ELECTRODEPOSITED COBALT

ALLOY COATINGS AND THEIR

USE ON HOT FORGING DIES

by

FRANK ANTHONY STILL, B.Sc.

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SUMMARY

Three cobalt alloy electro-plating solutions, cobalt-nickel, cobalt-molybdenum and cobalt-tungsten, were used to electrodeposit cobalt alloys onto hot forging dies made from heat treated Electem No.5. die steel. The cobalt-nickel alloy solutions had been formulated previously but the cobalt-molybdenum and cobalt-tungsten baths were developed from a new basic solution containing sodium heptonate as the complexing agent.

The plated dies, both flat and shaped, were evaluated by subjecting them to standard hot forging tests. The shaped die test was developed so that a closer simulation of industrial conditions could be achieved than was possible by using the flat dies. Techniques used to evaluate the extent of wear included:

i. The use of surface analyser methods to determine changes in surface profile.

ii. Taper sections to examine cracking of the coating and underlying die steel.

iii. The use of the S.E.M. to examine wear characteristics and scale formation.

A number of cobalt-molybdenum and cobalt-tungsten alloy coatings proved to be successful in increasing the life of flat and shaped experimental hot forging dies. These alloys were electrodeposited at fairly high cathode efficiency, they did not scale during forging and were relatively hard so that they were not easily eroded away in regions subjected to severe wear. The internal stress, hardness and structure of these coatings were

determined. The hardness of the deposits were measured in the as plated condition and after heat treatment at 130°C and 500°C. These heat treatment temperatures corresponded to the bulk die temperature and the approximate die surface temperature achieved during forging respectively.

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1.   INTRODUCTION

Dies for use in hot forging operations are required to withstand some of the most arduous service conditions encountered in any industrial process.   They are subjected to very high stresses, high surface temperatures, thermal shock and oxide abrasion.   The materials utilised for dies vary considerably from fairly cheap, low alloy to expensive highly alloyed steels. However, due mainly to economic considerations, the most widely used steel is a low alloy nickel-chromium-molybdenum type known as No.5 die steel (B.S.S. 224 1938, 1949).   This steel is not only used for the manufacture of the dies themselves but is also employed extensively as a bolster material for die inserts of other materials having higher wear resistance.

Irrespective of material a die will eventually wear out or fail in service and this may be brought about by several means:-

1.   General erosion of the die leading to out of tolerance forgings.

2.   Stress cracking on sections of the die containing stress raisers.

3.   Thermal fatigue cracking.

4.   Sticking of the forging within the die cavity is due to cracking caused by mechanisms 2 and/or 3. Subsequent additional damage to the die may be caused by the use of excessive force when removing the forging.

5.   Excessive use of lubricants.

6. Erosion of the 'flash lands' leading to a thick forging 'flash' which may not be removed easily.

7. Malpractice in the forging shop, i.e. forging of cold billets, etc.

Consideration of these factors reveals that certain of them, (i.e. 4, 5 & 7) may only be guarded against and minimised by strict control exercised by the forging shop manager; they cannot be eliminated by the introduction of improved materials. Other factors such as stress cracking may be difficult or impossible to control. The only method of removing a stress raiser, assuming that it is not caused by poor machining or bad die design, is to completely re-design the component. This may not be practicable since the component's shape may be such that stress raisers are unavoidable. This leaves factors 1, 3 and 6 as modes of failure which can be reduced in severity by modification of the die material.

The most obvious way in which to improve the properties which affect these factors and thus improve the life of the die is to use an alternative material for the manufacture of the whole die. This material may have a higher strength, toughness, wear resistance or thermal shock resistance than that of the material previously in use but its introduction will not necessarily lead to economies. For example, if an improvement in strength is considered, the substitution of an alternative material may prove expensive due to increased costs encountered from various areas even though its basic cost may not be significantly greater than the original die steel. These increased cost areas include:-

a. The higher initial cost of material. (This is

not important for dies of small size but where large

dies are concerned this becomes an increasingly

important factor).

b.   An increase in processing costs due to the more

complex heat treatment procedures required.

c.   An increase in machining costs.

It is also possible that the increased strength of the new
material is achieved at the expense of other properties such as
erosion and thermal fatigue resistance.   Thus the new die material
may produce more forgings than the former one due to its ability
to withstand higher stresses but the inferior properties associated
with die erosion or thermal fatigue may still not permit the die
to produce an economical number of forgings.   Similar problems
may be encountered if any of the other properties of the die steel
are to be improved, the improvement of one property being gained
at the expense of another.

A final factor which must be remembered is that if the
new die material does give an improved die life under laboratory
conditions this improvement must be large in order to overcome
the effects of the fairly wide scatter of die life encountered
in many industrial forges.

It is therefore a very difficult undertaking to produce a
new die material with sufficiently improved all-round properties
to replace any of the die steels currently in industrial use.
This is emphasised by the continued wide use of No.5 die steel,
the British Standard Specification for which was introduced in
1938. Consequently the choice of die material for a particular

component becomes one of compromise, an attempt being made to maximise the number of forgings possible from a die set while at the same time realising the inherent weaknesses, physical, mechanical and financial, of the material.

The alternative procedure to a change in bulk properties is to attempt to improve the surface layers of the die using a suitable coating. By this means it is possible to retain all the desirable properties of the bulk material while at the same time imparting to the surface of the die a characteristic which the bulk die may lack. Various coatings have been used either experimentally or on a limited industrial scale, the most well known example being the use of electrodeposited chromium coatings. However, conflicting evidence has been reported on the value of such coatings. In some instances the service life has been improved but in others premature failure has occurred at surface stress raisers. Other coatings or surface treatments known to have been studied, at least on an experimental scale, include electrodeposited composite coatings (cobalt matrix containing chromium carbide particles), sprayed metallic coatings and chromised or nitrided surfaces. Since electrodeposition affords an ideal means of applying coatings possessing unique properties it is surprising that so little work has been carried out in this field.

2. THE USE OF COBALT ALLOYS ON HOT FORGING DIES

This investigation was commenced using flat die sets of heat treated Electem* No.5 die steel. These dies were in the shape of discs 5cm. in diameter x 1.25cm. thick. Initially unplated Electem dies and die sets plated with various cobalt-nickel alloys were evaluated. The cobalt-nickel alloys, deposited from both sulphate and sulphamate baths, were employed because Belt et al[1] had reported that certain alloys in this system possessed good hot hardness. Cobalt-molybdenum and cobalt-tungsten alloys were later used as again they were reported[2] to retain their hardness at elevated temperatures. The results obtained from testing these die sets indicated that cracking of the die surface occurred in areas of negligible metal flow. This cracking was attributed to thermal fatigue of the die surface. It was also apparent that the extent of the cracking of the die steel was influenced by the particular coating applied. This type of defect is known to contribute to industrial die failure and it was therefore considered important to determine the effects of cyclic temperature fluctuations on the electrodeposits. This required the development of a thermal fatigue test which did not include the effects of deformation. In order that the thermal cycle should adequately simulate the conditions that occurred during forging, temperature measurements were made during the forging operation using both surface and sub-surface thermocouples. This enabled the upper and lower limits of the temperature cycle to be set and the subsequent construction of a simple thermal fatigue apparatus.

* Proprietary name of Walter Somers Ltd.

The properties of the cobalt-nickel alloys were determined only in a few instances as the baths employed were well known and had been extensively investigated by previous workers[3-8]. The cobalt-molybdenum and cobalt-tungsten alloys however were produced from baths which had not been previously formulated. It was therefore thought that selected properties of the electrodeposits which were of significance in this particular application should be investigated. These properties included, cathode current efficiency, internal stress and hardness as well as thermal fatigue resistance mentioned earlier.

As the possible number of bath formulations was very large the above properties could not be determined for each solution. A sorting procedure was therefore used to obtain the most useful alloy deposits. First a series of baths was evaluated using the Hull cell test and the deposits obtained from a number of the baths having satisfactory plating characteristics were analysed. In this way a small number of baths having the highest possible alloying element content coupled with acceptable plating characteristics was found. These baths were then used to deposit cobalt-molybdenum and cobalt-tungsten alloys onto flat die sets and evaluated in the experimental forging test. This reduced the number of suitable alloy baths still further as several of the coatings performed inadequately during testing. The determination of the properties mentioned earlier was then undertaken on this relatively small number of baths. The properties investigated were chosen because they were the ones which would govern the practical applications of the coatings for use on industrial dies.

Cathode current efficiency was considered to be of importance as many previously formulated cobalt-tungsten and cobalt-molybdenum alloy plating baths operated at low cathode efficiency. This made it impossible to obtain moderately thick electrodeposits in a reasonable plating time and so hindered their industrial application. It was therefore necessary that any new alloy plating bath should have a reasonably high cathode efficiency for it to be commercially viable.

The measurement of internal stress was undertaken in order that the effects of both the alloying elements and the complexing agent could be studied. The internal stress of the deposits could not be too high as severe cracking and flaking of the deposit would be likely to appear when depositing thick coatings.

On completion of evaluating the properties of the deposits it was decided that a more satisfactory indication of service life in an industrial forge could be obtained if the coatings were applied to shaped dies which incorporated edges and corners. The behaviour of the coating on these features was important since these were considered the most likely areas of coating failure. A die shape was therefore developed which could be utilised in the forging apparatus available and which could be evaluated easily for wear. This shaped component was also a test of the ability of the solution to plate complex shapes which would be encountered industrially. The most wear resistant coatings, as indicated by the flat die testing procedure, were therefore evaluated using these dies. The results obtained from these tests indicated two alloy deposits, one cobalt-molybdenum and one cobalt-tungsten,

to have very good wear resistance as compared with an unplated Electem die of the same shape.

3.   LITERATURE REVIEW OF ALLOY PLATING

The development of alloy electrodeposits began at almost
the same time as the development of single metal electroplating.
The deposition of thin layers of single metals was first done by
Elkington in Britain and de Ruolz in France in 1840.   The first
alloys produced were of brass and bronze and these were plated by
de Ruolz from a cyanide bath in 1842.   Progress in the field of
alloy deposition from this time has largely depended on the progress
made on single metal deposition as the variables which govern these
deposits also play a major role in alloy plating.

The production of alloy electrodeposits offers a range of
properties which are not obtainable by electrode deposition of single
metals.   The alloy deposits are often stronger, harder, more wear
resistant and have better magnetic properties.   The alloys
produced by electrodeposition are true metallurgical alloys in that
they normally contain phases which are indicated by the phase
diagram as stable for the temperature at which the electrodeposited
alloy was formed.   There appear to be only two exceptions to this
rule and these should therefore be noted.   One is the electro-
deposition of Speculum (copper-tin alloy) and the other electro-
deposited nickel-tin alloys.   Speculum deposits containing about
60% copper - 40% tin were found by Rooksby[9] and Raub and
Sautter[10] to contain a phase which was not present on the
equilibrium diagram and which could not be thermally prepared.
Similarly an intermetallic phase of nickel-tin which approached the
formula NiSn was found by Rooksby[11] and by Smart and Robins[12]
to be present in nickel-tin electrodeposits containing 63-67% tin.

Although different phases are not normally produced by electro-deposition differences in structure between the electro-deposited and thermally produced alloy may be apparent. These differences are mainly caused by differences in the range of composition or temperature over which the phase exists. Therefore it is sometimes found that a particular phase may be restricted or expanded in an electrodeposited alloy.

The codeposition of alloys may be split into five types:-

1. Regular codeposition

2. Irregular codeposition

3. Equilibrium codeposition

4. Anomalous codeposition

5. Induced codeposition.

Types 1-3 are known as normal codeposition and types 4-5 as abnormal codeposition as from elementary considerations it would seem that codeposition of these alloys was not possible.

The deposition of alloys from the regular codeposition type bath are normally under diffusion control and therefore the effects of plating variables on the metal ion content of the diffusion layer are predictable from simple diffusion theory. Regular codeposition usually occurs in baths containing simple ions and with metals whose static potentials are far apart. A typical example of this type of bath is the perchlorate bismuth-copper bath.

Irregular codeposition is normally controlled by the characteristics of the potentials of the metals against the solution rather than by diffusion processes. The solutions for

this type of codeposition usually contain complex ions and are markedly affected by the concentration of free complexing agent present in the bath. The copper-zinc cyanide bath is typical of this category.

Equilibrium codeposition is not very common and only a few of these systems have been investigated such as the copper-bismuth and lead-tin acid baths. The solutions are in chemical equilibrium with both of the parent metals and the ratio of metals in the deposit is the same as their ratio in the bath.

The anomalous codeposition type baths are fairly rare and usually contain one or more of the Iron group metals iron, cobalt or nickel. It is referred to as anomalous as the less noble metal deposits preferentially.

The last type of alloy bath listed is the induced codeposition type. These baths are characterised by the deposition of alloys containing molybdenum, tungsten and germanium which cannot be deposited from aqueous solution alone. The alloys most readily formed are those with the iron-group metals and the ions present in the bath are termed inducing metal ions (iron group metal ions) and reluctant metal ions (molybdenum, tungsten or germanium metal ions).

The latter two alloy systems are the concern of this work therefore in the following brief outline of the theory of alloy deposition specific reference will be made to these systems where possible.

In order that an alloy may be obtained from a plating

solution it is required that the deposition potentials of the two metals are fairly close together. The reason for this is that the more noble a metal the easier it will deposit and therefore if the difference in deposition potential of the two metals is great the more noble metal will deposit preferentially, frequently to the complete exclusion of the less noble metal. The static potential of each metal in the alloy bath may be given by a form of the Nernst equation:-

$$E^s = E_o + \frac{RT}{ZF} \ln a^{z+} \qquad (i)$$

where

E^s = static electrode potential

E_o = standard electrode potential

R = gas constant

T = absolute temperature

F = Faraday

Z = valency

a^{z+} = activity of metal cation

Although the static potential of a single metal can give no definite information as to whether or not an alloy system is feasible it may serve as a guide to alloy deposition from simple salt baths. If a list of the standard potentials of the elements is drawn up it may be observed that a considerable number of commonly deposited metals, such as lead, tin, nickel, cobalt, chromium and zinc have a potential more negative than hydrogen. It would therefore seem that none of these metals could be deposited from aqueous solution as electrolysis would result in the 'deposition' of the more noble hydrogen. However

in practice this is not found to be the case due to the high hydrogen overpotential required to liberate hydrogen. This effectively gives hydrogen a more negative potential than the metals under consideration. The two metals of particular interest in this work, tungsten and molybdenum, would also be expected to deposit as they have more negative potentials than hydrogen but are more noble than cobalt which deposits easily. In fact it is not possible to obtain thick deposits of either of these metals from aqueous solution, for reasons which are unknown at present. The deposition of very thin 'flash' deposits of both metals has been claimed[13-17] but the deposits obtained could not be built up above approximately 0.5 μm in thickness and it is questionable whether the deposits were pure metals, oxides or alloys. There are obviously severe limitations to the usefulness of standard electrode potentials in predicting alloy formation or for that matter single metal deposition. However some generalisations may be made on the formation of simple alloy baths by reference to the standard electrode potential table. For example simple alloy baths may be produced from metals whose standard potentials are close together, such as nickel and tin. Conversely metals whose potentials are far apart, such as silver and zinc, do not readily deposit. It can be said that in general alloy baths of simple salts, apart from some exceptions, give reasonably satisfactory alloy deposits if the static potentials of the two metals do not differ by more than 0.2v.

The activity of the depositing cation present in the cathode film, represented by a^{z+} in equation (i), is dependent

upon the concentration of depositing cations present in the bath
and therefore may be increased or decreased by altering the
concentration of these cations. This is very important in alloy
deposition as by lowering the concentration of the more noble
metal in the bath the static potentials of the two alloying
elements are brought closer together and alloy deposition is thus
encouraged. However if the activity in equation (i) is re-written
as a function of the concentration of metal ions present the
following equation results:-

$$E^s = E_o - \frac{0.059}{n} \log_{10} C_{f_a} \qquad (ii)$$

where C = molar concentration of the metal

f_a = activity coefficient of the ion

n = number of equivalents per mole.

This equation is controlled by the logarithmic function of salt
concentration and therefore if values are substituted in this
equation it is found that very high decreases in salt concentration
lead to relatively small decreases in electrode potential. It is
often the case that alloy baths containing simple salts are either
inoperable as the concentration of one element cannot be reduced
sufficiently to allow alloy deposition or the concentration of
one element is reduced to such an extent that poor deposits result.
In consequence some other means is required which will reduce the
effective concentration of the more noble metal such that good
alloy deposition may take place. This is done by the formation
of complex metal ions in the bath using a variety of complexing
agents. The use of complexing agents also has the effect of
shifting the electrode potentials of the metal ions in solution to

more negative values. This often brings the electrode potentials
closer together and therefore also promotes alloy formation. The
main use of complexing agents however is as mentioned above, in
altering the activity of the metals in the bath by reducing the
number of available metal ions, particularly of the more noble
metal. Therefore in the copper-zinc bath for example the use
of cyanide as a complexing agent makes possible the deposition of
copper-zinc alloys by reducing drastically the activity of the
copper ions present in the bath.

The Nernst equation quoted earlier, equation (j), holds
true for a condition of reversible equilibrium but as metal
deposition is usually an irreversible process this equation
cannot be used to determine the deposition or dynamic potential
of the metal. The deposition potential includes extra energy
which must be added to that of the static potential in order to
sustain the deposition rate under the dynamic conditions which
exist in the cathode film. This energy is effectively the energy
required to overcome polarisation effects. Therefore although
the use of static potentials gives some useful information
concerning the deposition of alloys the dynamic potential at which
the metals actually deposit are far more important for determining
alloy plating. In general the dynamic potentials are always
more negative than the static potentials because they include the
overvoltage due to polarisation effects. Dynamic potentials are
normally brought closer together by the same means as is used for
static potentials (i.e. by the use of complexing agents for
example). The deposition potentials of metals and alloys are

usually related to current density and plotted as current density - cathode potential curves. In this way the curve for both metals may be plotted and it is often found that the curve for the deposition of the alloy lies between them. That is, the co-deposition of the two metals allows the less noble metal to deposit at a more noble potential. However after studying many alloy systems in this way it has been found that there is no correlation between the types of curves produced and the alloy systems from which they come. It has also been found that the current density - cathode potential curves for codeposition often differ from those for individual deposition. The use of such curves for predicting the behaviour of an alloy system from data obtained from the parent metals is therefore limited. This is especially true for alloys of the induced deposition type.

As mentioned previously the metals tungsten and molybdenum cannot be deposited from aqueous solution therefore the construction of a current density - cathode potential curve of the parent metals for both the cobalt-molybdenum and cobalt-tungsten system is impossible and offers no means of predicting the position of the alloy curve. However current density - cathode potential curves for cobalt/cobalt-tungsten alloy and nickel/nickel-tungsten alloy have been produced by Brenner and Seegmiller[18] and Holt and Vaaler[19] respectively. The curves obtained for the cobalt-tungsten system showed that the alloy was more noble than the single metal and approached the cobalt curve with increasing tungsten content in the bath.

The above baths, as is the case with many of the alloy

baths from both the cobalt-tungsten and cobalt-molybdenum systems, were alkaline in nature. These studies therefore and those carried out by other workers[20-23] are not applicable to the acid solutions which are the main concern of this work. The few acid solutions which have been studied by Holt and Black[24] (iron-tungsten) and Nielsen and Holt[25] (nickel-tungsten) have shown that the potentials of alloy were not more noble than those of single metal deposition and that the differences in potential were small. Holt and Black[24] found that the difference in potential between the iron-tungsten alloy and pure iron was negligible within experimental error. Nielsen and Holt[25] showed that pH effected the difference in potential between the pure metal and the alloy as at pH 5.0 the deposition potential of the nickel-tungsten alloy and nickel were the same but at pH 2.0 the deposition potential of the alloy was 0.1v less noble than that of nickel.

Current density - cathode potential curves have been produced by Piontelli[3] for the anomalous deposition of cobalt-nickel alloys from the sulphamate bath. It was found that this system was temperature sensitive and at a temperature of 35°C the curve for the alloy was between those of the two parent metals while at 55°C and 80°C the alloy deposited at more noble potentials than the parent metals. The curves for the same alloy produced from the sulphate bath give similar curves to those obtained from the sulphamate bath.

Two of the major factors which determine the electro-deposition of an alloy are the thickness of the cathode diffusion

layer and the concentration of metal ions within it. Of these the concentration of metal ions within the diffusion layer is the most important. The diffusion layer is formed mainly due to the upward movement of the solution at the cathode/solution interface. This is because the depleted solution in this area is less dense than the solution in the main bulk of the bath and tends to rise. A horizontal component to this movement is also present caused by a horizontal flow of ions to the depleted region from the bath. The cathode layer therefore always contains a concentration gradient, with the lowest metal ion concentration occurring at the cathode/solution interface. The thickness of the layer is a function of many variables such as; the rate of solution flow over the cathode surface which will reduce the thickness of the layer[26]; an increase in the current density which slowly decreases the thickness of the layer[27]; the height at which it is above the bottom edge of the cathode as the higher up the cathode the thicker the diffusion layer[27]. These variables themselves are influenced by the degree of agitation employed in the bath and therefore a very complex situation exists in any normal plating bath.

