction where necessary, and electro-deposition. The latter has not been used to produce materials whose properties have been measured. Co-precipitation is commercially successful in T.D. Nickel, and mechanical mixing has been proven in the literature and in this work.

The process costs of each step in the production routes have been calculated. A thorough mix can be produced by ball-milling (0.7 £/kg) jet milling (0.07 £/kg) and dry dispersing (0.08 £/kg). Selective reduction can produce iron at £2.2 kg based on figures given for large scale natural gas direct reduction plants. This agrees well with the price of £0.14 kg of sub-micron haematite, which is £0.21 per kg iron plus £0.05 per kg calculated reduction cost (materials only) giving a minimum cost of £0.26 kg for reduced ultrafine iron powder. Cold isostatic compaction costs £0.23 kg for iron with the experimentally established compaction ratio of 8 for sub-micron powder. Extrusion costs about £0.4 kg, and hot isostatic pressing £0.16 kg. Co-precipitation of nickel-thoria powder is deduced to be about £5.50 kg, but the thoria may be a significant part of the cost.

The possible strategies of fundamental research have been derived by considering the S.W.O.T. approach. Within each strategy a set of objectives of fundamental research has been drawn up, as a function of product or process, and type of market. The relation of the results of the work in this thesis have been shown. Methods of evaluation, and the application of the D.C.F. method to research programs, have been discussed at length. It was concluded that the correct application for D.C.F. analysis was to evaluate individual projects which are technically proven and have known markets.

6.2. Discussion

Specific results were summarised in the previous section. It remains to bring out certain more general points, and make some suggestions for future work. The final section (6.3.) contains suggestions for further experimental work from a purely academic point of view. There is no attempt to relate them to GKN, as all research must be related to the company's requirements, and the future requirements of the company in relation to the present work is not yet decided.

The two literature reviews, one on plasma-chemistry and one on D.S. materials, correct deficiencies in the published literature. The scope and potential of the production of fine powders by plasma torches has been discussed. As at this stage it is unlikely that GKN wishes to go into the business of manufacturing ultrafine powders for direct sale, the only potential application at present is in D.S. materials. However, should the decision be taken to set up a production plant, the background information is now available as a result of this work. The cost model in particular would enable the costs of any powder to be calculated readily once the appropriate thermodynamic data is put into the program.

It is possible that GKN may decide to produce D.S. materials for internal or external use, or be asked to process them into components. In either case the previous knowledge has been reviewed, and the practical problems of producing and processing such materials have been identified. This work represents valuable groundwork if a decision to proceed is taken. In particular a method of producing firm green compacts from submicron powders has been established.

The discussion of the strategies and objectives of fundamental research is a useful contribution to the clearer understanding of a difficult area of management. The application of D.C.F. analysis to research is a controversial subject, however by the realistic use of the method as outlined in section 5.3.3. much of the controversy should disappear, and the technique will be less misused.

6.3. Suggestions for further academic work

Production of ultrafine powders by mechanical methods

The possibility of producing fine nitrides such as silicon nitride by ball milling coarse powders should be examined in more detail, as this process is technically feasible as a competitor to the plasma process.

Production of ultrafine powders using a plasma torch

1) The reaction rates between

   (a) $SiCl_4$ and NH_3

   (b) $TiCl_4$ and NH_3

are not known, neither is the rate of dissociation of the di-imide.

   (c) $Si(NH)_2 \longrightarrow Si_3N_4 + NH_3$

2) The formula of the intermediate compound proposed as $Ti(NH)_2$ has not been investigated.

3) The detailed way in which the reaction yields depend on variables such as the reactor temperature, profile, plasma gas composition etc should be established.

4) There is no theory to explain the production of non spheroidal particles such as lamellae and tubes.

5) It is possible that other inorganic nitrides can be produced using the method described in this thesis.

Densification of powder compacts

6) The effect of process variables such as heating atmosphere, forging temperature and forging pressure should be examined.

LIST OF TABLES

1) Commercially available sub-micron powders.
2) Summary of significant experimental results of Silicon Nitride production.
3) Results of analysis on silicon nitride specimen R9.
4) Comparison of experimental and calculated yields of silicon nitride
5) Values of coefficients of thermal expansion for various metal matrices and non-metallic dispersants
6) Summary of processing costs for D.S. materials
7) The powders used in the experimental work on D.S. materials
8) Properties of sintered compacts
9) Properties of hot forged compacts
10) List of FORTRAN variables used in the plasma cost program.

LIST OF FIGURES

APPENDIX ONE

USE OF THERMOCOUPLES AT HIGH TEMPERATURES

A thermocouple which is correctly made and connected may be used to measure any temperature within its useful range providing it is in thermal equilibrium with its environment, but is otherwise, i.e. chemically and electrically, inactive.

Thermal equilibrium requires that:

a) The rate of conduction of heat away from the junction by the couple wires and supports is negligible compared with the heat transfer rate from the environment to the junction assuming a temperature difference which is within the acceptable measuring error.

b) The nett rate of loss of heat by radiation from the junction is negligible compared with the heat transfer rate from the environment to the junction assuming a temperature difference which is within the acceptable measuring error.

Chemical inertia requires that:

a) The thermocouple is not destroyed by, for instance, oxidation. The attached sheet on silica coatings gives two instances of chemical reactions with Pt/Pt-Rh thermocouples.

b) The junction is not acting as a catalytic surface, and receiving heat from chemical reactions or recombination of atoms.

Electrical inactivity requires that:

The circuit including the thermocouple is electrically floating, to avoid any thermionic or voltage induced emission of electrons from the junctions.

The use of a thermocouple in the high enthalpy gas streams associated with the plasma jet exhaust should not suffer from lack of thermal equilibrium. An attempt can be made to calculate the heat transfer rates which occur under these conditions. As the junction is in a graphite enclosure with high wall temperatures and copious radiation from the plasma jet, the difference in temperature between the junction and local radiating surfaces will not be very great.

Oxygen is carefully excluded from the reacting gases, and it is likely that solids will condense on the junction and prevent catalytic recombination. The diatomic gases will have recombined at temperatures higher than those measurable by thermocouples, so will not cause a problem.

Against through-wall measurements is the observation that if the gas allowed to flow out past the thermocouple as it is removed from the reactor wall, an increase in temperature is recorded.

A thorough account of the problems of gas temperature measurement is given by the AMERICAN INSTITUTE of PHYSICS (1939). Of the methods used to overcome these problems the more relevant are:-

1) Use of a radiation shield around the junction.
2) Minimizing the size of the junction.
3) High velocity thermocouple - H.V.T.

Modern Thermocouples

In order to meet the demands of the space and aero industries in the last decade for high temperature (over 1650°C) measurements in gas streams, three classes of thermocouple have been developed (see MOELLER, NOLAND, and RHODES) using:

1) Noble metals
2) Refractory metals
3) Non-metals.

For use in air breathing engines up to 2150°C., Ir-Rh/Ir elements have been used, and the N.B.S. supplies reference tables for Ir-40Rh/Ir elements which are described by BLACKBURN and CALDWELL. The metallic thermocouples with the highest ranges are tungsten-molybdenum and tungsten-rhenium, of which the second is generally preferred, according to ERGARDT. The properties of wires made from W alloyed with from 1 to 25% Re i.e. VRI to VR25) have been investigated by DANISHEVSKII et. al. Thermocouples made from VR5-VR20 and VR10-VR20 wires have been tested and used for differential thermal analysis of high melting alloys up to 2600°C., for studying test specimens made of graphite in gas streams up to 2500°C. and for measurements of 2200-2300°C in a 2000 m.sec^{-1} gas stream. The commercially available thermocouple (ENGELHARD) is W-W26% Re and may be used continuously at 2,300°C. and intermittently up to 2,600°C, in inert or reducing atmospheres. N.A.S.A. experience is that although the W-W26% Re couple has a high emf at high temperature, the brittle nature of the W is a disadvantage, and for this reason W-5 Re/W-26 Re elements are widely used, the lower emf being accepted for a higher strength.

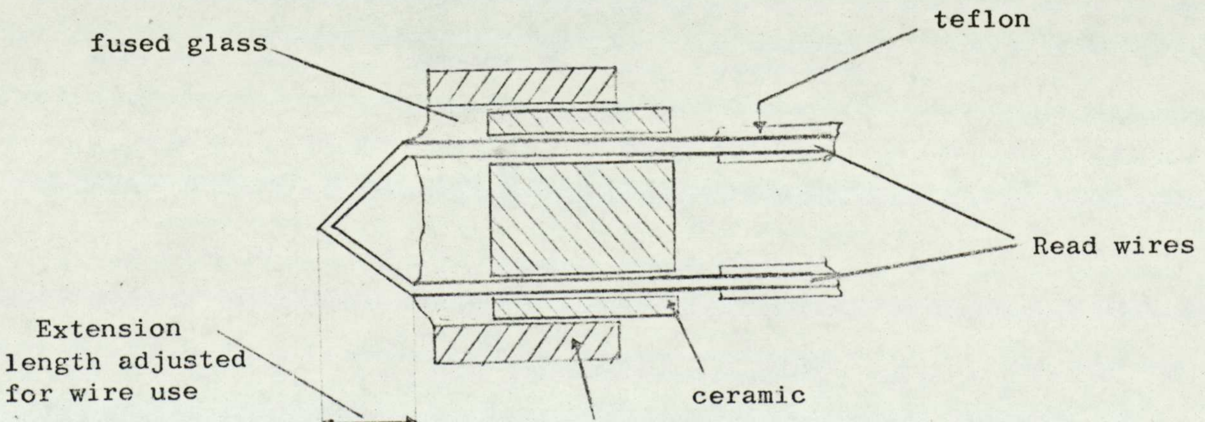
The W/Re junctions are made by capacitor discharge or inert gas welding and their properties may be summarised as having M.P's above 2,980°C., high thermal emfs, chemical stability in vacuo or inert gas and low vapour pressures.

The W/Re junctions need protective caps under certain conditions because they react vigorously with carbon and silicon, so a thermocouple based on graphite has been developed by MALYSHEV. The inner element is dense graphite, and the outer element is a concentric tube of silicized graphite. The two are insulated, and the hot junction is formed by a screw - on cap of silicized graphite. The cold junction is water cooled with copper connectors and leads.

It is important to remember that at these high temperatures it is likely that provision of a suitable sheath material will be a serious problem. Commonly used ceramics such as alumina and mullite fail above 1800°C., and chemical compatability has to be considered.

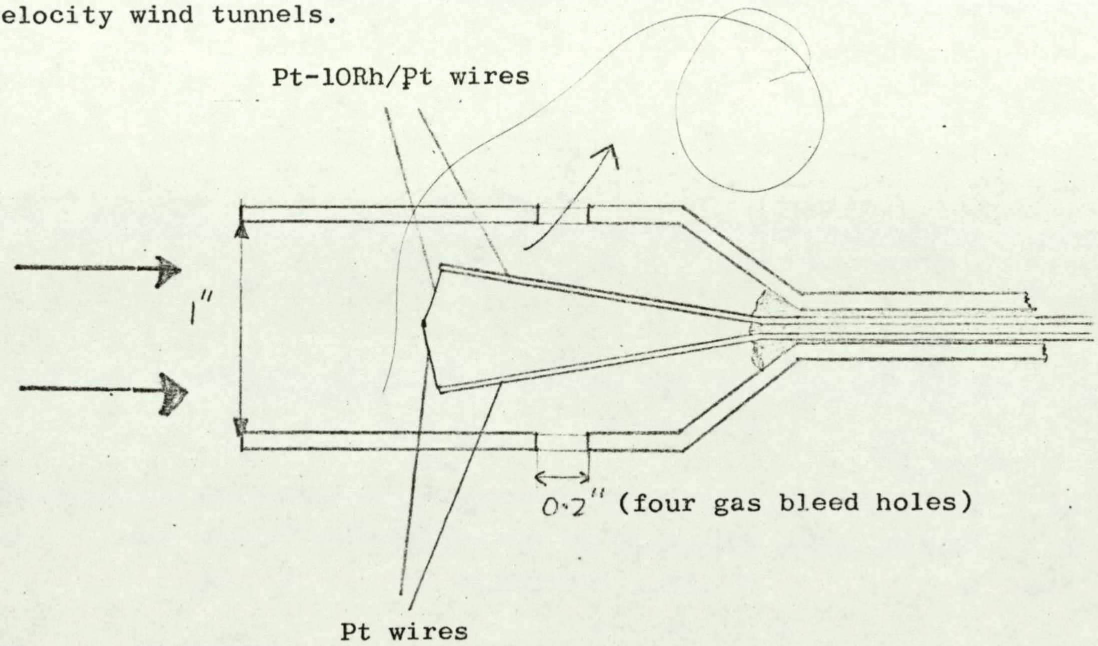
Design of Thermocouple Probes

The simplest probe tip is a bare wire junction, but this suffers from an uncertainty in the emittance of the surface. A two wire probe was developed for measuring hot nozzle gases on the NERVA nuclear rocket engine.