The most important aspect of the cathode diffusion layer when considering alloy deposition is the concentration gradient within the layer, as mentioned earlier. The transport of metal ions through the film is accomplished by diffusion, convection and electrical migration of the ions. However the relative concentration of each of these agencies to the transport of metal ions varies throughout the thickness of the layer. The effect of diffusion is greatest at the cathode/solution interface as the

concentration gradient is steepest here. The effect of convection at this point however is zero as there is zero flow at this point in the layer due to the lamellar flow of the cathode layer. The situation is reversed at the outer-edge of the layer where there is maximum convection but a very shallow concentration gradient. The movement of ions due to electrical migration is very similar throughout the layer and in fact does not vary significantly with distance from the cathode. The existence of the cathode layer gives rise to two phenomena which are important in both single metal and alloy deposition, namely concentration polarisation and activation polarisation. In order to overcome these polarising effects extra energy must be supplied to the reaction and it is this extra energy which accounts for the difference between the static and dynamic potentials of the metals. The concentration polarisation, as its name suggests, is caused by depletion of metal ions in the cathode layer which gives rise to the concentration gradient mentioned earlier. The Nernst equation shows that in dilute solution the deposition potential becomes more negative therefore the deposition of the metal becomes more difficult. If the current density is increased the diffusion layer becomes more denuded in metal ions and the concentration polarisation increases. A state is eventually reached at which the concentration polarisation approaches infinity (i.e. zero concentration of metal ions). The current density at this point is termed the limiting current density. This situation is not common as before it is reached an alternative electrode process takes place. In alloy plating codeposition may occur at a limiting current density greater than or equal to

the sum of the limiting current densities of the two metals or
at the limiting current density of the more noble metal, the
other metal being deposited below its limiting current density.
Alloy systems which are deposited in this way are under diffusion
control (i.e. regular alloy codeposition) as they rely on diffusion
and electrical migration through the cathode layer to supply ions
to the cathode. The effect of concentration polarisation may be
quite large in the case of alloy baths which contain complexing
agents as the deposition of the metal atom at the cathode results
in the formation of a high concentration of 'free' complexing
agent in this region. A high concentration of free complexing
agent in solution causes large negative shifts in potential and
this shift in potential, as compared with the static potential of
the 'normal' bath concentration, is considered as concentration
polarisation. The concentration of free complexing agent will
increase with increasing current density thereby making the cathode
more negative so that the potential for the discharge of hydrogen
is approached. In this way solutions containing complex ions
exhibit a decrease in the cathode current efficiency with increasing
current density.

Activation polarisation is associated with processes
occurring at the electrodes which require an activation energy.
Such processes for example include hydration and dehydration of
ions and the discharge of ions at electrodes. This type of
polarisation may again be particularly important for solutions
containing complex ions.

3.1 The Mechanisms of Anomalous and Induced Codeposition

The mechanisms involved in anomalous and induced codeposition are not fully understood and various theories have been put forward to explain the process. However as yet no suitable theory has been formulated which can explain all of the phenomena observed in these alloy systems.

The anomalous alloy systems formed by the iron-group metals, which includes the cobalt-nickel system used in this work, differ in their degree of anomaly depending on their particular combination. For example work by Glasstone and Speakman[4] on the alloy systems of cobalt-nickel, iron-nickel and cobalt-iron shows that the cobalt-nickel is the most anomalous and that the cobalt-iron system shows little anomaly. The theory put forward by Glasstone to explain the anomalous codeposition of the iron-group metals was essentially the same as he had postulated for the anomalous codeposition of zinc with the iron-group metals[28]. The explanation was that the anomalous deposition of nickel was due to a retarding effect of the iron or cobalt which caused the nickel to be initially deposited in a less noble form. Consequently a more negative potential was required to discharge the nickel than was required to discharge the other iron-group metal present in solution and anomalous deposition took place. This theory is unacceptable mainly due to the fact that there is no experimental evidence to show that two such forms of nickel exist. A possible explanation put forward by Brenner[2] assumes the adsorption of foreign material by the active surface of the iron-group metal. This hypothesis is suitable for alloys of the iron-group with

zinc and also the formation of alloys within the iron-group. The adsorption of ions or molecules onto the surface of the iron group metal prevents or hinders further deposition. The theory is particularly suitable for alloys containing nickel since nickel is very sensitive to such effects as is shown by the decrease in nickel content of nickel alloys when relatively small quantities of addition agent are added to the bath[29-30]. Accordingly, such alloys should show the most anomalous behaviour and in practice this is seen to be the case[4].

The mechanism for the induced codeposition of both tungsten and molybdenum with the iron-group metals has been fairly extensively stud ied and has resulted in the formation of several hypotheses. Most of these relate to both alloy systems although specific work has been carried out mainly on the cobalt-tungsten alloy system. There are one or two theories however which exist to explain certain aspects of the codeposition of molybdenum alloys alone but these either relate to specific solutions which are not of interest (i.e. pyrophosphate bath of Case and Krohn[31] or suffer the same limitations of cobalt-tungsten hypotheses (i.e. oxide formation theory of Ernst and Holt[32]).

The first hypothesis for induced codeposition is that the induced metal requires special surface conditions to enable it to deposit. This assumes that the reluctant metal ions cannot discharge on a tungsten surface but will discharge on the surface of an iron-group metal with relative ease. Holt and Vaaler[19] proposed that the alloy deposited in layers of iron-group metal and tungsten thereby producing the laminated structure characteristic

of this alloy system. This hypothesis is easily disproved however as x-ray examination shows the alloys to be solid solutions and not mixtures of two metals. It has also been proposed that tungsten will not deposit by itself due to the low overvoltage of hydrogen on tungsten and that the surface of the tungsten alloy has a sufficiently high overvoltage to allow the codeposition of tungsten. This hypothesis is again easily disproved as it is found that the cobalt-tungsten alloy has a lower overvoltage than either of its parent metals. There are several hypotheses which explain the phenomenon by referring to the iron-group metal as a 'catalyst' for the deposition of the tungsten or that the alloy has a favourable electronic structure for the deposition of tungsten[33]. These theories however have no experimental supporting evidence and therefore merely restate the unknown quantity in different terms.

The formation of complex ions of the iron-group metal and tungsten have also been postulated but polarographic studies by Holt and Vaaler[19] and Clark and Lietzke[34] have shown that this type of complex does not form.

A further hypothesis is the existence of a film of tungsten oxide on the cathode. This according to Glazunov and Jolkin[35] is then reduced to tungsten by atomic hydrogen, the iron-group metal acting as a catalyst. A cathode film was also postulated by Nielsen and Holt[25] who envisaged a semipermeable membrane of tungsten compounds over the cathode. The bath employed was an acid type for depositing nickel-tungsten alloys. The membrane allowed hydrogen atoms through to discharge when only tungsten

ions were present in the bath, thus explaining why tungsten will not deposit from aqueous solution, but was disrupted by the iron-group metals leading to the codeposition of tungsten.

The above theory and others which postulate on oxide membrane do not explain why tungsten alone cannot be deposited from an alkaline solution (in which the oxide is soluble) or why tungsten cannot be deposited readily on a stirred mercury cathode[36] (on which an oxide film does not form).

The most widely held hypothesis [15,22,23,37] for induced codeposition is based on the theory that the induced metal will not deposit from aqueous solutions because its deposition potential is too negative. The formation of a solid solution alloy with the iron-group metals is said to lead to a decrease in free energy sufficient to shift the deposition potential of tungsten or molybdenum to a more noble value. The main objection to this mechanism of induced codeposition is that it requires a very large shift in the deposition potential of tungsten and therefore a large decrease in free energy during formation of the alloy. Such large changes in free energy do not take place according to Sherfey and Brenner[38] who studied the heats of solution of electrodeposited cobalt-tungsten and nickel-tungsten alloys. A further argument put forward by Brenner[2] is that in the individual codeposition of tungsten the tungsten is always deposited preferentially as the percentage tungsten in the deposit is higher than the percentage tungsten metal in the bath. This is not in agreement with the supposition that the tungsten has a

deposition potential too negative to allow it to deposit alone as normally the more noble metal deposits preferentially. It could be reasoned that a mechanism similar to anomalous codeposition also occurs in induced codeposition but Brenner concludes that this cannot be so due to the positioning of the current density-cathode potential curves. In the case of true anomalous codeposition in the zinc-nickel system the deposition potentials of the alloys are more negative than the nickel whereas in the tungsten-nickel system the deposition potentials of the alloy are more positive than those of the nickel.

The hypothesis of Brenner[2], which he terms Transfer Polarisation, seems to offer the most comprehensive answer yet available concerning the mechanism of induced codeposition particularly as the bath conditions may be either acid or alkaline for its application. The Brenner hypothesis postulates that the energy of polarisation of the inducing element provides the activation energy required for the deposition of the reluctant metal ion. This theory may be used to explain several practical observations of alloy plating systems which other hypotheses are unable to do. The fact that there appears to be a limit to the amount of reluctant metal that can be obtained in the deposit is shown by the work of Holt and Black[24] and Ernst et al.[39] With increasing concentration of reluctant metal in solution the percentage reluctant element present in the deposit does not increase to 100% but tends to reach a limiting value. This effect may be explained using Brenner's hypothesis on the basis that as the codeposition of the reluctant element requires energy

supplied by the inducing metal then this is likely to occur on a one to one basis. A maximum of one atom of reluctant metal may therefore be discharged for each atom of inducing element thereby involving a maximum of one electron in the discharge of the reluctant metal. Therefore as only half of the current may be used for depositing the reluctant metal a limit is placed on the quantity of reluctant metal that may be deposited. This hypothesis may also be used to explain the fact that the reluctant metal is deposited preferentially in this type of alloy system. For example if the metal ratio of inducing element to reluctant element in the bath is considered it must be large for successful deposition of these alloys. Therefore if the current density is greater than the limiting current density for the reluctant ions but not greater than the limiting current density of the inducing ions a larger number of reluctant ions than inducing ions reaching the cathode would be activated. The rate of discharge of reluctant metal therefore would be greater than that of the inducing metal to give preferential discharge of the reluctant metal.

Although this hypothesis may be used to explain most of the phenomena observed in induced codeposition it cannot be used to explain the more positive positions of the current density – cathode potential curves for the alloys as compared to the individual iron-group metals. However it is thought by Brenner, from the data of Hoar and Bucklow[23,33], that this positive shift is accounted for by the overvoltage of the alloys as compared to the individual elements. Hoar and Bucklow[23,33] found that

the hydrogen overvoltage on the tungsten alloys was lower than that of the iron-group metals.

3.2 The Effects of Plating Variables on Alloy Baths of the Anomalous and Induced Codeposition Type

The effects of plating variables on the alloy systems used in this work have been studied by several workers. The following discussion will be confined, where possible, to acid type baths and to the alloy systems under investigation.

3.2.1

The effect of the metal ratio of the bath

The effect of the metal ratio of the bath on the alloy content of the deposit from the anomalous codeposition of cobalt-nickel has been investigated by numerous workers but the results obtained were all very similar. Piontelli et al[3,5] using a sulphamate bath and Glasstone et al[6,7] using a sulphate bath found that small percentages of cobalt present in the bath resulted in a high percentage of cobalt in the deposit. This effect is to be expected due to the anomalous nature of codeposition (i.e. the less noble cobalt deposits preferentially).

The concentration of alloying element in induced codeposition baths generally indicates that initially the baths behave in a similar manner to the anomalous type in that low metal ion concentrations of the reluctant metal in the bath produce higher concentrations of reluctant metal in the deposit. However as discussed in section 3.1. they eventually reach a limiting value for the percentage alloying element present in the deposit.

Typical examples of this are the iron-tungsten, cobalt-tungsten and nickel-molybdenum alloys deposited from acid solution by Holt and Black[24], Holt et al[40] and Seim and Holt[41] respectively.

3.2.2.

The effect of the total metal content of the bath.

The total metal content of the bath has little effect on the composition of alloys of the anomalous codeposition type. The work of Glasstone and Speakman[6] and Fink and Lah[8] show that in a simple sulphate bath for the deposition of cobalt-nickel alloys an increase in total metal content of approximately seven times produces only a slight increase in cobalt content of the deposit. The increase in concentration of the more readily deposited element in the deposit with an increase in the total metal ion content of the bath is typical of diffusion controlled systems due to the increase concentration gradient across the cathode film.

There appears to be no data concerning the effects of total metal content of the bath on the alloy concentration in the deposit for either cobalt-tungsten or cobalt-molybdenum deposited from an acid bath. The work of Roy et al[42] using an alkaline citrate bath to deposit a cobalt-tungsten alloy indicated that the tungsten content of the deposit increased with the total metal content of the bath. Similar results were produced by Franstsevich-Zabludovskaya and Zayats[43] for the deposition of nickel-tungsten alloys from an ammoniacal bath containing no organic hydroxyacid. The above results however can only be taken

as a guide to the possible effects which may be produced in the
solutions used in this work as there is such a great variation
in bath composition.

3.2.3

The effects of complexing agents

Although it is possible to produce cobalt-nickel alloys
from complex baths there is little point in doing so as simple
salt baths produce quite adequate results.   Consequently work
in this field is almost limited to the work of Sree and Rama Char[44,46]
on the deposition of the alloys from a pyrophosphate bath containing
ammonium citrate.   The effect of the complexing agents on the
bath was found to inhibit the deposition of cobalt with the result
that the metal ratio of cobalt-nickel in the deposit was almost
the same as in the bath over a wide range of current density.

The effects of complexing agents on induced codeposition
have again only been studied with respect to neutral or alkaline
baths and are therefore again only a guide to the possible effects
which may occur in this work.   The trends exhibited by the cobalt-
tungsten and nickel-molybdenum alloys investigated by Clark and
Holt[47] and Ernst et al[39] respectively are conflicting in nature.
Both baths contained citrates and ammonia or ammonium salts as complexing
agents and it was found by Clark and Holt[47] that an increase in
citrate produced a decrease in the tungsten content of the alloy
whereas Ernst et al[39] found the opposite to be true. These
results are characteristic of induced codeposition which frequently
shows anomalous results with changes in plating variables.

3.2.4

The effect of pH

The effect of pH on the anomalous deposition of cobalt-nickel is that the cobalt content of the deposit increases slightly at low pH values. This has been reported by Glasstone and Speakman[6,7] when investigating the sulphate bath and Piontelli and Patuzzi[3] when investigating the sulphamate bath. The largest increase in cobalt occurs below pH 2-3 and is accompanied by a decrease in cathode current efficiency. This effect was explained by Glasstone and Speakman[6,7] as being caused by disruption of the cathode film by hydrogen evolution due to the low cathode current efficiency experienced at these pH values.

The general effect of raising the pH in acid baths for the deposition of tungsten alloys is to increase the tungsten content a few percent as shown by the work of Holt and Nielsen[48] and Holt et al[40] when investigating the nickel-tungsten and cobalt-tungsten systems respectively. A citric acid cobalt-tungsten bath investigated by Clark and Holt[47] produced some interesting results as this bath is normally operated as a neutral solution. This alloy bath exhibited a maximum and minimum tungsten content in the deposit at approximately pH 7.0 and pH 3.0 respectively. Above pH 7.0 the tungsten content decreased and below pH 3.0 it increased. It is thought that these variations were caused by formation of various citrate complexes at the different pH values and by changes in the cathode current efficiency with pH.

3.2.5

<u>The effect of current density on the composition of the deposit</u>

In general the cobalt content of the nickel-cobalt alloys deposited from simple salt baths is found to decrease with increasing current density. However due to the anomalous nature of this system the effects of current density on the deposit may be divided into various current density levels. At very low current density levels Glasstone and Speakman[7] and Piontelli and Patuzzi[3] found that the alloy deposited normally (i.e. nickel deposited preferentially being more noble). Then at a higher range of current density (approximately 1-3 A/dm^2) the cobalt content in the deposit reached a maximum. This maximum was reached at approximately 1 A/dm^2 in the case of the sulphate bath of Glasstone and Speakman[7] and at approximately 3 A/dm^2 in the case of the sulphamate bath of Piontelli and Patuzzi[3]. These results show that the deposition of the alloy is initially normal and that anomalous deposition is only fully achieved at a particular current density. At higher current densities (i.e. 2-6 A/dm^2) the decrease in cobalt content mentioned above takes place. This is due to depletion of cobalt ions in the cathode diffusion layer causing the system to come under diffusion control. This current density range was investigated by Young and Struyk[30] (chloride bath) and Young and Egerman[49] (sulphate bath). If the current density was increased further the alloy composition curves became almost flat as shown by Young and Struyk[30]. This is important practically as it means that irregularly shaped objects may be coated with a uniform alloy composition if a sufficiently high current density is employed.

The relationship between current density and the composition of the deposit for the induced codeposition of tungsten and molybdenum varies with the type of bath employed. In general an increase in current density will reduce the percentage of reluctant metal present in the deposit. This is true of all of the alloys deposited from acid type baths, as reported by Holt and co-workers[24,40,41,48] when depositing tungsten and molybdenum with iron, cobalt and nickel, and most of those obtained from alkaline baths. Usually the decrease in alloying element in the deposit was fairly small (i.e. approximately 8% drop in molybdenum content between 2-22 A/dm^2 for the nickel-molybdenum alloy of Seim and Holt[41], 0.4% drop/ $1A/dm^2$) but there were two notable exceptions to this. The work of Holt et al[40] on cobalt tungsten alloys showed a drop in tungsten content of approximately 5% between 1-3 A/dm^2 (2.5% drop/$1A/dm^2$) and Holt and Black[24] found a drop in tungsten content in the iron-tungsten system of 22% between 1-10 A/dm^2 (2.2% drop/$1A/dm^2$).

3.2.6

The effect of bath temperature on the composition of the deposit

The effects of raising the bath temperature on anomalous deposition are not consistent. In the cobalt-nickel alloy system, as with other alloy systems of the anomalous type, there are two conflicting effects:-

1. Increasing the temperature, slightly relieves the polarisation of anomalous codeposition thereby increasing the nickel content of the deposit.

2. Increasing the temperature increases the diffusion rate of metals ions and replaces cobalt ions in the diffusion

layer at a faster rate leading to an increase in cobalt content of the deposit.

In consequence it is not possible to predict which effect will predominate in baths of this type. The relationship is further complicated by the fact that there is a complex interaction between current density and temperature as shown by Glasstone and Speakman[7]. Their work using an acid sulphate bath containing 10% cobalt metal showed that if the current density were greater than 1.3 A/dm^2 the cobalt content of the deposit increased with increasing temperature but at a current density of less than 0.3 A/dm^2 the opposite was the case. This behaviour is obviously very closely related to the change from normal to abnormal codeposition associated with the current density as outlined in section 3.2.5. The effect of raising the temperature appears to increase the current density at which the changeover takes place.

The relationship of bath temperature and alloy content for induced codeposition is surprisingly constant in view of the inconsistencies normally associated with these systems. In general a rise in temperature leads to a slight increase in alloy content of the deposit as would be expected from diffusion theory. This effect has been reported by Holt and Black[24] when depositing cobalt-iron alloys from an acid bath. Work by Brenner et al[50] on cobalt-tungsten alloys from an alkaline citrate bath and Lietzke and Holt[51] on iron-tungsten alloys from an alkaline citric acid bath also confirmed this observation. In addition to the slight increase in alloy content a rise in temperature also improved the quality of cobalt-tungsten electrodeposits as reported by Gol'tz

and Kharlamov[20] but had no noticeable effect on the quality of cobalt-molybdenum deposits obtained by Ernst et al[39].

The data outlined in the above sections illustrates the unpredictability of certain of the plating variables on the codeposition of alloys from the systems under investigation. The anomalous deposition of cobalt-nickel has been studied extensively due to its commercial use for many years and therefore the behaviour of the alloy deposition is better understood. The induced codeposition of tungsten and molybdenum however, particularly from the acid type bath, shows very unpredictable behaviour. This is undoubtedly due to the little work which has been carried out on these baths which does not enable any clear trends to be distinguished. In many cases the remarks on alloy behaviour of acid type baths stated above only relate to one or two solutions and therefore may not be true in the general case. If more clearly defined behaviour trends had been established previously there would have been no need to carry out certain aspects of the work undertaken. However this is an inevitable consequence of limited theoretical and practical knowledge.