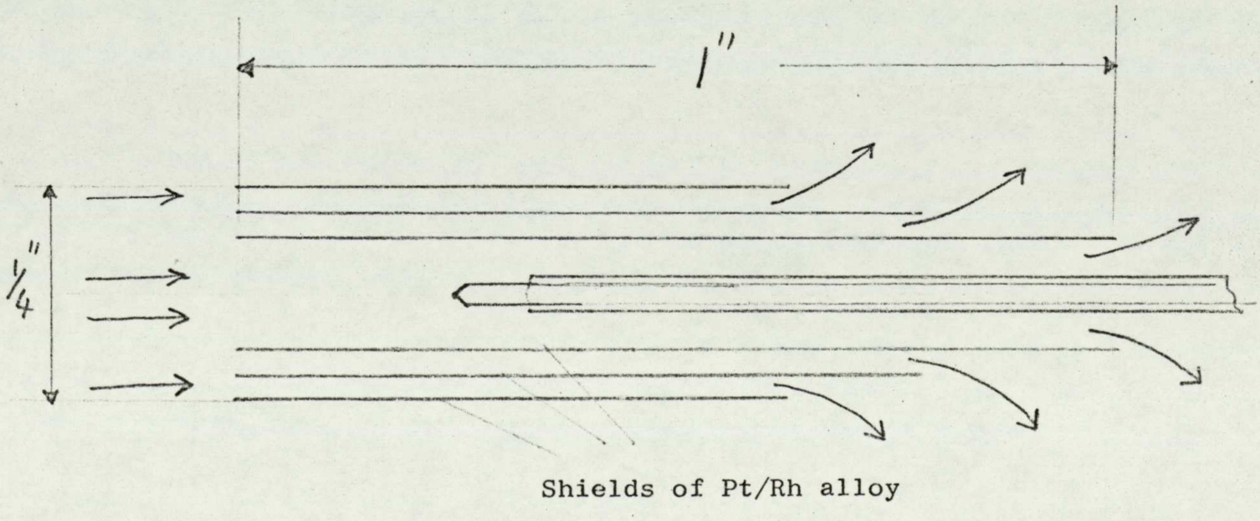


This device recorded 200 to 300°C. below calculated temperatures because of heat losses. A method of using bare wire probes to measure the transient temperature in an expanding nuclear fire ball has been developed which preheats the junction to near the expected temperature.

The error caused by radiation from the junction can be dealt with by a shield. The shield may be cold, with a high thermal capacity so that its temperature remains sufficiently low that radiation losses are calculable. This is used for short time measurements especially in low pressure high velocity wind tunnels.



Alternatively the shield is designed to reach the same temperature as the junction. This demands a steady state, and a triple shield may be required to attain the ambient temperature.



The high velocity thermocouple (H.V.T.) is a junction encased in a porcelain tube and surrounded by a water cooled tube. The gases being measured are sucked through the tube and exhausted. The junction itself is surrounded by a porcelain radiation shield. (The construction is similar to an enthalpy probe). The principal of operation is that the rapid gas flow imparts such a rate of heat flow to the junction that any losses are negligible. The method has been used with considerable success - its accuracy is tested by increasing the gas flow until no increase in temperature is observed.

A study of heat transfer to small spheres in a nitrogen plasma jet has been made by ROTHER. 1 mm diameter steel spheres were dropped through the horizontal jet into a calcrimeter at a velocity of 1m. S^{-1} and a rate of 40 spheres per second. The temperature of the spheres (from 10 to 60°C) was measured as they fell along chords of varying radius from the axis. The results were compared with the temperatures attained by an iron-constantan thermocouple made by spark-welding the wires to a similar 1 mm steel sphere. The junction was moved at an adjustable velocity along a chord. The thermoelectric voltage was passed through a 1 KHz chopper amplifier onto an oscilloscope. The results of the two experiments agreed within the limits of experimental error.

The data obtained was combined with a spectroscopic temperature measurement to give information on heat transfer rates which is compared with theory. The work is being extended to higher temperatures and velocities.

It may be that this work could be used to calculate heat transfer rates to much smaller particles injected into the plasma jet, but the difference in size between the spheres used and, e.g. 0.1μ particles, (which is a factor of 10^4) is likely to invalidate any comparisons.

APPENDIX TWO

Methods used for the Analysis of Silicon Nitride samples and reduced iron samples

SiO_2

A suitable sample weight is placed in a stainless steel beaker, together with 25mls of water, and 1grm of NaOH and heated for 5 minutes. The contents of the steel beaker are then transferred to a glass beaker containing 30mls of Perchloric acid and brought to the boil on the hot plate. The solution is evaporated to fumes, allowed to fume strongly for 10 minutes, and allowed to cool. The salts are dissolved in 25mls of hot distilled water containing a little HCl and filtered on a paper pulp pad, the SiO_2 adhering to the beaker is "bobbied" onto the pad, washed with warm dilute HCl, and finally with warm water. The pad is ignited in a platinum crucible at 1000°C for 30 minutes, allowed to cool, and weighed. The residue is treated with a little HF and taken down to dryness; after heating up to 1000°C again, the crucible is allowed to cool and reweighed.

The silica present = weight of Pt + residue before H.F. treatment, minus the weight of Pt after the H.F. treatment.

$$\% \; SiO_2 = \frac{\text{weight of } SiO_2 \times 100}{\text{weight of sample}}$$

Combined Nitrogen

A suitable sample is weighed into a small refractory boat together with 3 gms of NaOH and placed inside a protective silica sheath; this is to prevent molten NaOH from ruining the tube of the furnace. The addition of NaOH is best done immediately before placing into the furnace to avoid any loss of NH^+_3 salts.

A furnace is prepared for the determination by heating it to 700°C, and 'purging' the system by passing pure Nitrogen through it for 30 minutes. Two Dreschel bottles, each containing 15mls of a 0.1% solution of Boric Acid together with 150mls of distilled water, and 6 drops of a Methyl Red/Methylene Blue indicator, are attached to the end of the tube to absorb any NH^+_3 coming from the sample.

The sample is then introduced into the furnace, and Nitrogen passed through for one hour. After removing the absorption vessels, the solution is titrated to a green end point using the most suitable strength of HCl, N/100 or N/10.

$$1\text{ml N/100 HCl} = 0.00014 \text{ g N}$$

$$\therefore \% \text{ N} = \frac{\text{titre} \times 0.00014 \times 100}{\text{weight of sample}}$$

The Indicator is 0.125 Methyl Red, and 0.083 g Methylene Blue, dissolved in 100 ml of Absolute Alcohol

Ammonium Salts

A suitable sample weight is placed into a beaker together with 100mls N_2 free distilled water and thoroughly mixed, heated gently, avoiding heating strongly enough to lose any ammonia, the residue is filtered off, and washed with the N_2 free distilled water.

The steam distillation apparatus having being previously set up, 100mls of the NaOH/Tartaric solution (500/133 to 1250ml) are distilled for 5 minutes to remove any Ammonia present. The sample solution is then added, and distilled for 6 minutes, the Ammonia being absorbed in 10mls of 0.1 Boric Acid solution containing 6 drops of the Methyl Red/Methylene Blue indicator. On completion of the distillation, the solution is titrated to a green end point with N/100 HCl.

$$1\text{ml N/100 HCl} = 0.00014 \text{ g N.}$$

$$\therefore \% \text{ N} = \frac{\text{titre} \times 0.014}{\text{weight of sample}} -$$

Acid soluble chlorides

A suitable weight of sample is warmed gently with 25mls of 40% HNO_3, and stood in a warm place for two hours, filtered, and washed with warm water. The procedure after this, is the same as in Water Soluble Chlorides.

Iron

A suitable sample weight is simmered gently for 15 minutes with 25mls 50% HCl. The residue is filtered off, washing with warm dilute HCl, and the filtrate in then heated to boiling. After making ammoniacal with NH_4OH, the solution is boiled to coagulate the precipitate and filtered, washing with hot water. The precipitate is dissolved through the paper with hot 50% HCl, washing well with hot water. After reprecipitating with NH_4OH the precipitate is filtered again, washed, and redissolved. After being brought to the boil, the solution is reduced by the spot-wise addition of 1% $SiCl_2$ solution, and allowed to cool. After cooling, 10mls of a saturated solution of Mercuric Chloride are added together with 15mls of an $H_2SO_4/H_2PO_4/H_2O$ mixture (3/3/14) and 2 pellets of Sodium Diphenylamine Sulphate Indicator, and titrated with N/50 $K_2Cr_2O_7$ solution.

$$1\text{ml N/50 } K_2Cr_2O_7 \text{ solution} = 0.00112 \text{ g Fe}$$

$$\therefore \quad \%\text{ Fe} = \frac{\text{titre} \times 0.00112 \times 100}{\text{weight of sample}}$$

APPENDIX THREE

NOTES ON THE HANDLING OF $SiCl_4$ and $TiCl_4$

Containers

Glass containers are suitable for long term storage of these liquids, on the proviso that too much is not stored in any one container in case of breakage. The screw top bottle with the black plastic cap is not suitable, as $SiCl_4$ expands the plastic so much that it slips over the glass threads. A ground glass stoppered bottle is suitable, the stopper is best liberally coated with the red type silicone grease, and not pushed home tightly or it will stick. Natural rubber bungs will withstand attack for several weeks, but on removal are hardened and cannot be used again.

Tubing

Plastic tubing must be used with care, polythene is rapidly attacked, crazes and leaks, and P.V.C. is not much better. P.T.F.E. tubing should be quite unharmed but has not been tried. Copper tubing is attacked and covered with a layer of chloride, which if scraped off lifts into the air and is extremely unpleasant to breath in. It is not known if prolonged exposure to the vapour or liquid would destroy copper.

Metals

Brass appears resistant to attack, but analysed products showed over 5% Zinc, which must have been due to attack by $SiCl_4$ on brass fittings. All ferrous metals, including some stainless steels, chromium and cadmium plating, are strongly attacked by the vapour. Brazed joints are unaffected but on no account should soldered joints be relied on, as $SiCl_4$ appears to remove solder from joints leaving them loose.

Taps

Conical glass taps cannot be used, as they seal up solidly after a couple of days. The P.T.F.E. taps are suitable, but simplest of all are vacuum weir-type valves. So far Neoprene appears unaffected, as also does VITON, as the valve diaphragm. VITON-'O"-rings are less attacked than Neoprene, and should be used instead.

Transferring

When transferring one of these chlorides to a fresh vessel, it should be filled with an inert gas, preferably Argon because it is denser than air, and sealed up until pouring commences. In this way hydrolysing fumes can be almost eliminated. When a vessel is emptied, it should be flushed with water to make sure that all traces of vapour are removed. It is essential that all of these operations are carried out in well ventilated conditions, preferably in a fume cupboard. Protective clothing must be worn - rubber gloves and a gas mask. The rubber gloves should be tested for resistance before trusting them, and will probably have to be discarded if they have been in contact with the liquid. The vapour alone gives a painful skin burn. A suitable gas mask and cartridge is obtainable from Siebe Gorman Limited.

Spillage

If a spillage occurs, the area must immediately be evacuated as any exposure to the fumes is very dangerous. Only persons wearing gas masks should be allowed near the scene and they should proceed with care and liberally cover the liquid with Sodium Bicarbonate powder. It must be remembered that gas masks are not meant for high concentrations of gas, and cannot be relied on to give adequate protection in such conditions. So it is important that air extraction equipment is installed in any space where these liquids are handled, and can be switched on from outside. The point of discharge of the fumes should be considered - via a wet collector would be desirable. If a skin burn is experienced immediate application of Sodium Bicarbonate powder gives relief.