3.3 Previous Bath Formulations for the Electrodeposition of Cobalt-Nickel, Cobalt-Molybdenum and Cobalt-Tungsten Alloys

Cobalt-nickel alloy electrodeposits have been in commercial use for about 30 years as this alloy was one of the first successful methods of depositing 'bright-nickel' coatings when used in conjunction with either nickel formate[52] or nickel formate and formaldehyde[53]. Although the alloys have generally been

superceded by commercial bright nickel systems containing organic
brighteners interest is periodically revived in the alloys when
nickel is either in short supply or prohibitive in price.   Recent
work on this alloy for decorative purposes carried out by Mathieson
and Sedghi[54] was occasioned by such a shortage.   The alloy has
been successfully deposited from chloride[30], sulphate[6,7,49],
mixed chloride/sulphate[55] and sulphamate baths[3,56].   The most
recent work on this alloy system for electroforming purposes has
been carried out by Belt et al [1,56], McFarlen[57] and Wearmouth[58].
These investigators all used the sulphamate bath to produce alloys
over a wide range of compositions for engineering.applications.
These investigations illustrated that an alloy containing about
35% cobalt possessed the highest hardness and greatest strength.
The bath used by McFarlen[57] was the conventional sulphamate bath
containing 75g/l nickel and cobalt sulphamate whereas that employed
by Belt et al [1, 56] and Wearmouth[58] was the concentrated bath
based on the 'Ni-speed'* electrolyte (600g/l nickel sulphamate.)
The deposits obtained by McFarlen[54] gave slightly higher strengths
than those obtained by Belt et al[1] and reached a maximum at
38.5% cobalt.   This composition is very close to the composition
found by Belt et al[56] to give the highest hardness.   The work
of Wearmouth[58] is interesting as it is mainly a study of electro-
forming applications for the cobalt-nickel alloy solutions developed
by Belt and co-workers [1,56].   This work will be discussed in
more detail in section 4.

*Trade name of the International Nickel Co.Ltd.

Previously formulated baths for the deposition of cobalt-molybdenum and cobalt-tungsten have been both acid and alkaline. The work on cobalt-molybdenum alloys was commenced in 1949 and has been undertaken largely by three research groups led by Holt, Frantesvich and Krohn. Simple acid salt baths for the deposition of cobalt-molybdenum alloys were studied by Brenner and Riddell[59]. These systems were based on the cobalt alloy baths of Holt and co-workers[40,48] and contained the cobalt as sulphate or chloride and the molybdenum as molybdate. All of the baths tried produced very unsound deposits and suffered from chemical reaction of the molybdate with the Iron-group metal anode.

Acid baths were again used by Seim and Holt[41] when depositing the alloy from a citrate bath. They obtained alloys containing up to 3.0% molybdenum from a bath containing 1.9g/l molybdenum metal. However the cathode current efficiency of the bath was 27% and the deposits obtained were only several microns thick. Brenner and Riddell[59] have used baths based on tartaric and hydroxyacetic acid. They failed to produce satisfactory deposits of cobalt-molybdenum alloy from the tartrate bath but produced alloys containing up to 30% molybdenum from the hydroxy-acetic acid bath. The baths again suffered from low cathode current efficiency and Brenner reported that the quality of the deposits deteriorated with continued operation of the bath. There have been several other attempts to deposit cobalt-molybdenum alloys from other types of acid bath but they have all suffered from low cathode current efficiency and relatively low alloy content.

Work has also been carried out on the cobalt-molybdenum alloy system using alkaline baths. These fall into two categories; the ammoniacal citrate and tartrate baths and the pyrophosphate bath. Work has been carried out on the ammoniacal baths by Frantsevich-Zabludovskaya[60] and Ernst et al[39]. The solutions employed all contained free ammonia as this was considered essential but both Frantsevich-Zabludovskaya[61] and Ernst et al[39] considered the presence of ammonium ions in the bath detrimental. The current efficiency of the baths was fairly good at between 60-70% and alloy contents of up to 35% were obtained by Ernst et al[39]. These alloys were reported as being fairly dense but did contain inclusions. However Case and Krohn[31] stated that deposits obtained from both citrate and tartrate baths were dark and non-adherant.

The pyrophosphate bath was developed by Myers[62] and later investigated by Krohn et al[31,63]. The bath used pyrophosphate for complexing the cobalt and sodium bicarbonate for adjusting the pH to approximately pH 8.0. The cobalt-molybdenum baths of Myers[62] and Krohn and Brown[63] produced alloys containing high percentages of molybdenum (up to 60%) but contained up to 15% non-metallic inclusions.

A range of carbonate baths for the deposition of cobalt-molybdenum alloys is the subject of a patent held by Brenner and Burkhead[64]. These baths were based on the formation of a complex cobalt carbonate using potassium carbonate as the addition agent. They operated at high temperatures (up to $100^\circ C$) and had cathode current efficiencies of up to 78%. The deposits obtained from them

contained as much as 25% molybdenum but they were very cracked and mechanically weak. They also contained non-metallic inclusions.

The electrodeposition of cobalt-tungsten alloys has mainly been reported using alkaline baths of various types. There has been very little work carried out using acid baths except for that of Holt et al[40]. The bath used by Holt was essentially a sulphate bath (250g/l cobalt sulphate) containing solium tungstate (3.6g/l). The bath operated at pH 3-5 had a cathode current efficiency of 95% and produced alloys containing between 5-10% W. The deposits obtained however were brittle and contained non-metallic inclusions which increased to give a non-metallic coating if the sodium tungstate concentration was increased above a few grammes per litre. Brenner et al[50] attempted to obtain better deposits from the acid bath by adding the tungsten in the form of borotungstate, phosphotungstate and fluotungstate but the results obtained were no better than those of Holt et al[40].

Early work on the deposition of cobalt-tungsten from alkaline baths was carried out by Fink and Jones[13] and Holt and co-workers[65,66] using alkaline carbonate baths but the deposits obtained from these baths were very poor. Later developments were therefore concentrated on the use of ammoniacal baths of similar composition to those used for the deposition of cobalt-molybdenum alloys. One of the first successful tungsten alloy baths of this type (a nickel-tungsten bath containing no hydroxyacids) was formulated by Gol'tz and Karlamov[20]. They established that the bath must contain excess ammonia (as for the cobalt-molybdenum

baths) and also that ammonium salts in the bath were also essential
(in marked contrast to the cobalt-molybdenum baths of this type).
These workers also noted that high bath temperatures favoured
sounder deposits. This bath was later improved by various workers
using hydroxyacid additions to the baths giving the familiar
citrate and tartrate baths. The citrate and tartrate baths of
Brenner et al[50] both operated at pH 9.0 and 95°C. The current
efficiency was about 90% and the deposit contained 20-23% tungsten.
The alloys could be plated to a thickness of about 0.1mm. if low
concentrations of alloying element could be tolerated but contained
non-metallic inclusions giving rise to brittleness. The deposits
obtained by Brenner et al[50] were typical of those obtainable
from this type of bath. The thickness of the deposit obtained
depended upon the alloy content and some of the alloy baths
employed would only give very thin coatings due to low cathode
current efficiencies (of the order of 20%). Other citrate baths
employed by Clark and Holt[47], Hoar and Bucklow[23] and Roy et
al[42] gave similar results but the coatings were very thin in
most cases. The bath used by Hoar and Bucklow[23] used an
interrupted current cycle of 1 second on 1.5 seconds off.

The survey of bath formulations outlined above for the
deposition of cobalt-tungsten and cobalt-molybdenum alloys shows
that none of the baths could be operated on a commercial scale.
The acid systems for the deposition of cobalt-tungsten have failed
to produce a deposit of sufficient soundness to be of any practical
importance and many of the alkaline baths for the deposition of
both alloys suffer from non-metallic inclusions and extreme

brittleness. Of the two alloy systems the baths formulated for the deposition of cobalt-tungsten appear to produce the sounder deposits as it appears that fairly thick coatings have been obtained from them. However the drawback of these baths is that they are required to have an excess of ammonia present in the bath at temperatures approaching $100^{\circ}C$. Such operating conditions could not be tolerated on a commercial scale due to both fume hazards and high operating costs. In order to make the plating of these alloys a practicable proposition a suitable bath is required which operates at normal plating temperatures and conditions, produces a sound coherent deposit, contains reasonably cheap complexing agents and does not require constant attention. For these reasons an acid type bath operating at a fairly low temperature was chosen for this work and the complexing agent employed, sodium heptonate, is cheap and easily obtainable.

4.   THE PREVIOUS USE OF ELECTRODEPOSITED DIE COATINGS

The use of nickel to electroform dies operating at fairly
low temperatures and stresses has been practiced for some time[67].
Recently work by Belt et al[1,56] has shown that cobalt additions
to the nickel sulphamate bath give a range of cobalt-nickel alloys
having superior properties to pure nickel electrodeposits at
elevated temperatures.   These alloys have been used by Wearmouth
and Belt[58] to produce zinc base die-casting dies.   These dies have
been employed only for limited production runs but it appears that
they have performed at least as well as steel dies used for the
same period.

The chromium plating of carbon steel forging dies is
confined largely to the Sheffield cutlery industry in this country
and has been practiced for many years.   This process is used by
several European firms for hot forging dies and is also employed
in Japan.   However quantitative data on the performance of coated
dies has not been published and therefore it is impossible to assess
the improvements obtained by using such dies.   It has been found
that not all die shapes are suited to the coating process.   In
general if the die contains large flat areas with a relatively
shallow sink and small changes in cross-sectional thickness then
chromium plating can give a substantial increase in die life.
However if the die is more complex and particularly if it contains
a projection (i.e. a central 'peg' as in a gear blanking die)
then the plating can drastically reduce the life below that of the
unplated die.   In such cases massive cracking at the projections
resulted in failure of the die in service.   It is possible that

cracks, which are always present in chromium deposits, act as stress raisers thus causing severe cracking of the die.

The cobalt alloys of molybdenum and tungsten although appearing to have desirable properties for this application (i.e. hot hardness[68]) have hardly ever beem used commercially. The only use reported is in a recent patent by Prosser[69] for the use of cobalt-tungsten alloys to improve the life of forging dies made from a 5% chromium die steel. The application of a coating to such a relatively expensive and inherently wear resistant steel is somewhat puzzling. The solution used to deposit the alloys is of the alkaline citrate type and is based on another patent held by I.C.I. (Australia) Ltd[70] which describes the use of tungsten and molybdenum alloys of the iron-group metals for coating titanium fuel cell elements. It is claimed by Prosser[69] that the bath gives good deposits which substantially enhance the wear resistance of the forging dies.

Although the above investigations were the only commercial applications found in which cobalt-alloys had been successfully used as die materials they indicate that a large potential market exists for an easily deposited heat and wear resistant alloy. The work of Belt et al[1] has shown that the cobalt-nickel system contains some useful alloys and therefore this alloy system was chosen as one to be investigated under the more arduous conditions of hot forging. Similarly the Prosser[69] patent indicated that cobalt-tungsten coatings could be successfully applied to hot forging dies.

5. PREPARATION OF PLATING BATHS

5.1 Sulphate Baths of Cobalt, Cobalt-Nickel and Nickel

The sulphate bath for the deposition of cobalt, nickel/ cobalt or nickel is well known being based on the Watts bath ($240g/l$ Ni SO_4. $7H_2O$, $20g/l$ Ni Cl_2.$6H_2O$ and $20g/l$ H_3 BO_3). The alloy plating baths were prepared by adding the appropriate quantity of cobaltous sulphate solution ($300g/l$ Co SO_4.$7H_2O$, $28g/l$ Na Cl and $40g/l$ H_3 BO_3) to a Watts type nickel solution containing $300g/l$ Ni SO_4.$7H_2O$, $28g/l$ Na Cl and $40g/l$ H_3 BO_3. both solutions were purified before use by treating with $20g/l$ activated carbon to remove organic impurity and by plating at low current density ($0.5 - 1.0A/dm^2$) for several hours to remove metallic contamination.

As cobalt is preferentially deposited in the presence of nickel a calibration curve of concentration of cobalt in solution against % cobalt in the alloy deposit was required. This was constructed initially by formulating solutions which would give alloy deposits containing approximately 5-10% Co, 10-15% Co, 25-30% Co and 35-40% Co. The data for this was obtained from a paper by Belt[1] et al. This paper was concerned with cobalt-nickel alloys obtained from a sulphamate bath but it was considered that the two solutions would probably behave in a very similar manner. These solutions were used to deposit alloys onto brass plates which were then sectioned and the alloy content determined by electron probe microanalysis. Alloys containing higher cobalt contents than these were deposited on die sets and again analysed

by electron probe microanalysis using samples obtained from the die after forging. The cobalt content of the solutions used to produce these die sets was found using an optical spectrophotometer. The results obtained enabled the construction of the graph shown in Fig.1.

5.2. Sulphamate Baths of Cobalt-Nickel and Nickel.

The sulphamate baths for alloy deposition of cobalt-nickel and nickel were prepared in a similar manner to the sulphate ones; that is by adding an appropriate quantity of cobaltous sulphamate to a nickel sulphamate bath containing 600g/l nickel sulphamate, 10g/l Ni $Cl_2.6H_2O$ and 40g/l H_3BO_3. However it was necessary to produce the cobaltous sulphamate by allowing sulphamic acid to react with cobaltous carbonate since cobaltous sulphamate could not be purchased. The sulphamic acid was dissolved in the minimum quantity of water at $65^{\circ}C$ (this was approcimately 600g/l) and neutralised to pH 4.0 with cobaltous carbonate according to the reaction:-

$$2NH_2 SO_3H + Co Co_3 \rightleftharpoons Co(NH_2 SO_3)_2 + CO_2 + H_2O \qquad (iii)$$
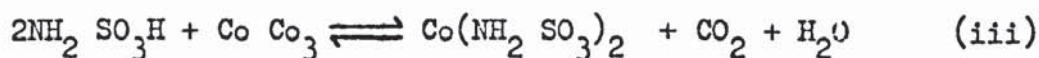
The solution was filtered to remove excess carbonate and then treated with 20g/l activated carbon. It was filtered again and plated for 12 hours at low current density ($\frac{1}{2}$-1.0A/dm^2) using a pure cobalt anode.

The nickel sulphamate prepared from a commercially available concentrate was purified by activated carbon treatment and low current density plating out as for the sulphate baths.
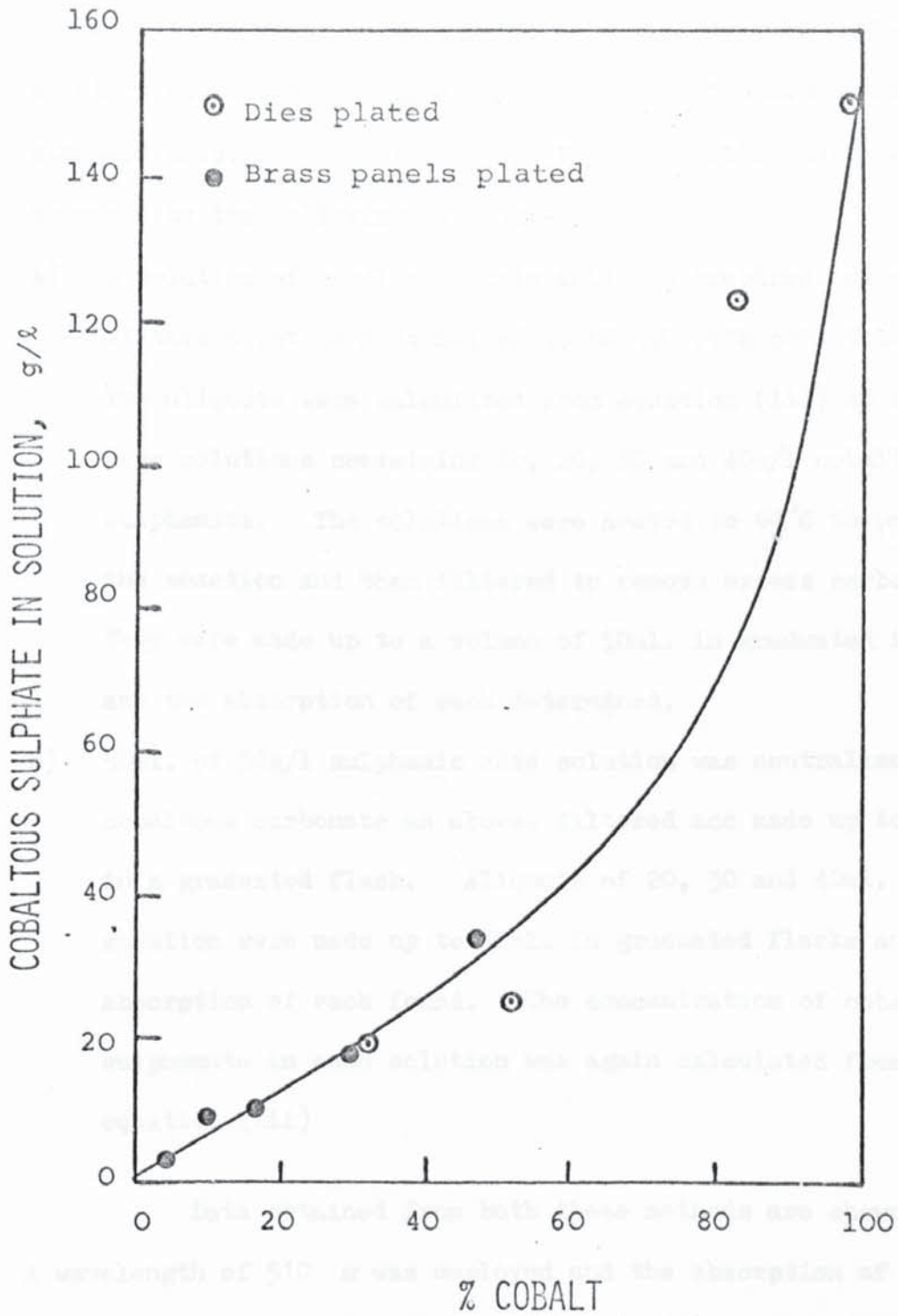
Fig.1.   Relationship between the concentration
          of cobaltous sulphate in solution and the
          percentage cobalt obtained in the deposit

The exact concentration of cobaltous sulphamate in solution was determined using an optical spectrophotometer. The standard solutions used to produce the calibration curve were prepared by the following methods:-

a) A solution of 50g/l sulphamic acid was prepared and aliquots of this solution neutralised to pH 4.0 with cobaltous carbonate. The aliquots were calculated from equation (iii) so as to give solutions containing 10, 20, 30 and 40g/l cobaltous sulphamate. The solutions were heated to 60°C to promote the reaction and then filtered to remove excess carbonate. They were made up to a volume of 50ml. in graduated flasks and the absorption of each determined.

b) 50ml. of 50g/l sulphamic acid solution was neutralised with cobaltous carbonate as above, filtered and made up to 100ml. in a graduated flask. Aliquots of 20, 30 and 40ml. of this solution were made up to 50ml. in graduated flasks and the absorption of each found. The concentration of cobaltous sulphamate in each solution was again calculated from equation (iii)

Data obtained from both these methods are shown in Fig.2. A wavelength of 510 m was employed and the absorption of the nickel sulphamate solution at this wavelength (0.19) was added to all readings.

Fig.3 shows the relationship between cobalt content in solution and percentage cobalt in the deposit. This graph includes results obtained by Belt et al[1] as well as those obtained in this present work.
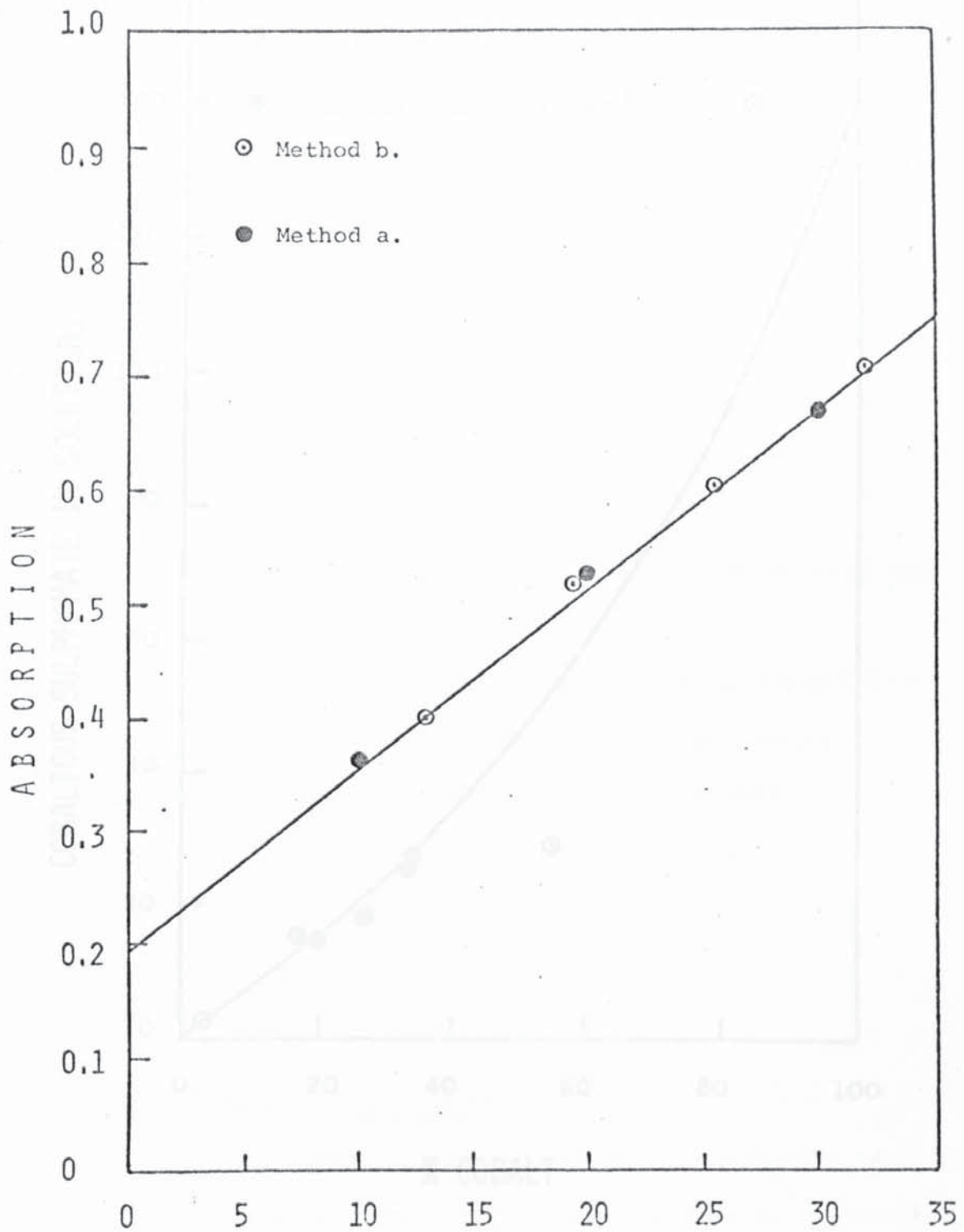
Fig.2. Calibration curve for the determination of
cobaltous sulphamate in nickel sulphamate
solution.
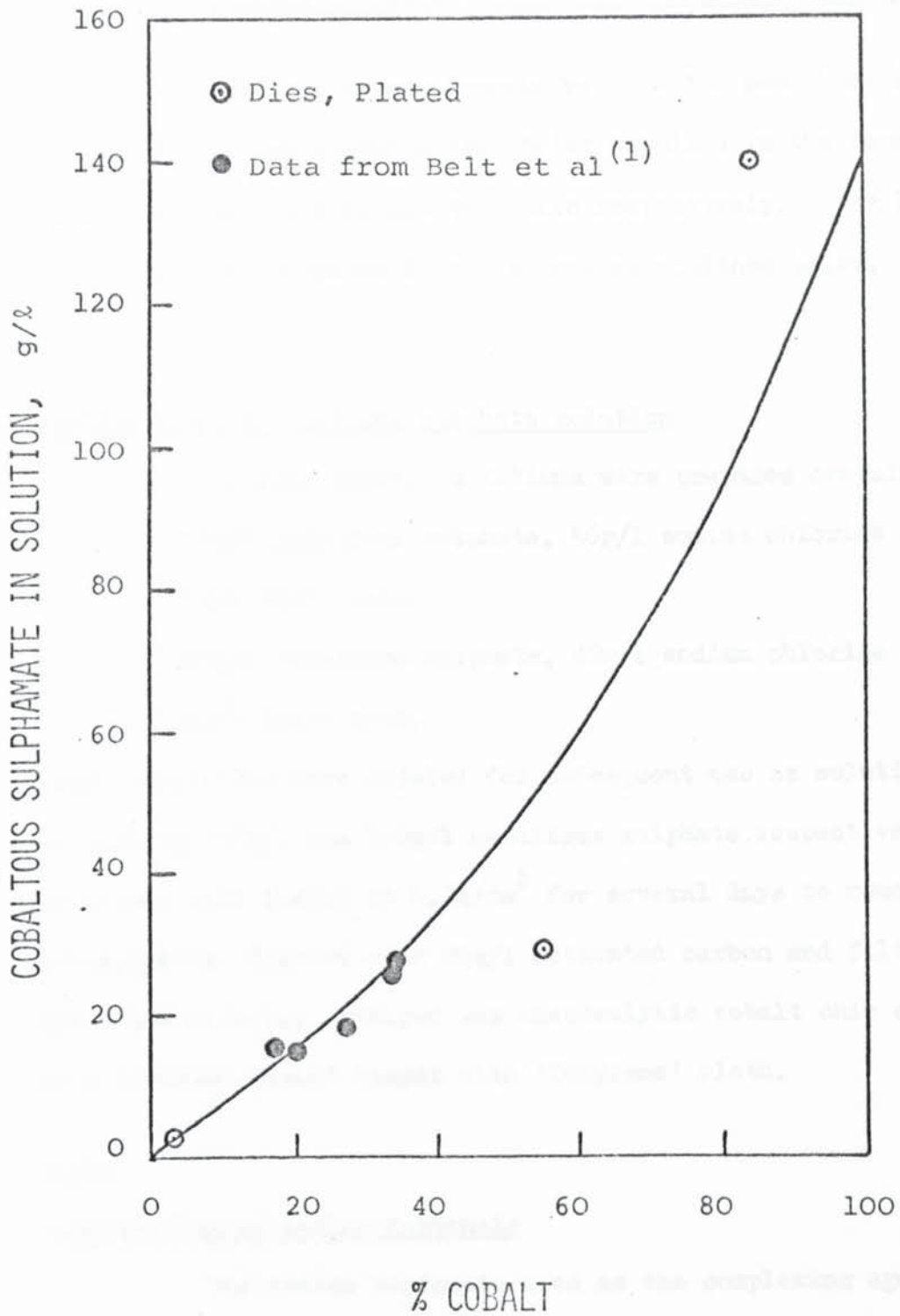
Fig.3. Relationship between the concentration of cobaltous sulphamate in solution and the percentage cobalt obtained in the deposit.

5.3   Complex Baths of Cobalt-Molybdenum and Cobalt-Tungsten

These baths were formulated from the same base solution, the molybdenum and tungsten ions being supplied in the form of sodium molybdate and sodium tungstate respectively. The basis electrolyte was prepared in two stages as outlined below.

5.3.1

Purification of cobaltous sulphate solution

Two concentrated solutions were prepared containing,

(i)   300g/l cobaltous sulphate, 56g/l sodium chloride and 80g/l boric acid.

(ii)   450g/l cobaltous sulphate, 42g/l sodium chloride and 60g/l boric acid.

(These solutions were diluted for subsequent use as solutions containing 150g/l and 300g/l cobaltous sulphate respectively.) The solutions were plated at $0.2A/dm^2$ for several days to remove metallic contaminants, treated with 20g/l activated carbon and filtered. The anode material employed was electrolytic cobalt chip contained in a titanium basket bagged with 'Terylene' cloth.

5.3.2

Purification of sodium heptonate

The sodium heptonate used as the complexing agent in these baths also required purification and this was achieved by re-crystallisation of the salts. A super-saturated solution of sodium heptonate at $70^{\circ}C$ was prepared (approximately 1000g/l) and treated with 50g/l activated carbon. The solution was filtered and allowed to cool slowly producing pure crystals of sodium

heptonate.   The supernatent liquid was decanted and the crystals washed and dried.

The alloy baths were prepared from the above purified constituents plus appropriate general purpose reagent additions of sodium molybdate and sodium tungstate.

6. MANUFACTURE AND PLATING OF DIES

6.1 Die Manufacture

6.1.1

Flat Dies

The Electem No.5. die steel was purchased as 5.7 cm. diameter forged bar in the annealed condition. The manufacturer's chemical specification for this steel is given in Table 1. The bar was turned to 5 cm. diameter and discs, approximately 1.25 cm. thick, were sliced from this stock. The dies were then heat treated, to the manufacturer's directions, in batches of sixteen. They were first soaked for 50 minutes in a salt bath maintained at $840^{\circ}C$. This was followed by oil quenching and tempering for 20 minutes at $600^{\circ}C$. This heat treatment operation produced a tempered martensite structure having a hardness of between 388-411 H_v. The steel is widely used industrially in this condition. After tempering a random sample of four dies was taken and their hardness determined using a Rockwell machine. If the hardness was satisfactory the die sets were then turned to approximately 0.06 cm. oversize. The bulk of the excess material was machined from the working face to ensure the removal of any decarbonised layer which may have formed during tempering. Final machining, to approximately 0.025 cm. oversize, was carried out by surface grinding, a fine ground finish being applied to the working face. A Vickers hardness was then determined on the working face of each die before plating to ensure that the hardness was within specification.

TABLE I.   Chemical Composition of Electem No.5. Die Steel

Element	%
C	0.5 - 0.6
Si	0.3 max
Mn	0.5 - 0.8
S	0.04
P	0.04
Ni	1.25 - 1.75
Cr	0.5 - 0.8
Mo	0.25 - 0.3

6.1.2

Small shaped dies

These dies were machined from heat treated flat dies prepared as outlined in the previous section. The horizontal surfaces which were used as datum points for wear measurements were finely surface ground parallel to the back of the die. Machining allowances were made so that dies when plated and finish ground were 1.25 cm. thick.

6.1.3

Large shaped dies

The Electem 5 steel used to make these dies was purchased in the form of 8.3cm diameter forged bar supplied heat treated to a hardness of 388-411 H_v by the manufacturer. The dies were machined all over to a finished size of 5.1 cm. high x 7.6 cm. diameter. The die cavity was fine turned in a lathe and the surface finished by hand polishing with emery, diamond paste and jewellers rouge. The flash land was surface ground parallel to the back surface of the die.

6.2 Jigging of Dies for Plating

The two jigging techniques illustrated in Fig.4 were investigated prior to the plating of die sets in order to obtain the most favourable plate distribution. A die was plated, using each of these jigging techniques, for 3 hours in a Watts nickel solution after which a thickness survey was carried out using a B.N.F. coulometric instrument. The results obtained from this survey showed that the general thickness distribution was concave
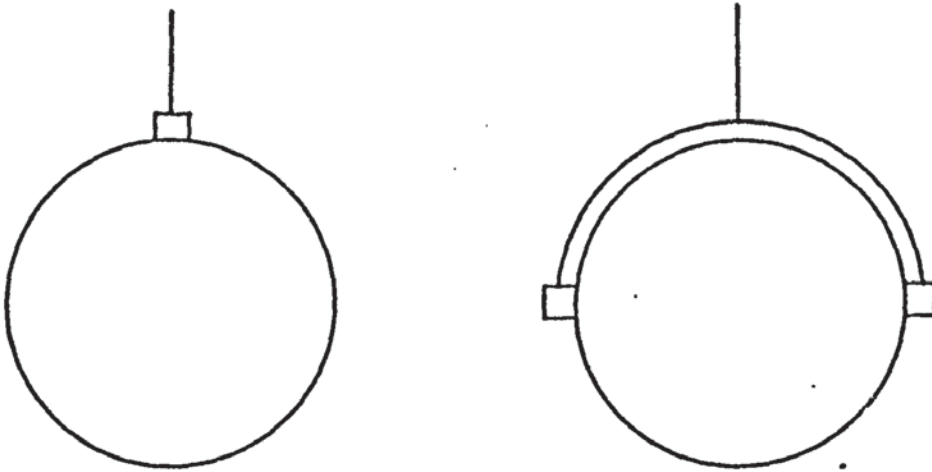
Fig.4. Single contact and double contact
jigging techniques used for plating
flat dies.

in nature. The areas near to the jigging points tended to give thinner deposits than at other edge areas and the deposit was thinnest at the centre of the die. On comparison of the two jigging procedures it was found that a slightly more even distribution was achieved with the two contact points but as this improvement was so slight a single contact point was used for all subsequent die plating in order to simplify die manufacture.

6.3 Pre-Treatment of Dies

In order to obtain good adhesion of the plate to the substrate an etching operation in 50% sulphuric acid was included in the plating pre-treatment sequence. This cleaning cycle and etching treatment, which is shown below, was used on several types of die steel and produced good adhesion of the electrodeposit in all cases. However the chemical composition of the die steel had an effect on the etching time. This was as low as 45 secs. for carbon steel and up to 4 mins. for steels having high nickel and/or chromium contents. An etch time of between $1\frac{1}{2}-1\frac{3}{4}$ min. was required for Electem No.5.

Pre-electroplating sequence

1. Anodic treatment in hot commercial alkaline solution, $4A/dm^2$, $85^{\circ}C$.

2. Rinse in water.

3. Dip in hydrochloric acid solution, 50% V/V concentrated acid.

4. Rinse in water.

5. Anodic treatment in commercial cyanide solution; $4A/dm^2$; room temperature.

6. Rinse in water.

7. Dip in sulphuric acid solution, 20 % V/V concentrated acid.

8. Rinse in water.

9. Anodic etch in sulphuric acid solution, 50 %V/V concentrated acid, at 6.5 V (approx. 60A/dm^2) until the surface attained a light grey-white appearance.

10. Rinse in water.

11. Anodic treatment in commercial cyanide solution, 4A/dm^2; room temperature.

12. Rinse in water.

13. Dip in sulphuric acid solution, 20 % V/V concentrated acid.

14. Rinse in water.

15. Electroplate.

6.4   Plating of Dies and their Preparation for the Forging Test

6.4.1

Flat dies

The dies were jigged, the sides and back 'stopped off' with a suitable lacquer and plated for periods of between 6-8 hours to ensure that a deposit thickness of between 50-75 µm was obtained in the centre of the die.   This thickness was considered necessary as preliminary work carried out using a die plated with a 25 µm thick coating of Watts nickel had shown plate penetration over the entire wear area on completion of the 1000 billet forging test. However a 75 µm thick coating of Watts nickel completed the forging test with no plate penetration.

The concave nature of the electrodeposit, as mentioned in section 6.2., was removed by surface grinding. A completely

flat working face was required for the forging test. This was essential to allow the automatic billet feed mechanism to function correctly and to fix a datum surface for subsequent wear measurements. The surface grinding was carried out such that the least possible thickness of electrodeposit was removed from the centre of the die. The 0.025cm. oversize of the die was corrected at this stage by surface grinding the back of the die to obtain an overall die thickness of 1.25cm. A final 0.0005 cm. was then removed from the working face to give a fine ground surface for the forging test.

6.4.2

Small shaped dies

The plating of these dies was carried out in the same manner as that used for the flat dies. After plating the die cavity was hand polished with emery and jeweller's rouge. In order to detect the existence of plate build up on the inside edges of the die cavity trial forgings were made in lead. The dir surfaces were lightly smeared with oil and a lead billet hammered into the cavity. The die was then inverted to release the forging. If sticking of the lead forging occurred the die was re-polished and another lead forging made. This process was repeated until the forging fell from the cavity when the die was inverted.

The flat surfaces of the dies were surface ground to a fine finish, removing as little of the electrodeposit as possible.

6.4.3

Large shaped dies

The plating procedure for these dies was again the same as that used for the flat dies. The polishing however could not be done by hand due to the size of the die therefore build up of electrodeposit at the edge of the cavity was removed using a universal grinding machine. This ensured an exact taper to the cavity sides and therefore lead test forgings were not required to check for sticking in the die. The inside of the die cavity was then polished with 600 grit wet and dry paper followed by jewellers rouge and the flash land surface ground parallel to the bottom face of the die.

7. EVALUATION OF PLATING BATHS AND DEPOSITS

7.1   Hull Cell Tests

The standard Hull cell technique was employed, brass
panels 7.5 cm x 10 cm being plated in a perspex cell immersed
in a water bath to maintain the temperature of the plating bath
at 55°C.   Vigorous air agitation was used and 1A was passed
through the cell for 15 min. unless otherwise stated.   The
cleaning sequence given below was used and Hull cell panels were
plated in each solution over the pH range pH 1-5.

Cleaning sequence

1.   Soak clean in hot alkaline cleaner, $1\frac{1}{2}$ min.

2.   Water rinse.

3.   Cathodic treatment in cold cyanide solution, $1\frac{1}{2}$ min 4A/dm^2.

4.   Water rinse.

5.   Acid dip (20% V/V H$_2$SO$_4$).

6.   Water rinse.

7.   Electroplate.

7.2   Cathode Current Efficiency of Alloy Plating Baths

The cathode efficiency of the baths was determined by
plating a brass test panel, 5cm x 5cm in series with a similar panel
immersed in an acidified copper sulphate solution acting as a copper
coulometer.   The copper sulphate bath contained 150g/l Cu SO$_4$.7H$_2$O
and 50g/l H$_2$SO$_4$.   The test panels were electrolytically cleaned
in the same way as the Hull cell panels, dried in acetone and
weighed.   They were then cleaned once more and plated for 20 min.
at 4A/dm^2 and 55°C.   Air agitation was used in both the alloy

bath and the copper coulometer. After plating the panels were washed thoroughly in hot water, dried in acetone and re-weighed. The difference in the weights gave the quantity of copper and the quantity of cobalt alloy deposited by the same current. The weights of each element present in the alloy deposited were calculated from the chemical analysis and the 'effective' cathode efficiency of each of these elements found using the method described by Brenner[2].

The following assumptions were made when calculating the efficiency:-

a) The copper bath was 100% efficient.

b) The total current was used to deposit or liberate the three relevant elements cobalt, molybdenum/tungsten and hydrogen, that being used to liberate hydrogen representing the wasted energy.

c) 1 Faraday (F) deposits the gram equivalent weight of each element which is:-

$$\frac{63.5}{2} = 31.77 \text{ grms} \quad \text{copper}$$

$$\frac{58.94}{2} = 29.97 \text{ grm} \quad \text{cobalt}$$

$$\frac{95.95}{6} = 15.97 \text{ grm} \quad \text{molybdenum}$$

$$\frac{183.86}{6} = 30.64 \text{ grm} \quad \text{tungsten}$$

A valency of six was used for the molybdenum and tungsten as this was the valency state of the ions present in sodium molybdate and sodium tungstate.

If x coulombs are passed through the cell the weight of copper deposited will be:-

$$x \left(\frac{31.77}{F}\right) \ \text{grm} \tag{iv}$$

and the weight of cobalt deposited will be:-

$$x \left(\frac{29.97}{F}\right) \ \text{grm} \tag{v}$$

Now efficiency $= \dfrac{\text{Weight of cobalt deposited}}{\text{Theoretical weight of cobalt deposited}}$ (vi)

$\therefore$ % Efficiency of Cobalt $= \dfrac{\text{weight of cobalt}}{\text{weight of copper}} \times \dfrac{31.77}{29.97} \times 100$ (vii)

Similar equations may be constructed for molybdenum and tungsten and the total cathode efficiency of the alloy obtained by adding the efficiencies of the individual elements.