APPENDIX FOUR

THE COST EQUATION

The object of a cost equation is to combine all the cost components of a process into one general expression, which providing nothing has been omitted, is accurate. To evaluate a particular case, the relevant values are substituted, and the accuracy of the costing depends on the quality of the cost data.

Both cost accountants and economists find it convenient to distinguish between fixed and variable costs. Fixed costs are those incurred once the plant has been set up, whether it is used or not. They include capital depreciation, maintenance, labour and overheads. Variable costs are subdivided into material related e.g. fuel, and consumables, such as machine components that wear at some rate proportional to their usage.

Fixed costs are time related, the convenient period being one hour, so production rate is calculated on an hourly basis, and may be in terms of numbers of pieces, kilograms, or volume.

Labour charges are based on one year's salary per man, and include overheads. The annual cost per man is taken throughout to be £3000. The numbers of working hours on a shift is taken as 2000 hours per year, and a machine utilisation factor makes allowances for all the usual stoppages.

Capital charges are based on amortisation over a seven year period, and a percentage is added to the annual depreciation to cover the cost of maintenance. This percentage varies according to the nature of the process.

Materials' costs and consumables are expressed in terms of whatever production units are being used. Finally the production units are transformed to units of kg, or cubic metres, to give the processing cost in terms of £ per kg, or £ per m^3 respectively.

The following examples serve as an illustration:

1) $$\text{P.C.} = \frac{1}{\text{Kg per batch}}\left[\text{Electrical costs per batch} + \frac{\text{Cost of component}}{\text{Life of component in batches}} + \right.$$

P.T.O.

$$+ \frac{1}{\text{No batches per yr}} \cdot \left(\frac{\text{Capital cost}}{\text{Yrs life of plant}} + \text{Maintenance} + \begin{matrix}\text{Annual} \\ \text{labour} \\ \text{\& overheads}\end{matrix} \right) \Bigg]$$

$$\text{2) } \begin{matrix}\text{P.C.} \\ \text{£/kg}\end{matrix} = \frac{1}{\text{Kg per hour.}} \left[\text{Hourly electrical costs} + \frac{\text{cost of component}}{\text{Life of Component in hours}} + \frac{\text{Annual depreciation \& Maintenance + Annual labour and overheads}}{\text{Annual working hrs x machine utilisation}} \right]$$

$$\text{3) } \begin{matrix}\text{P.C.} \\ \text{£/m}^3\end{matrix} = \frac{1}{\text{Volume of piece in m}^3} \left[\frac{\text{Power costs per hr}}{\text{Pieces per hr}} + \frac{\text{component cost}}{\text{component life in hrs.}} + \frac{\text{Annual depreciation and maintenance + annual labour and overheads}}{\text{Pieces per hr x working hrs. per yr x utilisation.}} \right.$$

The symbols which are used throughout are,

P.C. = Processing cost (units as states)

C = Capital expenditure (£)

C_d = Capital depreciation (£p.a.)

C_{dm} = Capital depreciation and maintenance (£p.a.)

C_{LOH} = Annual labour and overheads charges (£p.a.)

E = Electrical charge (£per hour or batch)

$\bar{S}$ = Hourly production rate (pieces per hour)

n = Annual production rate (pieces or batches per year)

D = Cost of a consumable die set (£)

x = Life of a consumable item (units as stated)

η = Machine utilisation

H = Number of working hours per year (Hours p.a.)

V = Volume of a piece (cm^3 or m^3 as stated)

c = compaction ratio

d = final density, expressed as a fraction of theoretical density.

y = amortisation period in years.

Other quantities are defined as required.

APPENDIX FIVE

THE PROPERTIES AND USES OF DISPERSION STRENGTHENED MATERIALS

A survey has been made of the literature and is presented here in tabular form. Although the review does not pretend to be exhaustive, it gives a good representation of the present state of the art. In each case the matrix and dispersant are given, with particle size and percentage concentration in either volume or weight per cent if this appears in the original paper. There is no consistent method in the literature of describing the characteristics of the materials, so these are quoted as given except that all strengths have been converted to MN/m^2, sizes to microns and temperatures to ^{o}C. Applications are given if these are described by the authors, and as much detail on production method as available or space allows.

The usual abbreviations for yield strength (Y.S.) tensile strength (T.S.) and ultimate tensile strength (U.T.S.) are used.

MATRIX	DISPERSANT %	USEFUL CHARACTERISTIC	APPLICATION	METHOD	SOURCE & REFERENCE
Aluminium (atomised)	SiO_2 0.5μ 6$^{w/o}$ TiO_2 0.5μ 6$^{w/o}$	U.T.S. 20^{o}C 172 MN/m^2 " 400^{o}C 61 " " 20^{o}C 203 " 400^{o}C 68 "	Substitute for S.A.P.	High speed blending for 30 mins, cold pressed, hot pressed 5 mins at 550^{o}C and extruded at 500^{o}C	ATOMENERGI -KOMMISSIONEN
Aluminium	Al_2O_3 6%	(S.A.P.) Marked resistance to recovery & recrystallization	See section 3.4.2.	Surface oxidation of alumina flakes, cold pressed,hot extruded	CREMANS BRYAN GRANT.
Aluminium	Al_2O_3 1-10μ	Need further development as inferior to S.A.P.	Applications with moderate thermal stab & low costs.	Plasma sprayed	KELLERER and LOOMAN
Beryllium	carbon 0.8% i.e. 2.5% Be_2C	Good high T props			GREENSPAN (Nuclear Metals Inc)
Cr-Mo Very coarse powder.	MgO 40mμ Y_2O_3 1 μ ThO_2 10mμ	The dispersant was unstable during heat treatments, and there was considerable contamination in the microstructure from the ball mill. Generall inferior properties		Ball milling metal and oxide powders in Molybdenum mill at -45^{o}C in argon and tolvene 99%. was 0.5μ after 450 hrs. Encapsulated and hot pressed at 1100^{o}C for 2 hrs at 70 MN/m^2, machined, re-encapsulated and extruded at 1100^{o}C & 18:1	ALLEN (GENERAL ELECTRIC)
Cr-Mo4% 50% <2μ	ThO_2 70mμ 4$^{v/o}$	Exceptionally high tensile properties up to 1300^{o}C	substitution for chromium in gas turbines with higher ductile/brittle transition	Ball milling for shorter period	