7.3   Measurement of Internal Stress

The technique of stress measurement chosen was based on the Hoar-Arrowsmith[71] principle. A commercial instrument of this type is not available therefore an instrument was constructed for this work, Figs.5-8. The particular advantages of this instrument over others which have been constructed are listed below:-

1. It is compact and self contained.

2. It can be operated in a fairly well lighted room.

3. The coils are partially submerged to reduce the unplated length from solution line to armature.

4. The armature can be attached quickly by plastic clips.

5. Robbers are incorporated to enable a uniform coating thickness to be deposited on the test strip.

The main disadvantage of the instrument is that agitation cannot be employed.
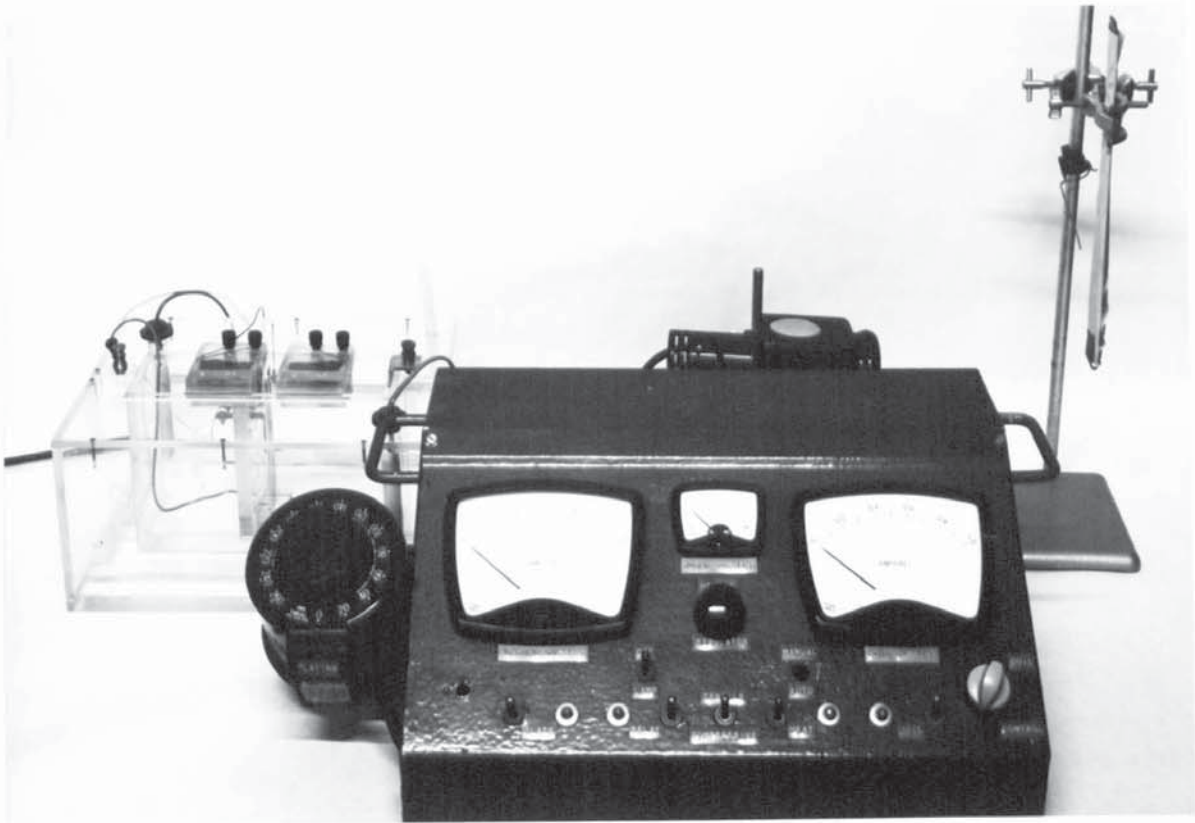
Fig.5.   General view of stress apparatus.
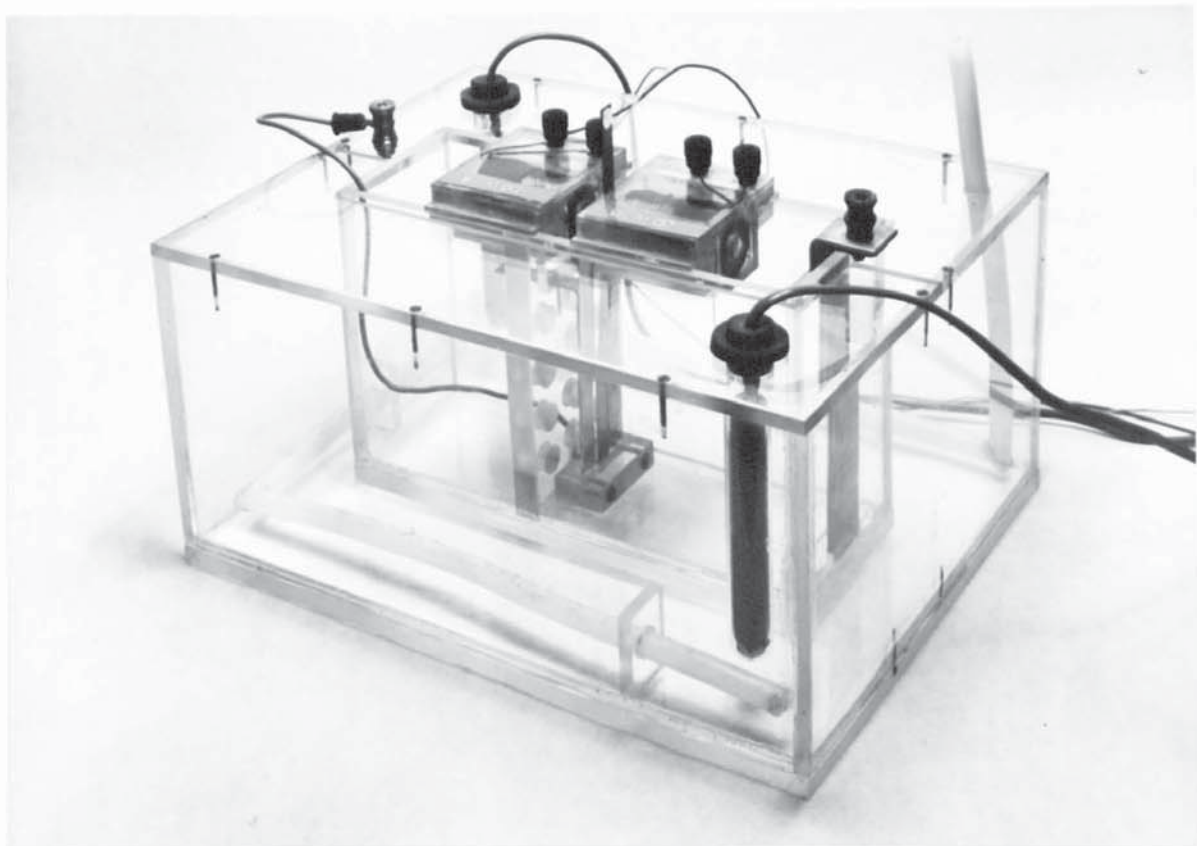
Fig.6.   Stress apparatus: water bath and plating cell.
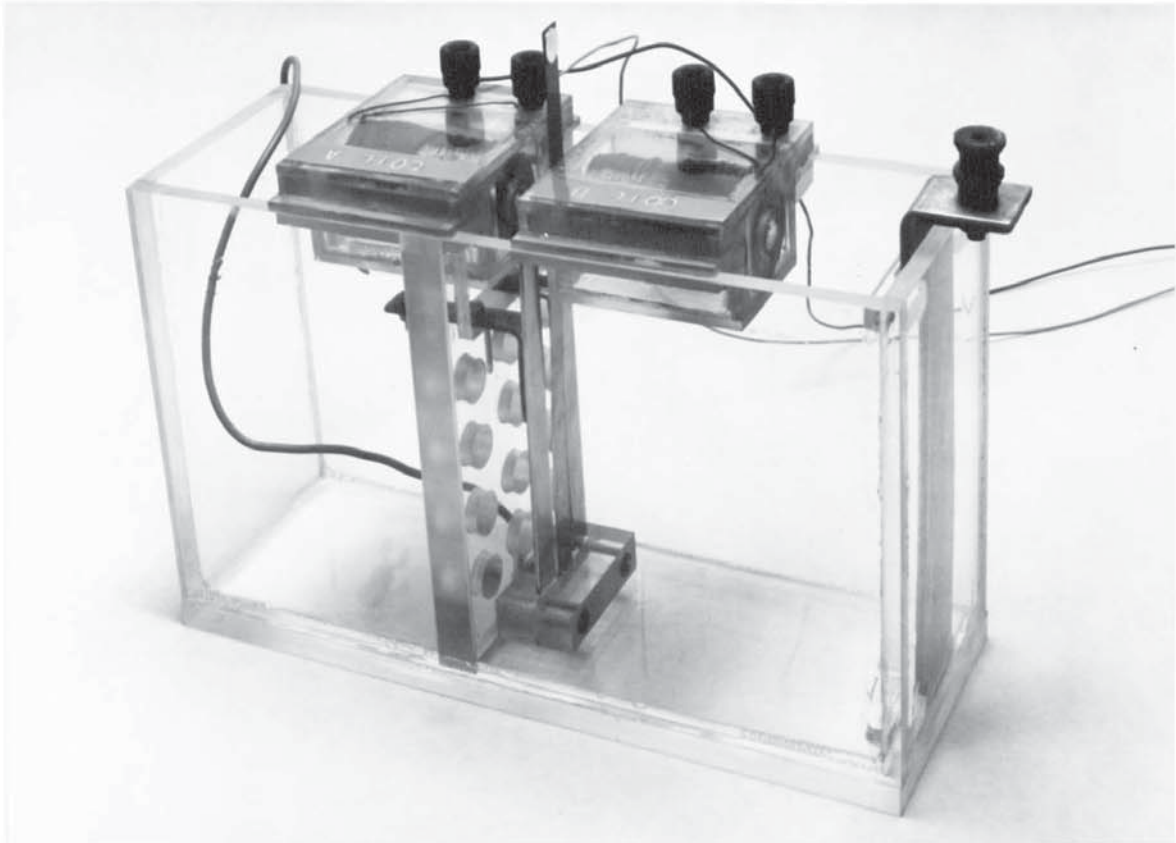
Fig.7.   Plating cell showing specimen and coils in position.
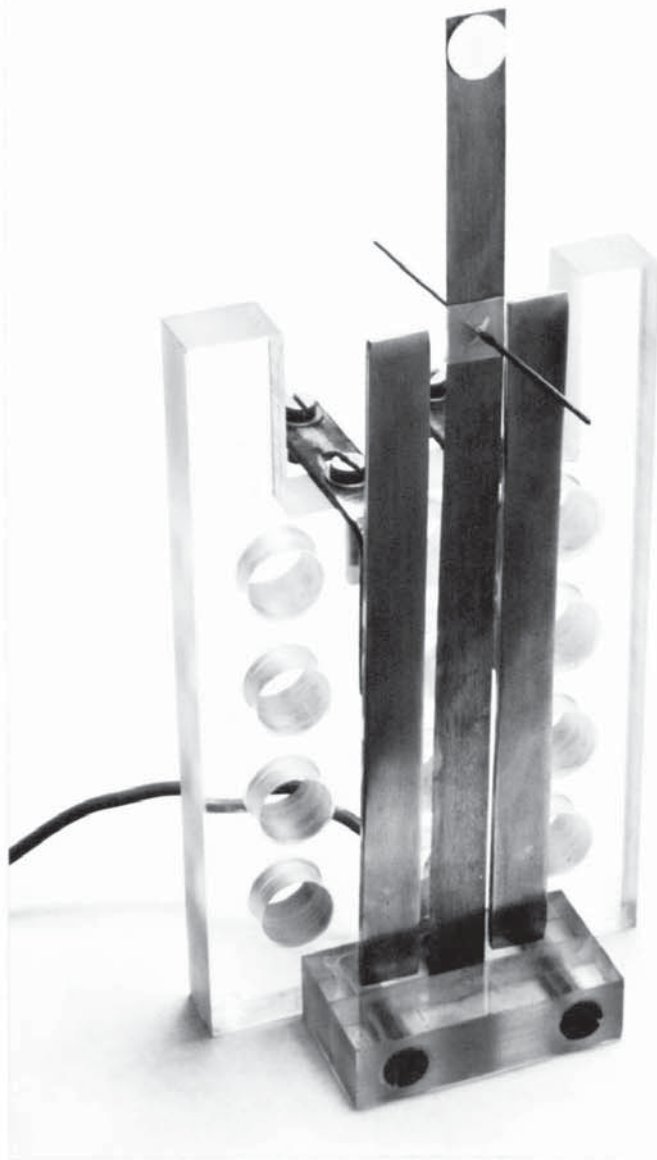
Fig.8.   Specimen jig showing the use of 'robbers'.

The principle of operation is that one side of a thin steel strip is plated at uniform current density. The strip is held in a jig at its base and bends into an arc under the influence of the stress in the deposit as it becomes thicker. A mirror attached to the top of the strip provides an optical lever which detects this bending. The optical lever is maintained in the 'null' position throughout the plating operation by the application of a restoring force. The restoring force is applied by means of a solenoid to a soft iron armature attached to the free end of the strip, Figs. 7 and 8.

The solenoid was calibrated using fractional gram weights so that the coil current applied could be converted to a restoring force, the calibration curve is shown in Fig. 9.

The strip material used was mild steel 0.01 cm. thick and it was cut into lengths 16cm. x 1.0cm. The front of each strip was prepared using a greased felt bob dressed with 240 grit emery followed by a sisal mop and a proprietary composition. Final polishing was carried out using a soft mop. The strips were then de-greased in acetone and given the following cleaning treatment:-

1. Anodic clean in hot alkaline cleaner, $4A/dm^2$.

2. Water rinse.

3. Acid dip (50% V/V H Cl).

4. Water rinse.

5. Anodic treatment in cold cyanide cleaner, $4A/dm^2$.

6. Water rinse.

7. Acid dip (20% V/V H_2SO_4).

8. Water rinse.
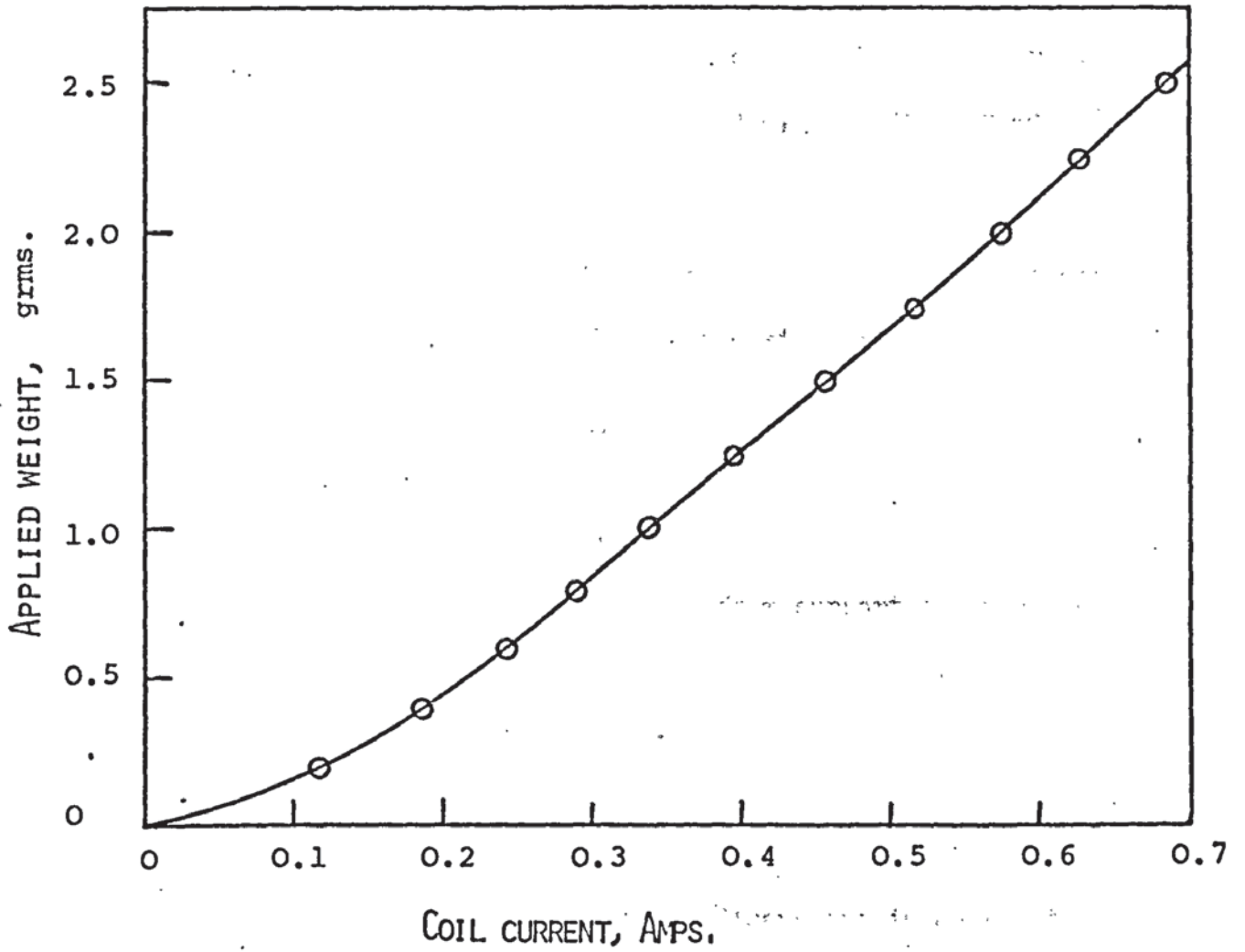
Fig.9.   Calibration curve for the determination of
internal stress.

After cleaning the strips were dried in acetone, weighed and stored in a desicator. Prior to use the back of each strip was stopped off with P.V.C. tape and the front face swabbed with magnesium oxide slurry to remove any accidental finger marks. After plating the P.V.C. tape was removed, the strip dried and re-weighed.

The formula used for calculation of the mean stress values was that discussed by Gabe and West[72]:-

$$S = \frac{4M^3 G}{10^6 \times BTL (3M-L) x} \qquad \text{(viii)}$$

where   G = restoring force

       M = length of steel strip from support to armature.

       B = width of strip.

       T = thickness of strip.

       L = plated length.

       x = thickness of plate.

If G is expressed in newtons and all dimensions in metres the stress is determined as N/mm^2.

As many of the values in equation (viii) remain constant it may be simplified to:-

$$S = K \frac{G}{W} \qquad \text{(ix)}$$

where   K = constant

       W = weight of metal deposited.

7.4   Hardness of Electrodeposits

7.4.1

Hardness of coatings applied to dies

Micro-hardness determinations were carried out on the taper sections at 1mm. intervals along a radius from the centre of the die to the edge of the wear ring.   The indentations were made as close to the surface as possible.

7.4.2

Hardness of cobalt-molybdenum and cobalt-tungsten alloy deposits in the as plated and heat treated condition

The hardness of the deposits was measured in three conditions, as plated, heat-treated for $4\frac{1}{2}$ hrs at $150^{o}C$ and heat-treated for 15 mins at $500^{o}C$. These temperatures were chosen because measurements taken during forging indicated that they were the maximum and minimum temperatures obtained on the die surface. The $4\frac{1}{2}$ hr. heat treatment at $150^{o}C$ was employed as this was the approximate duration of the test and the die surface was at this temperature for a considerable part of this time.   The duration of the $500^{o}C$ heat treatment was considerably in excess of the time the die surface was actually at this temperature during the forging test.   However as it was thought that the surface temperature was likely to be one of the controlling factors of die wear the 'long term' effects of this temperature on the deposit was important.

Samples for heat-treatment were obtained by plating brass panels, 5cm x 5cm. for approximately 5 hrs.   The brass panels were given the same cleaning treatment as the Hull cell panels and

plated under the same conditions as were used to plate dies.
Three specimens 2.5cm x 1 cm. were cut from the centre of each
panel and two heat-treated as described above.   Cross sections of
all three samples were mounted in bakelite and hardness tests
carried out using a micro-hardness tester.

7.5   Structure of Electrodeposits

7.5.1

Optical examination of deposits plated onto dies

The structure of deposits plated onto die sets was
examined optically by taking cross-sections from the die just
outside the wear ring region.   The specimens were mounted and
polished in the usual manner and etched in 1:3 nitric acid -
acetic acid mixture.

7.5.2

Optical examination of deposits as plated and heat-treated

The structures of electrodeposits in the as plated
and heat treated conditions were examined by etching the specimens
used for hardness determinations in 1:5 nitric acid - acetic acid
mixture.

7.5.3

Surface topography of the electrodeposits in the as plated condition

The scanning electron microscope (S.E.M.) was used to
examine samples cut from the centre of panels used to determine the
cathode efficiency of the electrodeposits.   Samples 2cm x 1cm
were cut from the panels using a guillotine, mounted on stubs and
viewed directly.

7.6 Analysis of Electrodeposits

7.6.1

Foils for chemical analysis

A convenient technique to obtain electrodeposits for analysis is to plate onto a stainless steel cathode. This produces a coating which usually may be peeled easily from the substrate as a metal foil since the oxide film present on the stainless steel prevents good adhesion. However, this method of foil preparation proved impossible in this instance, either the deposit flaked off or at low pH adhered strongly to the sunstrate. An alternative method of foil preparation was therefore devised which involved using aluminium foil as the substrate. The foil was attached to a brass plate for support using insulating tape. It was then treated with a proprietary solution of the type used to provide an immersion alloy zinc deposit to facilitate the plating of aluminium.

The foil was electroplated for 1½ minutes in a Watts nickel solution, (pH 4.0). This was used as it was thought that at low pH the thin zinc alloy film would be dissolved. Subsequently the foil was plated for half an hour in the alloy bath. After plating it was thoroughly rinsed and the aluminium dissolved from the back of the foil using 25% sodium hydroxide. The electrodeposit was dried and analysed for molybdenum or tungsten.

The small quantity of Watts nickel deposited in the early stages of foil preparation can be allowed for when weighing the sample for analysis but may be ignored for all practical purposes.

7.6.2

Samples for electron probe microanalysis

The electron probe micro analyser was employed to check the composition of electrodeposited coatings applied to dies. Using this technique it was possible to determine the composition after the forging test. A sample approximately 3mm. high by 6mm. diameter was required and ideally this should be cut from as near to the worn region as possible. This ensured that the sample was taken from a region having the same composition as that subjected to wear. If a sample is cut from the edge of the die, the composition may not be representative of the major part of the coating since the composition of many alloy electrodeposits is influenced by current density.

It was decided that the most convenient method of obtaining the specimen was to use a spark erosion technique. The die was first cut, using a slitting wheel, into six pieces so that the samples could be prepared for various types of examination (i.e. taper sections and S.E.M. examination). The specimen for electron probe micro analysis was bored from one of the 'quadrants' using a spark erosion technique. A thin-walled copper tube was employed as the 'cutting tool', the specimen being bored out as shown in Fig. 10. A specimen of the required length was cut off, using a thin copper sheet as the electrode in the spark erosion equipment. The specimens were mounted in perspex and polished by conventional methods. Finally they were removed from the mounting material, inserted in the specimen holder of the instrument and the coating analysed.
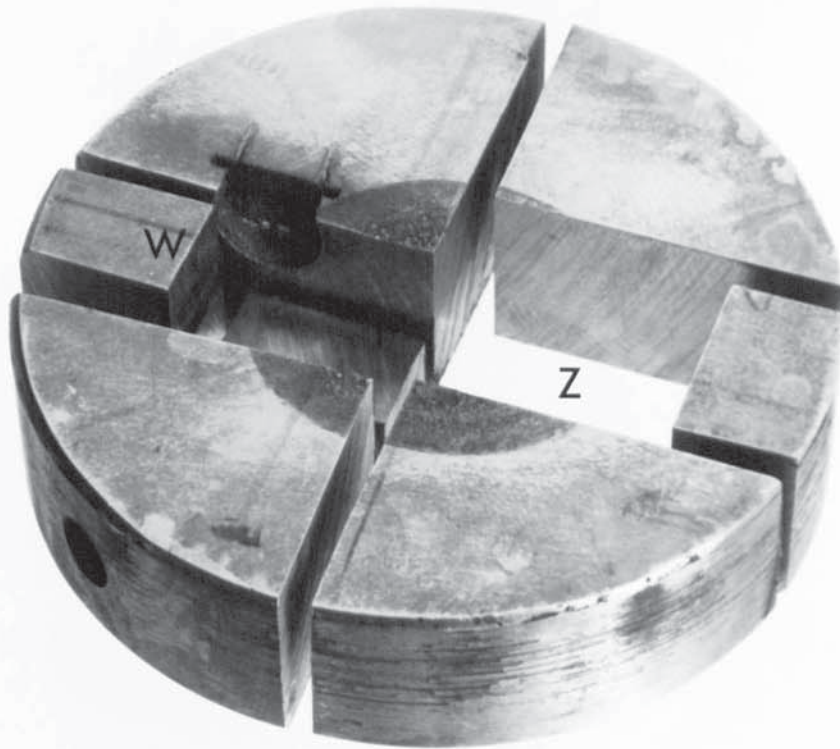
Fig.10.   Sectioned die after forging.

       W   Sample removed for E.P.M.A. analysis
              using new equipment.

       X   Sample removed by spark machining for
              E.P.M.A. analysis using old equipment.

       Y   Sample removed for S.E.M. examination.

       Z   Sample removed for taper section.

This technique was later modified when a more modern instrument became available. This instrument had a much larger specimen chamber which considerably simplified specimen preparation. Normal sized, mounted specimens could be used and therefore die sections for analysis were cut from the die with an abrasive slitting wheel, then mounted and polished in the usual way.

7.6.3

S.E.M.-analysis using the dispersive x-ray technique

Analysis of the electrodeposits was carried out on surface topography specimens using dispersive x-ray analysis equipment attached to the S.E.M. The surface topography specimen required no additional preparation and analysis spectra were printed out with the aid of an x-y graph plotter. The spectra produced by this instrument were calibrated by analysing samples from the same specimen using the E.P.M.A. as standard alloys could not be obtained. This particular analytical investigation was carried out in order to determine any large variations of alloy composition occurring particularly where changes in surface topography were evident.

7.7 Thermal Fatigue

As mentioned previously in section 2, it was found at an early stage in this investigation that several of the cobalt-nickel alloys reduced the incidence of surface thermal fatigue cracks. It was decided therefore that a test should be developed which would enable the effects of thermal cycling alone to be evaluated. The simple apparatus illustrated in Fig.11 was
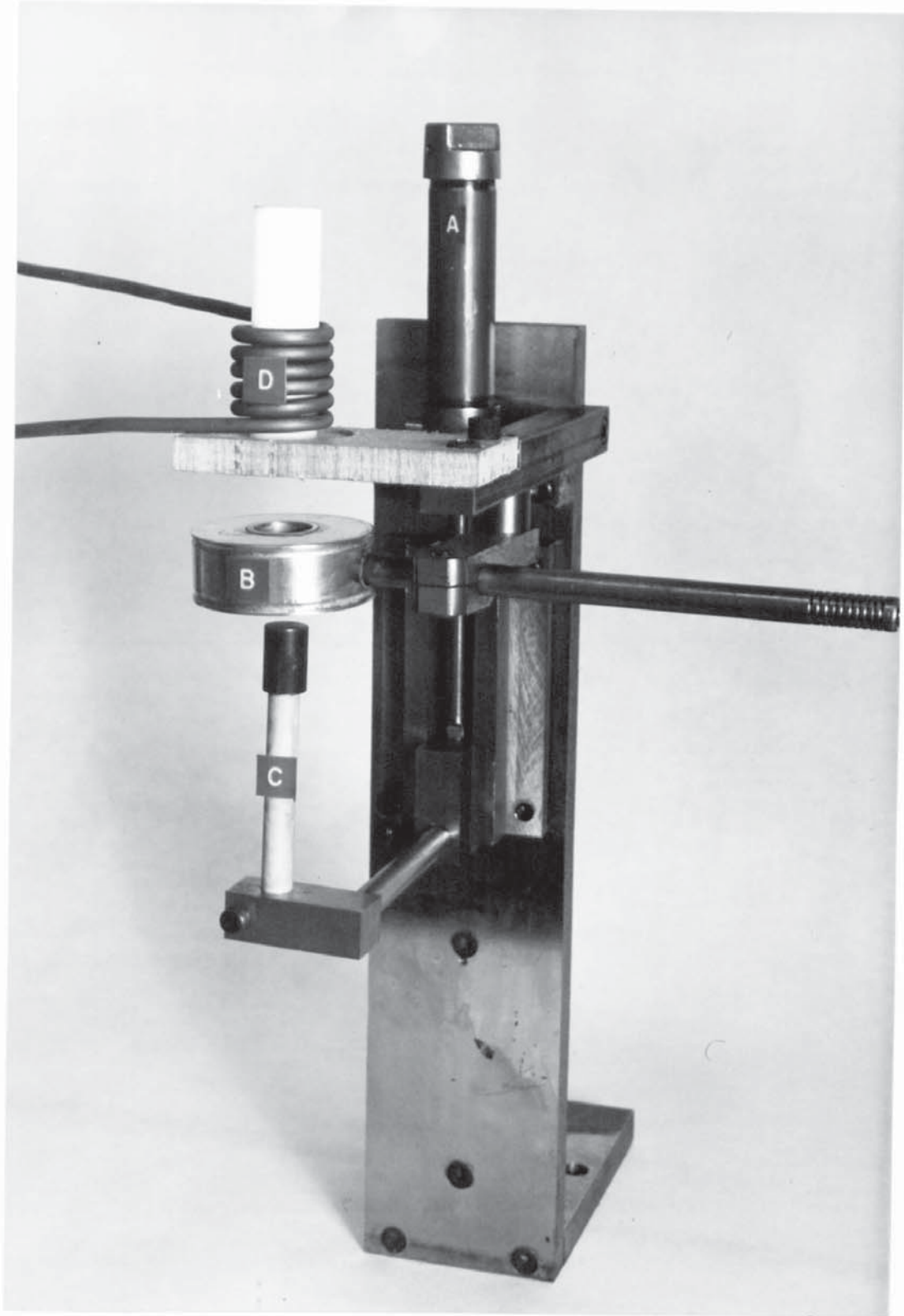
Fig.11. Thermal fatigue apparatus.

A - Air Cylinder
B - Water/Air spray
C - Ceramic tube
D - H.F. coil

devised for this purpose.

The specimen consisted of a cylinder of heat treated Electem No.5 die steel (or any other die steel required to be tested) 19mm high x 13mm diameter with a 7mm externally threaded peg on one end and a 7mm internally threaded peg on the other end, Fig.12. The specimens were plated and ground under the same conditions as those used for a normal die. To ensure an even electrodeposit three specimens were screwed into each other by means of the pegs on either end and rotated in the plating bath using the apparatus shown in Fig.13. After plating and grinding the top peg was machined off. The specimen was located on top of a ceramic tube by means of the externally threaded peg. This tube was moved up and down using an air cylinder so that on the upward stroke the specimen was moved into a high frequency induction coil and on the downward stroke into a fine water spray or air blast depending on the degree of cooling required. The apparatus was completely automatic and could be set to run for any number of cycles so that simulation of a normal forge shift could be obtained.

The heating operation represents the heating of the die surface by the hot billet while the water spray represents the water/graphite lubricant usually employed in forges between each forging operation. The air blast which could also be used for cooling was closer to the conditions prevailing on the experimental forge as no lubrication was employed and an air blast was used to remove loose scale from the die surface between each forging operation. The surface of the specimen was thus rapidly heated and cooled and by adjusting the time cycle, forging conditions

Fig.12.   Thermal fatigue specimen.
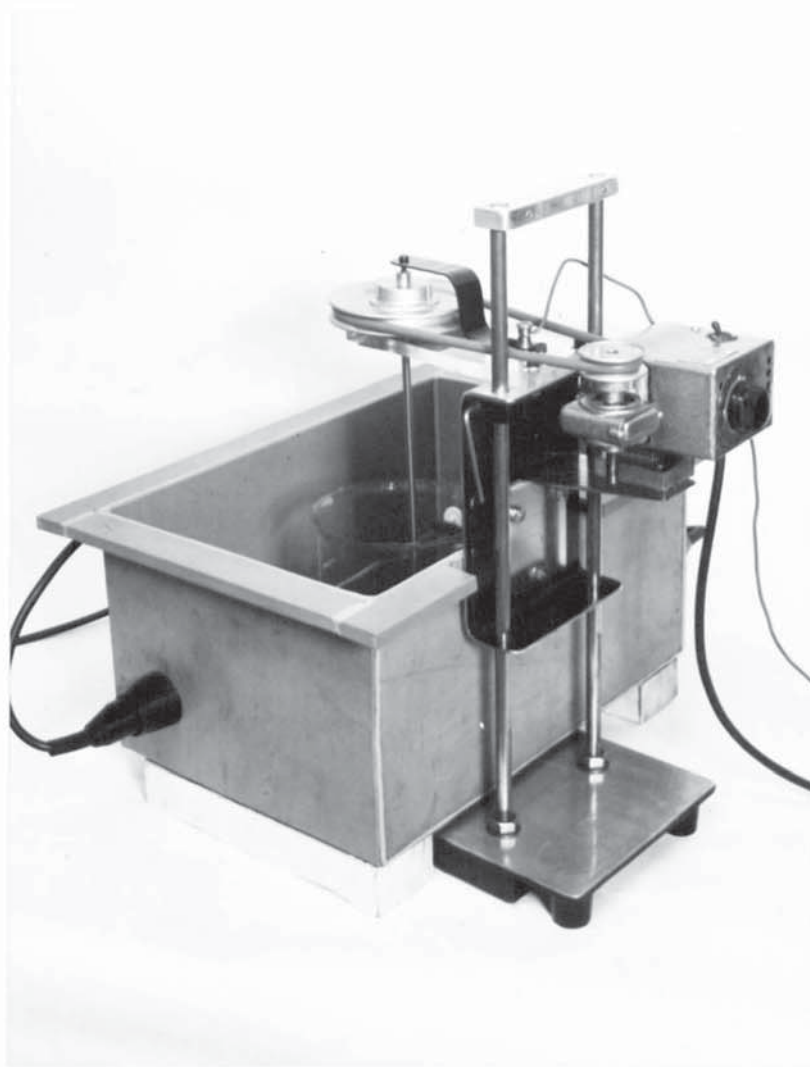
Fig.13. Apparatus used for plating thermal fatigue specimens.

could be simulated quite closely.

The temperatures used for the simulated forging sequence were obtained from measurements taken during the experimental forging operation as outlined in the following section. They were set before each test using an unplated electem sample to which a chromel/alumel thermocouple had been welded.

7.7.1

Measurement of die surface temperature

The measurement of die surface temperature during the forging operation is extremely difficult due to the arduous conditions encountered. The temperature measurement device employed must be able to withstand considerable mechanical stress and the temperature recording equipment must have a very short response time in view of the brief die/billet contact time. It is also important that the measurement technique should not influence the heat flow characteristics of the die thus giving false temperature values. Several methods have been reported in the literature[73,74] which are claimed to satisfy the above requirements but all suffer from certain limitations. One of these methods, that due to Kellow, Bramley and Bannister,[74] was chosen for the present work. This method was based on one devised by Vigor and Hornaday[73] but the apparatus was of simpler construction. It consisted of a single constantan wire which was embedded in the die and insulated from it using a suitable insulating material. The wire was held in position by deforming an insert of the die material around it. The deformation process

was also used to secure an iron wire to the die, close to the
eventual hot junction.   Finally the surface of the die was
ground flat, this resulted in a very thin smear of Constantan
over the die surface in the vicinity of the Constantan wire.   This
smeared contact between the Constantan wire and the die functioned
as the hot junction of an iron/Constantan thermocouple.   The
junction so formed was extremely small and thin thus giving the
thermocouple a very short response time.   The distortion of the
heat flow passing through the die was also minimised due to the
thinness of the wire and insulating material.   Thermocouples
of this design are relatively fragile although Kellow et al[74]
claim that they can be used for a considerable time and yet still
give accurate temperature readings.   However, in the present work
the number of forging operations was restricted to the minimum
necessary to provide consistent results.   This was also advisable
in order to limit scale formation over the thermocouple which would
lead to spurious results.

The thermocouple was connected initially to a pen
recorder but this proved incapable of a fast enough response time
to the temperature rise and so a cathode ray oscilloscope having
a polaroid camera attachment was used for all subsequent
measurements.   The oscilloscope was of the dual trace type which
permitted the inclusion of a marker on all the photographic records.
This was achieved by connecting the second channel to a micro-
switch connected across a low voltage supply which was operated
when the forging press reached "bottom dead centre" on the forging
stroke.   Thus on each photograph the marker indicated exactly

the same position of the forging stroke and measurements could be made using it as a reference point. The initial measurements were unsatisfactory due to interference on the oscilloscope traces; this made accurate temperature determinations impossible. The high frequency induction unit used for heating the billets prior to forging and the heaters in the die bolsters were found to be responsible for this interference. The following sequence of operations was used to record each trace. Five billets were first forged so as to attain a stable die temperature. (Preliminary investigation had shown that an equilibrium bulk die temperature was reached after forging four billets). On the sixth forging operation the billet was heated and immediately prior to forging all power to the heating circuits was switched off. This procedure enabled a clearly defined trace to be recorded. Several tests were carried out to obtain an average temperature value.

In view of the problems associated with direct methods such as the one just described it was decided to devise an indirect technique. This was carried out using a subsurface thermocouple and the same sequence of operations was employed as in the direct method. The thermocouple was set initially at approximately 1750 µm below the die surface. After each trace was recorded 250 µm was ground from the surface until 1000 µm of die steel remained above the couple. Increments of 125 µm were then removed until only 500 µm remained and finally the die steel was removed in increments of 50 µm until it was considered that the thermocouple tip was close to the surface. At this stage the forging

tests were halted and a cross-section through the thermocouple
insert was mounted and polished thus enabling the exact thickness
of metal remaining above the thermocouple to be measured.
Consequently the accurate depth of the couple, corresponding to
each temperature measurement, could be calculated. A method of
interpretation of the oscilloscope was devised using information
published in the paper by Kellow et al[74] and from practical
consideration of the forging operation. Kellow et al report
that the heat flux across a given area is dependent upon the real
area of contact between the hot billet and the die surface. From
these results it is apparent that 98% of the maximum possible heat
flux across a given area is achieved with a ratio of real/nominal
area of contact of 80% and that for a ratio of 75% (giving
approximately 96% of the maximum heat flux across a given area)
the amount of plastic strain required is 0.5. Therefore it may
be assumed when evaluating oscilloscope traces that the "starting
point" for measuring the temperature rise of the die surface
occurred after this degree of deformation had taken place. A
typical oscilloscope trace is illustrated in diagrammatic form in
Fig.14. The curve is shown divided into four regions. The
distance 1-2 was disregarded since the real contact area during
this time must have been small since little deformation had occurred
and hence a small percentage of the total heat flux would be used
to heat the die. Region 4-5 was ignored as the billet had been
ejected from the die surface and so the die was cooling down.
The time base still recorded that the top die was in the "bottom
dead centre" position because of the dwell time of the press as
it changed direction from down to up. The micro-switch was not
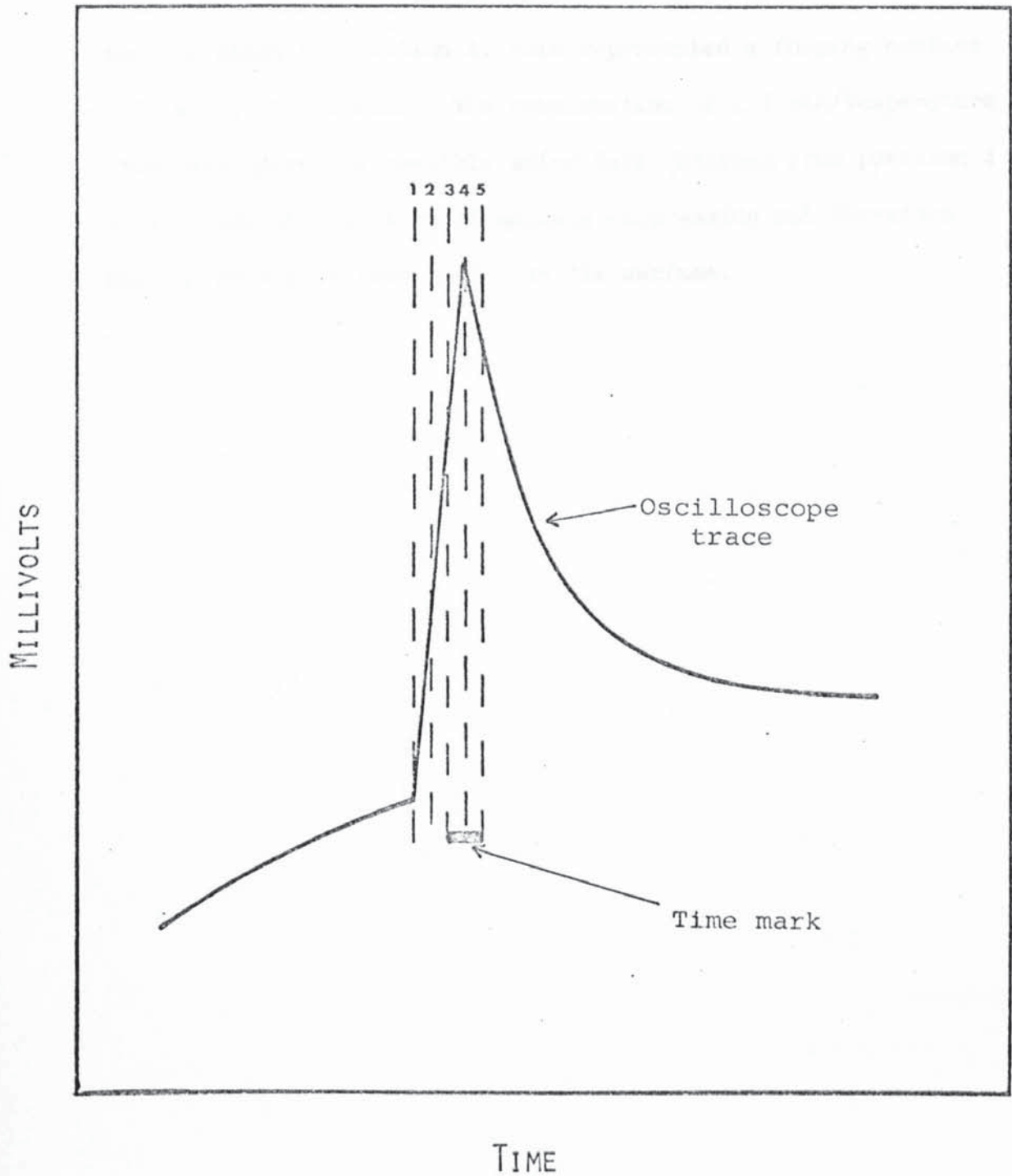
Fig.14.   Oscilloscope trace of surface temperature measurement.

operated until the top die was definitely moving upwards. The zero time for the forging operation was taken as position 2 and the end point as position 4, this represented a forging contact time of 0.105 seconds. The construction of a depth/temperature graph was therefore possible using data obtained from position 4 as this was the position of maximum compression and therefore maximum heat flow from billet to die surface.