MATRIX	DISPERSANT %	USEFUL CHARACTERISTICS	APPLICATION	METHOD	SOURCE & REFERENCE
Cobalt 80% Co-20% Cr 2μ 80% Co-20% Cr 80% Co-20% Cr (3μ) 80% Co-20% Cr (2μ and 5μ)	Al_2O_3 $10^{v}/o$ Thoria $6.5^{v}/o$ Al_2O_3 $10^{v}/o$ Thoria $6.5^{v}/o$ Thoria $10^{v}/o$	U.T.S. at 20°C 750 MN/m^2		Mechanical mixing Ground under H_2O. Flash coated Thermal decomposition of thorium nitride onto alloy powder	BUFFERD and GRANT (New England Materials Lab Inc. and M.I.T.)
Copper and Copper/Silver 150μ.	Alumina $4^{v}/o$	High electrical conductivity with hardness and resistance to thermal softening 99.8% full density	Spot or seam welding electrodes	Internal oxidation. Form oxide film at 300°C in O_2 then allow to diffuse at 700°C in argon. Reduce at 350°C in hydrogen. Green press, sinter, hot press at 924MN m^2 and 700°C..density 99.8%	A.E.I. LTD
Copper (CuO 1.0μ)	Al_2O_3 $5^{v}/o$	strength	High temperature electrical conductors	Ball milling under argon with solution of aluminium isopropoxide in toluene Alternately milled & heated to drive off tolerence. Water vapour passed through mill to convert isopropoxide to Al_2O_3 nH_2O. Compacted and sintered in H_2 for selected reduction. Extruded	HEAP and WILSON (E.E. CO. LTD)

MATRIX	DISPERSANT %	USEFUL CHARACTERISTIC	APPLICATION	METHOD	SOURCE & REFERENCE
Copper 6.6µ " 3.7µ Copper + Al8%	Al_2O_3 5 to 30mµ $2.2^{v/o}$ ThO_2 5 to 15mµ $2.2^{v/o}$ Al_2O_3 $4^{v/o}$	U.T.S. 20°C 406 MN/m^2 600°C 66.4 " " 20°C 371 " 600°C 133 " " 20°C 679 " 400°C 337 "	85% I.A.C.S. conductivity. Spark machining electrodes	Coprecipitation (described in detail) Washed & dried at 120°C. Heated to 250°C to produce mixed oxides Selective reduction 400°C in H_2. Compaction, uniaxial at 390 MN/m^2. Sinter at 850°C in H_2. Extrude at 600°C at 60 to 90 MN/m^2, anneal in HN_3 1 hour at 750°C. swage. Anneal and swage again. Draw to 3.18 mm diameter	GRAHAM EDGE and MOORE (I.M.I.)
Copper 0.2µ	Al_2O_3 $10^{v/o}$	.		As for S.A.P.	GRANT BLUCHER GIESSEN et. al.

MATRIX	DISPERSANT %	USEFUL CHARACTERISTICS	APPLICATION	METHOD	SOURCE & REFERENCE
Copper - 74µ	Al_2O_3 300mµ $10^{v/o}$	Y.S. 20°C, 210 MN/m^2	Aircraft parts-de-icing elements. Electronic component heat sinks. Electrical contacts	Dry mixing of powders in a ball mill or high speed Waringblender, for 15 mins at 15,000 r.p.m. Hydrogen reduction of residual oxide at 300°C Hydrostatic compaction in rubber sac at 270 MN/m^2, after evacuating air from sac. Sintered at 500°C for 1 hour, then 2 hours at 950°C in H_2. Canned in copper and extruded at 760°C at 20 to 30:1. Density 98% but 96% with -74µ Cu. Iron compacts sintered for min.10 hours at 830°C. canned in mild steel, extruded 16:1 at 820°C. Nickel compacts sintered as for Cu, then canned in Ni and heated to 1100°C for one hour then extruded at 16:-	GRANT and ZWILSKY
"	" 18mµ	" " 195 "			
" 5µ	" 300mµ "	" " 266 "			
"	" 33mµ "	" " 408 "			
" 1µ	" 300mµ "	" " 230 "			
" "	" 33mµ "	" " 418 "			
Iron 3µ	Al_2O_3 30mµ $10^{v/o}$	Y.S. 20°C 717 MN/m^2			
		" 520°C 185 "			
"	$0^{v/o}$	" 20°C 173 "			
		" 430°C 45.5 "			
"	MgO 50 100mµ $10^{v/o}$	20°C 890 "			
		520°C 211 "			
Nickel 5µ	Al_2O_3 20mµ $9^{v/o}$	Improved high temperature creep properties.			
Copper 1µ	SiO_2 20mµ $7.5^{v/o}$				
Copper	Beryllia	Does not embrittle in a hydrogen atmosphere	High temperature conductors High cond. brazed components such as welding electrode tips Die casting mould core pins	Method not disclosed but all stock is extruded	HANDY & HARMAN INC

MATRIX	DISPERSANT %	USEFUL CHARACTERISTICS	APPLICATION	METHOD	SOURCE & REFERENCE
Copper	BeO 'Triangular platelets 5 to 10mμ long'	U.T.S. twice that of the powder unoxidised, but at 20°C only 280MN/m^2	Experimental only	Copper 0.38% Be atomised powder 76μ internally oxidised, pressed in a double acting die at 540MN/m^2 and sintered at 1000°C. Density 80%	LEWIS SEEBOMM and MARTIN
	BeO 'Triangular platelets 5 to 10mμ long'	U.TS. 20°C 620 MN/m^2 Hardness maintained up to 0.9T_M		Powder prepared as before then canned and extruded at 800°C under 1400MN/m^2. Density 99%	
Nickel	Al_2O_3	U.T.S. 20°C 510MN/m^2		As above extruded at 950°C, 1400MN/m^2	
Copper	Al_2O_3	U.T.S. 20°C 386MN/m^2		As above extruded at 800°C, 930MN/m^2	
Graphite	Niobium Carbide	'Dense well bonded minimising the undesirable props. of pure carbides while exploiting their high strength	At high temperatures	Tumbled for 16 hrs. cold pressed, hot pressed at 3000°C for 15 mins under 21MN/m^2	HARADA (N.A.S.A.)

MATRIX	DISPERSANT %	USUAL CHARACTERISTICS			APPLICATION	METHOD	SOURCE & REFERENCE
Iron			at $20^{o}C(MN/M^2)$				
	Al_2O_3 10 to 50μ $16^{w/o}$	0.2% Y.S.	U.T.S.	El%		Oxidation-reduction Fe+8%Al atomised to <150μ, oxidised in air at $1250^{o}C$ for 16 hrs. Reduced in H_2 at $500^{o}C$ for 4 hrs, then ½hr at $1000^{o}C$. Compacted uniaxially at $386MN/m^2$ Sintered at $1200^{o}C$ in H_2 for 16 hrs. Canned in low carbon steel and extruded at $1200^{o}C$ at 16:1	GATTI (General Electric)
		458	510	1			
			at $650^{o}C$				
		180	190	5			
			at $20^{o}C$				
	Al_2O_3 10 to 100μ $16^{w/o}$	350	350	0		Co-precipitation of $FeAl_3$ and $AlCl_3$ with NH_4OH. Filtered, dried then reduced, compacted etc. as above.	
			at $650^{o}C$				
		220	220	0.5			
			at $20^{o}C$				
	Al_2O_3 1 to 50μ $8^{w/o}$	300	360	2.5		Selective reduction of mixed oxides, 0.1μ Fe_2O_3 and 0.1μ Al_2O_3 mixed in a colloid mill for ½ hr filtered, dried reduced etc as above.	
			at $650^{o}C$				
		90	100	15			
			at $20^{o}C$				
	Al_2O_3 10 to 50μ $8^{w/o}$	290	310	4.5		Colloidal mixing of 3μ Fe and 0.1μ Al_2O_3 treated as above.	
			at $650^{o}C$				
		72	79	20			
Iron <150μ	For comparison no alumina)		at $20^{o}C$			Compaced, sintered and extruded as above.	
		110	215	27			
			at $650^{o}C$				

MATRIX	DISPERSANT %	USUAL CHARACTERISTICS		APPLICATION	METHOD	SOURCE & REFERENCE
		at 20°C				
Iron	Al_2O3	0.2% Y.S.	U.T.S.		Mixed nitrates decomposed at 500°C. Reduced in H_2 at 500 $\longrightarrow$ 800°C. Powder density 0.7 gm cm^{-3}, all < 40μ	BOVARNICK and FLOOD
	0.41 $^w/o$	455 MN/m^2	550MN/m^2			
	2.8 "	482 "	655 "			
	6.25 "	606 "	703 "			
		at 650°C			Compacted into steel cans at 862 MN/m^2 evacuated, outgassed at 425°C, sealed heated to 1075°C for 2 hours and then extruded at 19:1 under 1000MN/m^2. Swaged to straighten.	
	0.41 "		83 "			
	2.8 "		152 "			
	6.25 "		165 "			
		at 980°C				
	0.41 "		34 "			
	2.8 "		59 "			
	6.25 "		69 "			

MATRIX	DISPERSANT %	USUAL CHARACTERISTICS	APPLICATION	METHOD	SOURCE & REFERENCE
Iron 5μ	Al_2O_3 $2^{v/o}$	1% proof stress shows a Substantial fall at the - transition temp at 910°C. Value at 20°C is $820 MN/m^2$	Limited to under 900°C due to grain growth.	Iron oxide 'doped' with Aluminium nitrate solution, dried and ignited at 1250°C for 36 hrs to form solution of Al_2O_3 in Fe_2O_3. Reduced at 400°C in H_2 for 4 hrs then at 600°C in H_2 for 2 hrs. Hydrostatically pressed at 540 MN/m^2 and sintered in H_2 for 4 hrs. Hot rolled & swaged at 800°C, coldrawn to 0.3 mm wire with annealing.	GRIMWADE and JACKSON
Nickel 1μ	Al_2O_3 5 to 50mμ $2^{v/o}$	U.T.S. 20°C $720 MN/m^2$ (as sintered)			
Copper 50μ	Mg O $2^{V/o}$	1% P.S. 20°C $540 MN/m^2$ (fibrous structure, 1μ grain size)	Recrystallised if heated in H_2 at 1000°C but <u>not</u> in N_2		
Iron Ferritic And austenitic steels	Al_2O_3 MgO SiO_2 1μ up to $15^{v/o}$	13% Cr 1% Si 0.5% Al 15% Al_2O_3 has T.S. 4 x cast alloy with decreased elongation.		Ball mill, compacted and sintered in H_2 for 4 hrs at 1350°C	IMAI and HIROTANI (Tokoku University)
Stainless Steel 1-5μ (22%Cr 22%Ni)	Alumina 16mμ 30mμ Titanium 26mμ Thoria 20mμ Zirconia 25mμ	Better retention of properties over long periods.		Planetary mill, dispersoid & alcohol in argon. Mean particle size 5μ. Extruded.	SANDS PHELPS MORGAN (B.S.A.)

MATRIX	DISPERSANT %	USUAL CHARACTERISTICS			APPLICATION	METHOD	SOURCE & REFERENCE
		at 20°C Y.S. MN/m^2	U.T.S. MN/m^2	%el		Ball milled under acetone for 40 hrs. Pressed at 600MN/m^2 with camphor lubricant. Pre-sintered at 880°C 1 hr, then 1350°C 1 hr under H_2 Density 90% 6 p.p.m of H_2 in compact. Then cold swaged to 50% reduction	SCHÖNBAUER MITSCHE and BENESOVSKY
Iron 4 to 6μ (carbonyl	CaO 1 to 2μ 0.2$^{w/o}$	130	250	50			
	1.0$^{w/o}$	120	260	20			
	5.0$^{w/o}$	120	250	30			
	0$^{w/o}$	160	240	50			
		at 300°C					
	0.2$^{w/o}$	150	220	250			
	1.0$^{w/o}$	100	230	230			
	5.0$^{w/o}$	120	200	200			
	0$^{w/o}$	90	260	270			
		at 20°C					
	MgO 1μ	Y.S. MN/m^2	U.T.S.MN/m^2	%el		As above	
	0.2$^{w/o}$	150	250	40			
	1.0$^{w/o}$	170	280	20			
	0$^{w/o}$	160	240	50			
		at 300°C					
	0.2$^{w/o}$	100	190	25			
	1.0$^{w/o}$	80	240	30			
	0$^{w/o}$	90	260	27			

IRON: see also under Copper (GRANT and ZWILSKY).

MATRIX	DISPERSANT %	USEFUL CHARACTERISTICS	APPLICATION	METHOD	SOURCE & REFERENCE
Nickel 75% Cr 20%	Thoria 0.08µ 2.35$^{w/o}$		As above	Cr is converted to CrN before compaction. De-nitrided before extrusion. Avoids Cr_2O_3	LAMBERT (Fansteel Inc)
Nickel 58% Cobalt 20% Molybdenum 10% Tungsten 10%	ThO_2 50mµ 3$^{v/o}$	None tested. The size and spacing of the dispersant was of the required specification for D.S. materials.	Experimental	High intensity arc process. Electrodes prepared by mixing - 74µ metal and oxide powders with carbon and an organic binder. Extruded and baked at 900°C for 4 hrs The 2cm diam 1 m long electrode vapourised at 40kW as the anode of an arc. Submicron powder collected by cyclons and bag filter then reduced in H_2 at 750°C for 3 hrs. Isostatically pressed and sintered in H_2 3 hrs at 1300°C	McCULLOUGH and GRAND (N.A.S.A.)
Nickel aluminide	ThO_2 5 to 15mµ 1 to 5$^{v/o}$	Excellant corrosion resistance and high strength at high temperatures.	Gas turbine components	'Pack diffusion of aluminium into T.D. nickel powder, by reaction with AlF_3 vapour at 1100°C. hot pressed in vacuo at 1570°C and $42MN/m^2$	MILLER (General motors)

MATRIX	DISPERSANT %	USEFUL CHARACTERISTIC	APPLICATION	METHOD	SOURCE & REFERENCE
Nickel 2.5µ	ThO_2 0.03µ $4^{v/o}$ Zirconium $0.4^{v/o}$ ThO_2 $4^{v/o}$ Al_2O_3 0.03µ $2^{v/o}$	T.S. 182 MN/m^2 at 1100°C T.S. 157 MN/m^2 at 1100°C T.S. 87 MN/m^2 at 1100°C	Showed that their method produced a T.D. nickel as good and better than commercial grades.	Milled, cold pressed, sintered, hot rolled, then 7-12 cold-roll/ anneal cycles.	QUATINETZ and WEETON (N.A.S.A.)
Silver	CdO $10^{w/o}$	Uniform properties. contact surfaces resist welding during overload conditions. Withstand cold work well	Relay contacts for the air-craft industry	Co-precipitation of carbonates-heated in air, when $Ag_2CO_3 \longrightarrow 2Ag$ and $CdCO_3 \longrightarrow CdO$ Then 'powder met. methods.'	LEVER F.M. (Mallory & Co.)
Silver	MgO $10^{w/o}$			As above.	
Titanium	Silicon	Higher strength required at 550-650°C. Hardness 150 D.P.H.		See paper	SCHWOPE (Clevite Corp)
Titanium 2.5µ	ThO_2 1.5µ $2.8^{v/o}$ TiC 5.0µ $5.5^{v/o}$ Ti_5Si_3 0.8µ $6.3^{v/o}$ Al_2O_3 0.3µ $2.8^{v/o}$	No effect (No bonding) 75% inc in T.S. 100-300% inc. in T.S.		Ball Milling	
Zirconium 50-150µ	Al_2O_3 0.3µ $2^{v/o}$	Coining and hot pressing not necessary. T.S. greatly improved.		Ball Milling	
Tungsten	ThO_2 0.045µ 3.8%	Y.S. up to 3 x pure W.		Co-precipitation	KING (Westinghouse)

NICKEL: see also under Iron (GRIMWADE and JACKSON) and under Copper (LEWIS et. al)

MATRIX	DISPERSANT %	USEFUL CHARACTERISTICS	APPLICATION	METHOD	SOURCE & REFERENCE
Tungsten	HFN 1.4at%	No grain growth at 1650°C for 1 hour in H_2	In a high pressure of N_2 as components in nuclear reactors	Cp-vapour deposition of $HFCl_4$ and ECl_6 with NH_3 at 900°C	KANE (Lawrence Radiation Lab.
Tungsten Molybdenum Rhenium (and their alloys)	Nitrides of aluminium, titanium hafnium, Zirconium, vanadium, niobium, tantalum plus refractory. additives.	Tool lives of order 10 times those of conventional cemented carbides when used at high cutting temperatures. Resistance to thermal cracking.	Metal cutting tools	Various considerably in detail with material, but in general ball milling followed by hot pressing at 1000°C to 2000°C at $28MN/m^2$ N.B. Thermal Expansion coefficients of constituents must not differ by greater than factor of 2.	YEATES (du Pont de Nemours & Co)
see the original for details. 64 examples given of great variety - impossible to select one which is representative					
Zinc 30μ	Zn 0.5μ $9^{v}/o$ 0.9μ $15^{v}/o$ 1.6μ $25^{v}/o$ Al_2O_3 Carbon tungsten	The hardest dispersed phase gave the greatest increase in ductility	Experimental only	Oxidised, hot pressed at 390°C at $210MN/m^2$ Tumbled then as above.	MCCARTHY SHYNE AND SHERBY (Lockheed)

MATRIX	DISPERSANT %	USEFUL CHARACTERISTICS	APPLICATION	METHOD	SOURCE & REFERENCE
Zirconium	Y_2O_3 .05 to 5μ $10^{v/o}$ (fused) $0^{v/o}$	U.T.S. at 500°C 236MN/m^2 " " " 172 " comprehensive creep data given.	Substitute for pure zirconium	ZrH_4 and Y_2O_3 milled for 24 hrs in rod mill under A. Pressed at 926MN/m^2 vacuum sintered 8 hrs at 1200°C, when $ZrH_4 \longrightarrow$ Zr. Rehydrided, and process repeated once, or twice. Additional step of hot rolling in vacuo at 950°C.	REZEK
	Y_2O_3 $<$0.5μ $3^{v/o}$		" " ""		

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