8. EVALUATION OF DIE WEAR

8.1 Simulated Forging Operation

8.1.1

The use of flat dies

In order that comparisons could be made between the present work and other die wear studies which had been carried out at the University of Aston, the forging equipment used for these previous investigations was also employed to evaluate the wear resistance of dies having electrodeposited coatings.

The wear test itself was essentially an upset forging operation carried out between two flat dies made from the material under investigation and was carried out on a mechanical press which had been modified such that automatic feeding of hot billets and ejection of forgings was possible. The essential features of the equipment are shown in Fig. 15. The complete forging cycle occupied only 10 seconds thus enabling a large number of forging operations to be carried out in a relatively short time. A billet of EN3B steel 1.2cm dia. x 1.8cm long was fed into an H. F. coil and heated to approximately 1200°C. It was transferred to forging dies by tongs. An optical pyrometer determined the billet temperature and activated the forging stroke, but only if the billet temperature was within the range 1110 - 1140°C. The billet was upset forged from 1.8cm to 0.6cm in height and ejected. A counter mechanism operated by the forging stroke determined the number of forging operations. A standard test of a thousand forging operations was employed since this was the same as in the earlier work. The dies were held in the press in bolsters which
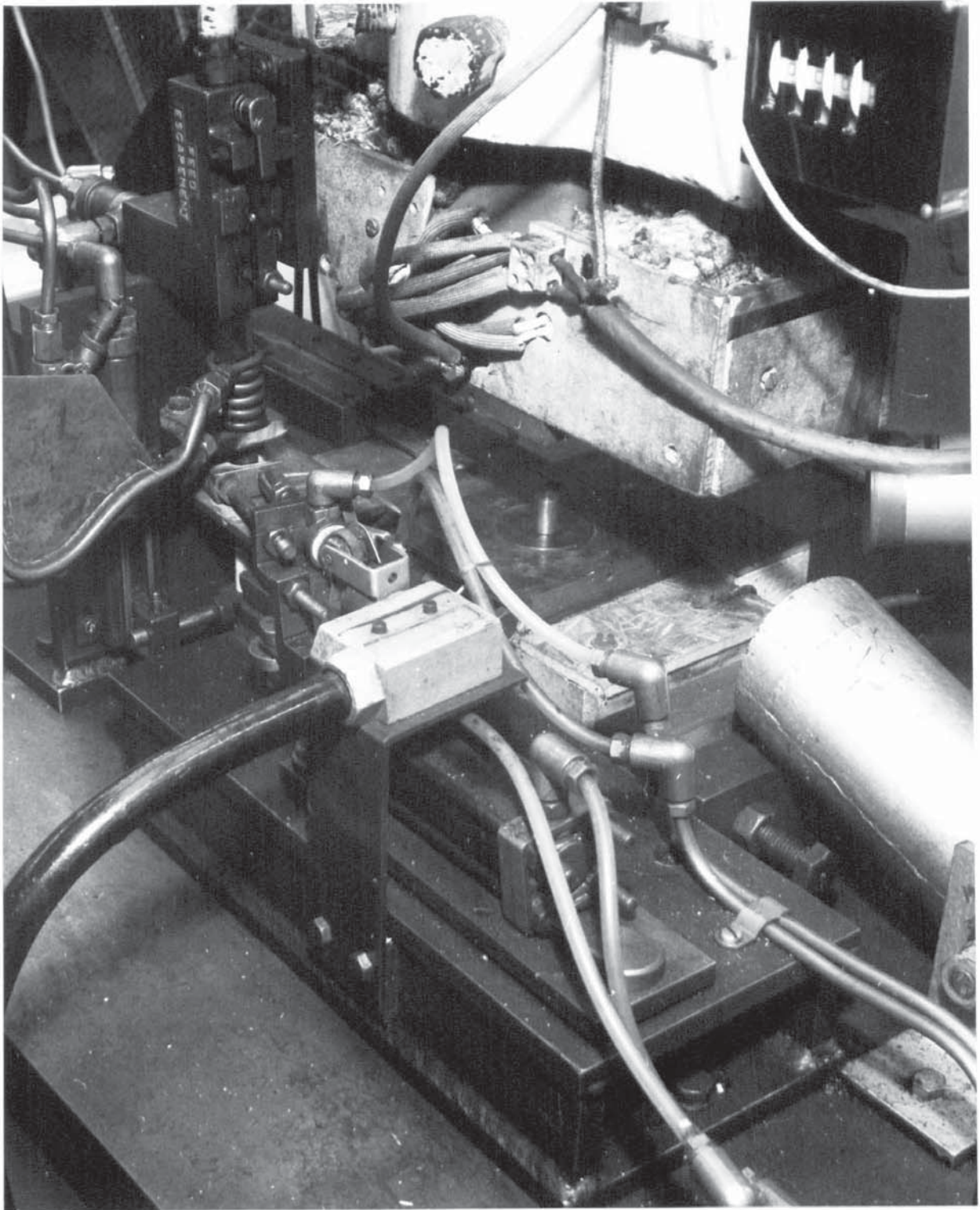
Fig.15. Forging equipment showing billet in position
on die prior to forging.

were electrically heated to 130°C. Heating of the die bolsters
was necessary as without auxiliary heating the bulk die temperature
only rose to about 60°C due to the small billet/bolster mass
ratio. Such a low temperature rise during forging was not
consistent with industrial experience where the billet/bolster
mass ratio is higher leading to a much greater heat input to the
die.

8.1.2

The use of small shaped dies

The use of the flat dies described above had one
significant limitation in that the thousand slug test was not
sufficiently severe to differentiate between highly wear resistant
die steels or coatings. Very small wear volumes were recorded
for such materials and, as described in section 8.3.1, it was
difficult in these cases to assess accurately the degree of wear
since some deformation also occurred. The spread of wear volumes
for the wear resistant materials could be increased, thereby
making comparisons easier, by increasing the severity of the
forging test. This could be achieved by increasing the bulk
die temperature, increasing the amount of deformation of the billet,
or by altering both of these variables simultaneously. It was
decided that a more satisfactory indication of service life in
an industrial forge could be obtained by the introduction of edges
and corners on the dies, however, it was important that these
features could be evaluated easily. The behaviour on edges and
corners was considered to be of particular importance in the case
of coated dies since failure of the coating was likely to be
initiated at these regions. The ease with which such dies could

be successfully coated was also thought to be an important factor when considering the process for industrial applications.

It was decided that the shaped die should be the top one of the pair normally used for the upsetting test. The same diameter of die was used so as to utilize the existing die bolster arrangements. The top die was chosen as the shaped one because the forgings would tend to fall from the cavity thus discouraging sticking of forgings in the die, the die cavity would not fill with loose scale, and the automatic billet feed system could still be used. The last of these points was by far the most important if the test was to be completed with reasonable speed.

The forging conditions were set so that the maximum reduction, which still allowed effective ejection of the forging, was used. (This gave approximately 0.3cm thick 'flash' to the forgings.) The bulk die temperature was set at 250°C, somewhat higher than for the flat dies.

The initial shapes used were essentially milled or turned round bottomed grooves let into the die surface. A single groove (shape 1), cross (shape 2) and circular configuration (shape 3) were tried, Fig.16. After forging between 50 and 100 billets on each die it was found that little wear had taken place and that which did was situated in very difficult positions for taking wear measurements. Another feature of these shapes was that if the billet was not placed centrally on the bottom die it was moved sideways during the forging operation due to the uneven forces generated by the shape. This had the effect of
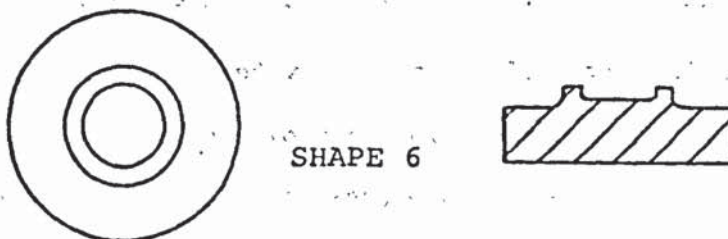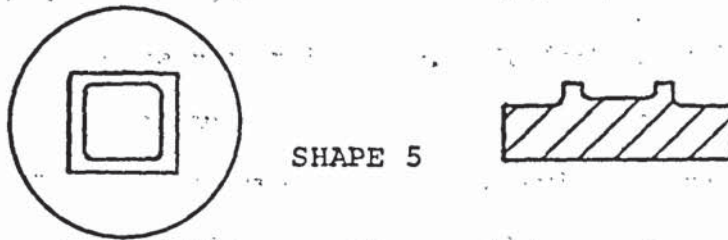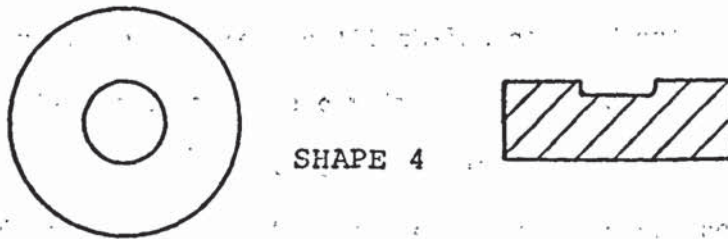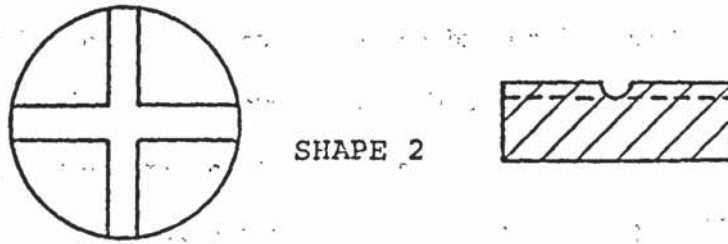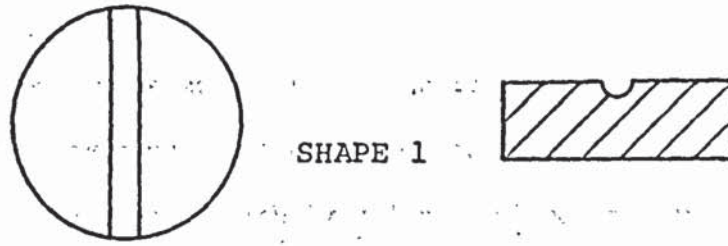
Fig.16.   Small experimental shaped dies.

slightly moving the most severe wear areas about the surface of
the die thus evening out their effects.   For this reason it was
decided that a recess slightly wider in diameter than the unforged
billet, should be an essential feature of the die shape so as to
give a 'self-centring' action to the billet during the initial
stages of the forging operation.   This led to the use of shape 4
(Fig.16).   The depth of the impression was varied considerably
but it was found that a sink of only approximately 0.125cm was
possible above which sticking of the forging in the cavity occurred
making automatic ejection impossible.   The dimensions shown in
Fig.17 were thus employed and easily measurable wear was detected
after forging only 50 billets.

Industrial experience shows that the areas which suffer
the most erosive wear are the 'flash-lands'.   These are flat
surfaces adjacent to the die cavity over which excess metal flows
when the die cavity is filled.   This area is usually fairly
narrow and is bounded on its outer edge by a recess known as the
'flash-gutter' which accommodates this excess metal and allows the
dies to close to the required degree.   To further simulate industrial
conditions therefore and to increase the wear rate shape 5 was
devised.   This had the same shallow 'hollow' as shape 4 but a
'flash-land' was introduced by relieving back the main bulk of
the die to a depth of approximately 0.2cm thus leaving a wall
0.47cm wide.   This proved very successful, giving high rates
of wear but was difficult to machine.   Shape 6 was therefore
introduced to overcome the lengthy machining operations required
when manufacturing the previous die shape.   This die shape was
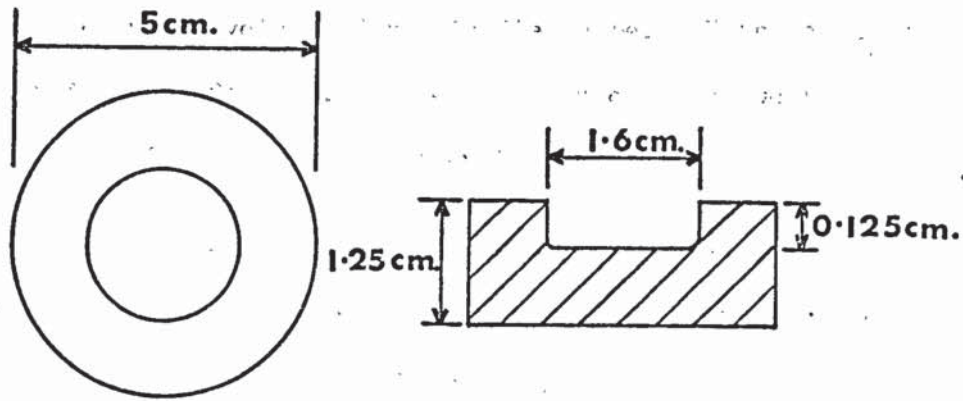
Fig.17.   Dimensions of Shape 4.

essentially a circular shape 5 and only required a turning operation
for its manufacture. However difficulties in wear measurement
were encountered with this shape. The Talylin could not be used
therefore a measuring system based on the use of a Taylor/Hobson
Talyrond was developed for this die shape. This measuring system
proved successful in practice and good circular wear traces were
obtained after forging small numbers of billets.

To obtain a relationship between the number of billets
forged and the wear obtained on die shapes 4, 5 and 6, a series
of 50, 50, 100 and 100 billets was forged and wear measurements
taken after each batch of forgings.

Die shapes 4 and 6 were ultimately assessed as the
best impressions to use as they were both relatively easy to machine
and measure for wear. They were therefore employed to evaluate
the most wear resistant alloy coatings found using flat dies.

8.1.3

The use of large shaped dies

Relatively large dies had been used at the University
of Aston by Balogun[75] to measure stresses in dies. This work
was closely linked with industrial forging practice and the dies
operated under comparable stress conditions to those encountered
in industry. It was therefore decided that die sets of the same
shape as those used by Balogun should be plated and tested under
the same forging conditions. This would give valuable information
as to the performance of the coatings in an industrial situation.
The shapes chosen are shown in Fig.18 plated, polished and ready
for forging.

Fig.18.   Photograph showing large shaped dies.
          Approximately three-quarters actual size.

Examination of the dies used by Balogun showed that appreciable wear of the die had taken place after only 30-40 forging operations had been carried out. Therefore a standard test of 50 forgings was used for the die sets. A graphite/water lubricant was sprayed onto the die during the forging operation. The forging stock used was EN3B bright drawn round bar and was heated to 1200°C in a furnace. Prior to forging excess scale was removed from the billets by hammering. The extra metal allowed for the flash was approximately 15% and the flash thickness set at 0.38cm. This gave a nominal forging load on the pressure gauge fitted to the press of approximately 650 kN.

8.2   Measurement of Wear

8.2.1

Flat dies

The amount of wear occurring during the forging operation was evaluated by obtaining a wear pattern from the surface of the die using a Taylor Hobson Talylin surface analyser. After forging, the surface of the die was descaled electrolytically. The back and sides of the die were coated with a suitable lacquer and using a carbon rod as anode, the surface of the die was cleaned cathodically in a solution of 5% V/V H_2SO_4 containing 0.1% by wt. o - tolythiourea as an inhibitor. The solution temperature was 75°C and the applied current 18-30 A/dm^2. The maximum time permitted for descaling was 1.5 minutes; this was divided into 30 second periods, each being followed by vigorous brushing of the die surface with a hard brush. After descaling the surface, four

wear traces were taken at 45° to each other, as shown in Fig.19.
It was possible to alter the sensitivity of the apparatus so that
varying degrees of wear could be evaluated.   The length of the
trace obtained could also be expanded by x 2, x 5, and x 10, (i.e.
when set at x 10, for each 1cm. traversed by the stylus, 10cm.
of trace were produced).   In the present work the greatest
expansion was always used.   Typical traces are shown in Fig.20.
The central plateau region was of approximately the same size as
the billet diameter, i.e. 1.25cm.   This represented the area of
sticking friction associated with the upset forging operation;
it was therefore an area of almost zero metal flow and remained
virtually unworn on completion of the forging test.   The wear ring
extended outwards from the edge of the central plateau almost
to the diameter of the forged billet, approximately 2.5cm.   This
area was one of metal flow during the forging operation and
consequently severe wear of the die surface occurred.   The extent
of wear as assessed in terms of the mean wear volume was evaluated
by the method described in section 8.3.1.

8.2.2

Small shaped dies

It was initially thought that the most convenient
method of measuring the wear occurring on shaped dies would be by
taking plastic casts of the impression before and after forging
and comparing the contours.   This technique had proved successful
when used on fairly large, highly worn dies but it was inadequate
when dealing with these small experimental ones having relatively
little wear.   The methods of wear measurement were therefore
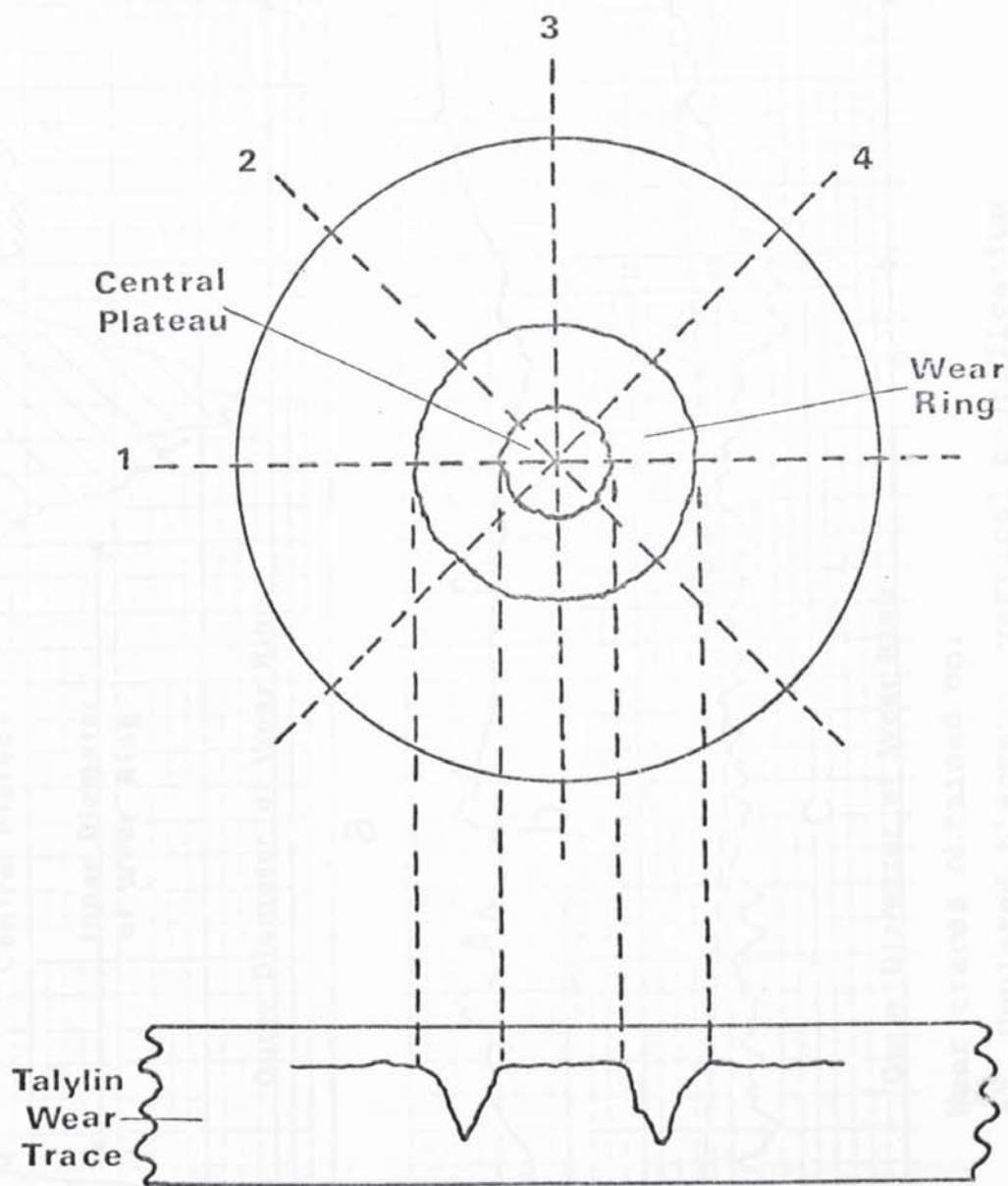
Fig.19. Positions at which wear traces were obtained on die surface.
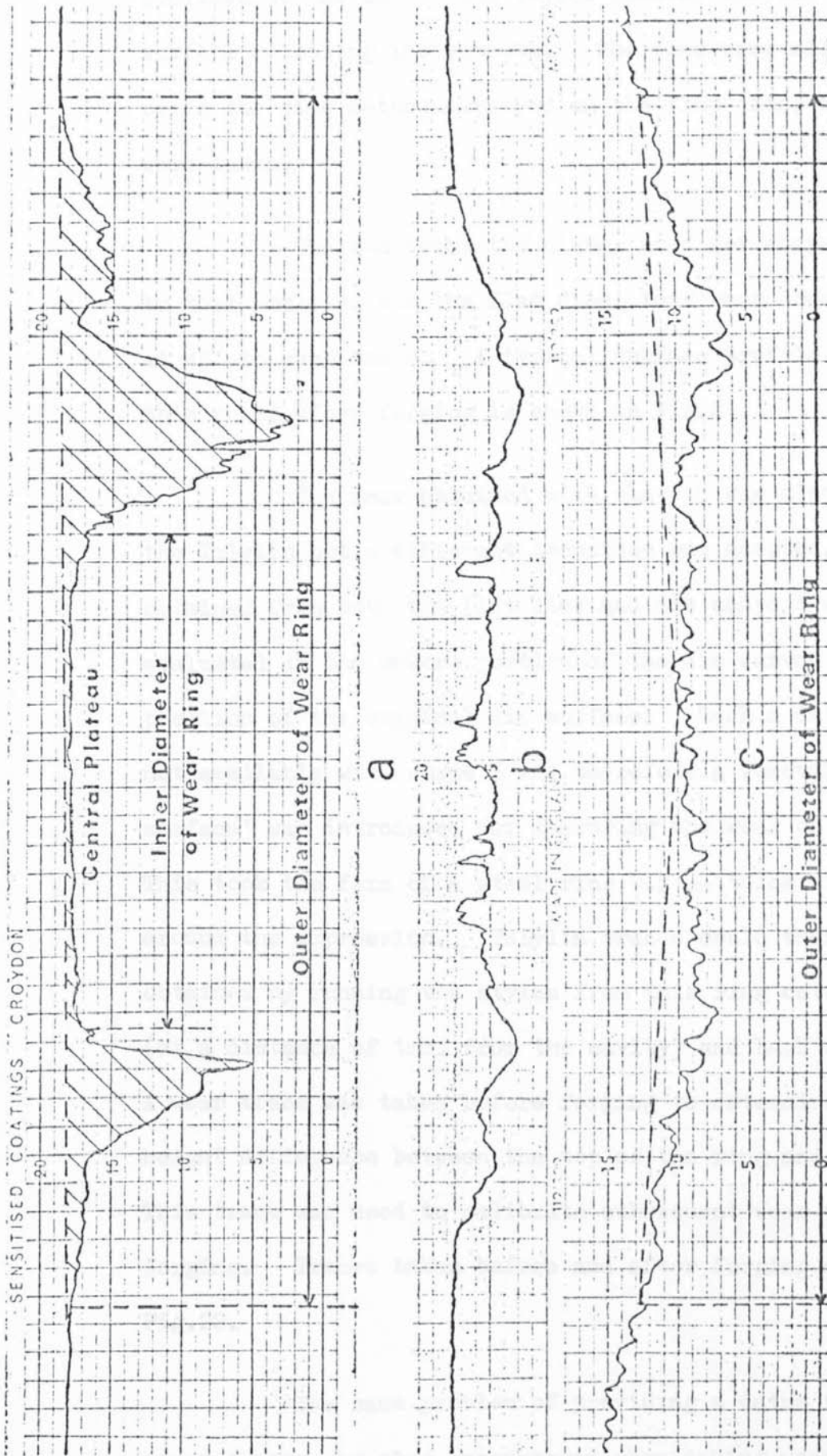
Fig.20. Wear traces obtained on:

a) Unplated Electem; vertical magnification x 1000

b) Die plated in solution W11; vertical magnification x 1000

c) Die plated in solution M19; vertical magnification x 4000

confined to the use of the Taylor-Hobson, Talylin and Talyrond surface measuring instruments. The dies were all de-scaled, using the same method employed on the flat dies, before measurements were taken.

The measuring techniques used for shape 4 was identical to that employed for the flat dies, four wear traces being taken at 45° to each other. A typical surface profile obtained from this shape after forging is shown in Fig.21.

The wear obtained with shape 5 was also measured with the Talylin but a different technique was adopted. The wear traces obtained from both the flat dies and die shape 4 were easily evaluated as the unworn portion of the die served to mark the position of the original die surface. Such a datum point was not available with shape 5 and therefore a removable 'original surface' was introduced for measuring the wear on the flash land. This took the form of a steel ring 0.2 cm thick which was placed around the impression. Talylin traces could therefore be obtained by running the stylus from this ring onto the flash land (at a distance of 1mm. from the cavity) and back onto the ring. A wear trace was taken before forging to determine the exact height difference between the top of the ring and the flash land. This trace was used to calibrate subsequent wear traces taken after forging. Traces taken before and after forging are shown in Fig.22.

The same problem of providing a datum from which to measure wear was also encountered when taking wear measurements
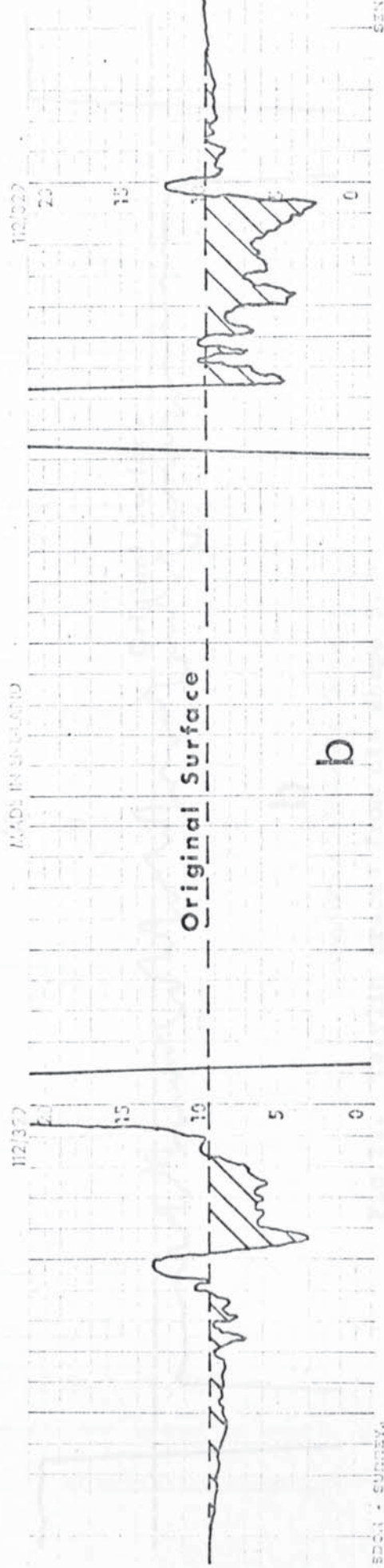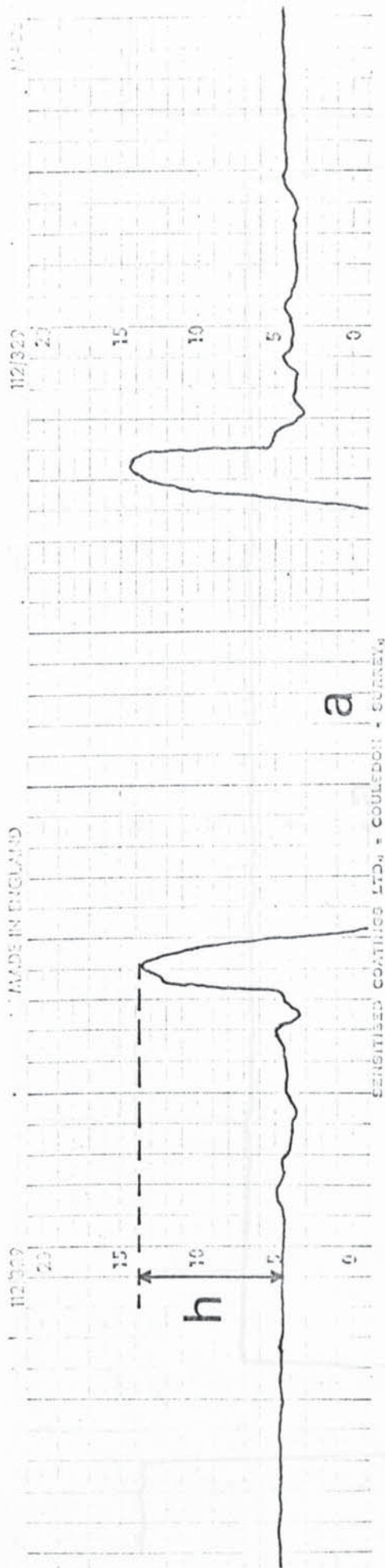
Fig. 21. Talylin traces from die shape 4.
Unplated Electem. 300 billets forged.

a) Vertical magnification x 100

b) Vertical magnification x 1000
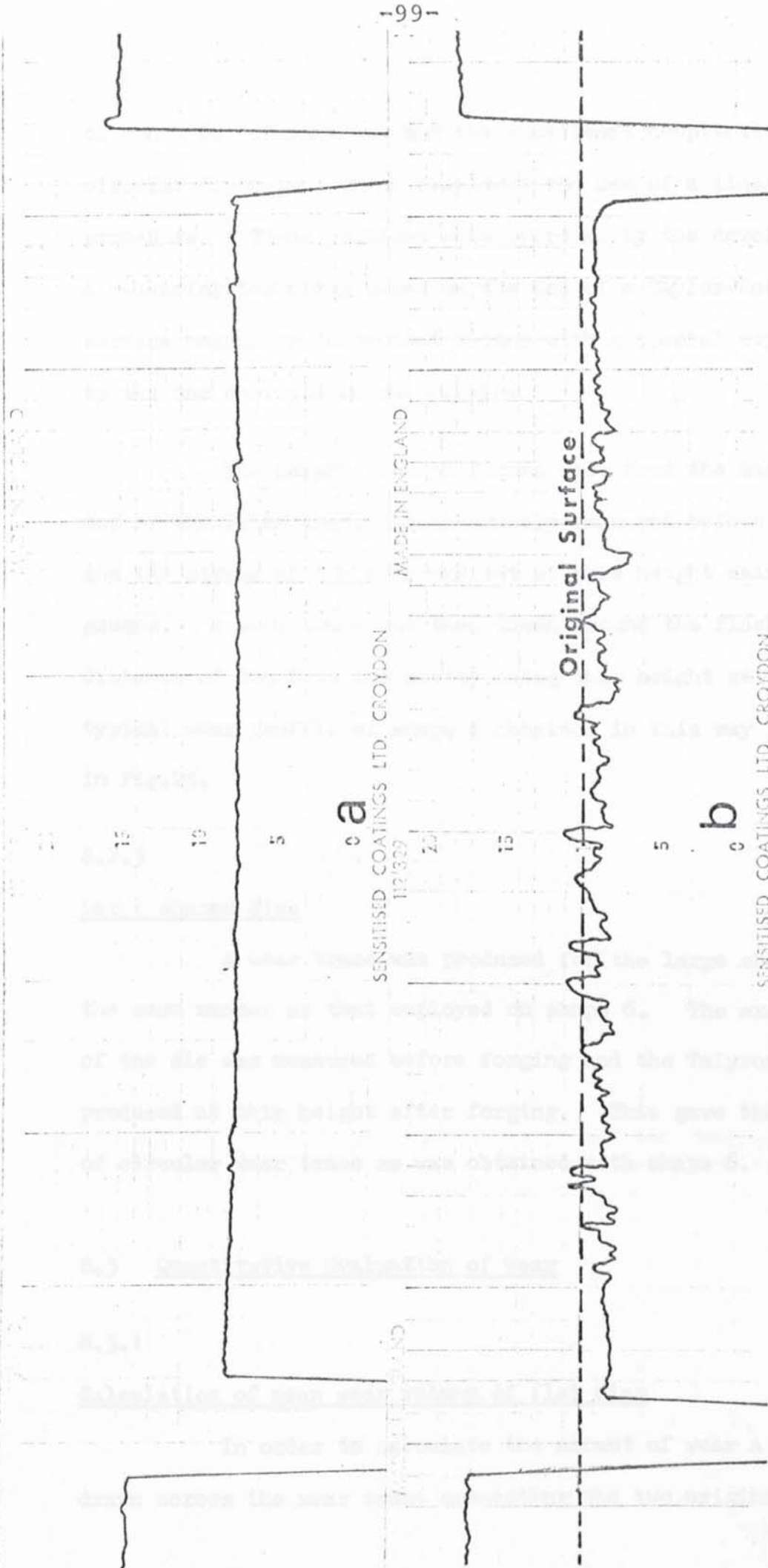
Fig.22. Talylin traces from die shape 5.
Unplated Electem.
a) Before forging; vertical magnification x 500
b) After forging 50 billets; vertical magnification x 500

of shape 6. This shape had the additional complication of a circular flash-land which precluded the use of a linear measuring procedure. These problems were overcome by the development of a measuring technique based on the use of a Taylor-Hobson Talyrond surface measuring instrument fitted with a special stylus similar to the one employed in the Talylin.

The height of each formed die, from the base to the top of the flash land, was accurately measured before forging and the stylus of the Talyrond set at this height using slip gauges. A wear trace was then taken around the flash land, at a distance of 1mm from the cavity using this height setting. A typical wear profile of shape 6 obtained in this way is shown in Fig.23.

8.2.3

Large shaped dies

A wear trace was produced for the large shaped die in the same manner as that employed on shape 6. The exact height of the die was measured before forging and the Talyrond trace was produced at this height after forging. This gave the same type of circular wear trace as was obtained with shape 6.

8.3   Quantitative Evaluation of Wear

8.3.1

Calculation of mean wear volume of flat dies

In order to calculate the amount of wear a line was drawn across the wear trace connecting the two original surfaces,
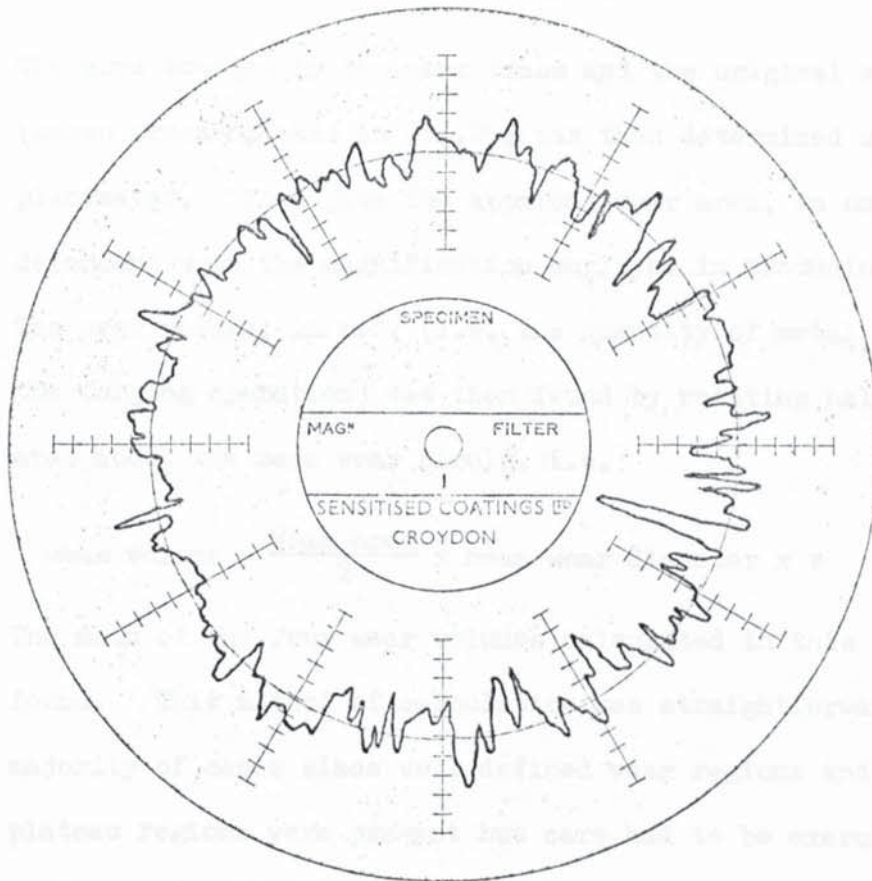
Fig.23.   Typical Talyrond trace from die shape 6.
          Unplated Electem.   200 billets forged.
          Vertical magnification x 1000

Fig.20a. The outer and inner extremities of the wear ring were then marked and the diameters measured. From these measurements the mean wear diameter was calculated using the expression:-

mean wear diameter = inner diameter + $\frac{(\text{outer diameter} - \text{inner diameter})}{2}$

The area bounded by the wear trace and the original surface line (shown cross-hatched in Fig.20a) was then determined using a planimeter. This gave the apparent wear area, in cm^2, which was dependent upon the magnification employed in producing the trace. The wear volume, in cm^3, (i.e. the quantity of metal lost during the forging operation) was then found by rotating half the wear area about the mean wear circle, i.e.

wear volume = $\frac{\text{Wear area}}{2}$ x mean wear diameter x π

The mean of the four wear volumes calculated in this way was then found. This method of calculation was straightforward in the majority of cases since well defined wear regions and central plateau regions were present but care had to be exercised in certain instances, particularly where little wear had taken place. Typical traces from this type of situation are shown in Figs.20b and 20c. Fig.20b represents a fairly low magnification wear trace of a die which had suffered little wear; it shows that clearly defined regions are not detected on the die surface as they are in the example shown in Fig.20a. Consequently, the mean wear diameter is very difficult to measure due to the uncertainty of the diameter of the central plateau. If high magnifications are used in order to achieve reasonable wear traces another problem is introduced. Fig.20c illustrates a typical trace of this type; the original surface profile is sloping at a small angle to the

horizontal because during the forging operation the die deforms
very slightly into a saucer shape and the magnification is so
high that apparent wear is recorded. The original surface line
could not be positioned accurately.

When these types of wear trace were encountered the
wear volumes were calculated by adopting various techniques which
the author had found successful, in a previous investigation, for
the evaluation of alloy die steels of high wear resistance. In
the case of wear traces similar to types shown in Fig.20b the
measurements required for the calculation of the mean wear diameter
were obtained both by inspection of the wear trace and of the die.
Evaluation of wear volumes from traces similar to those shown in
Fig.20c was done by extending the sloping 'original surface' line
to the centre of the die as shown and measuring the wear area
bounded by this line. Combinations of the above two techniques
were also required in certain instances.

It may be argued that the deformation mentioned above
should be included in the 'wear volume' as this represents a loss
of dimensional tolerance just as much as that caused by erosion
of the die. However this effect is only brought into prominence
by raising the wear trace magnification and traces taken at lower
magnifications are not sensitive enough to record the deformation.
It was therefore thought that it should be excluded from the wear
volume when measuring wear traces of this type.

It is fortunate that such traces are only produced from
dies which have suffered little wear and therefore does not mean

that a wear resistant material may be overlooked by miscalculation of the wear volume.

8.3.2

Calculation of wear area of small shaped dies

The Talylin wear traces obtained from shape 4, shown in Fig.21, illustrate the two quantitative measurements taken. The low magnification trace, Fig.21a, was used to measure deformation, height h, occurring on the inner edge of the die cavity. The height of the deformed regions above the original surface were measured on each trace and the mean height found. The high magnification trace shown in Fig.21b illustrates the erosion of the die surface extending outwards from the die cavity. This erosion was measured, as a wear area, in a similar manner to that used for the flat dies. A line was drawn joining the two original surfaces and the area bounded by this line and the wear trace (shown cross-hatched Fig.21b) was determined using a planimeter. A mean wear area was then determined from the four wear traces.

A wear profile obtained from shape 5 is shown in Fig.22. The original surface was again marked and the height of the wear trace, as measured against the original surface, was determined.

A talyrond wear trace obtained from shape 6 is illustrated in Fig.23 and shows the wear pattern superimposed on a master circle. The master circle represents the position of the original surface of the die and divides the wear pattern into two areas, one above and one below, the circle. The area above the master

circle was considered to represent deformation while the area below the circle represented erosion. These areas were both measured using a planimeter.

8.3.3

Large shaped dies

No quantitative wear measurements were made on the wear traces obtained from the large die shapes.

8.4   Evaluation of Coatings After the Forging Test

8.4.1

Preparation and examination of taper sections

Taper sections were prepared in a similar manner to that devised by Samuels[76] and were used primarily to detect cracking in the surface layers of the die, to observe the soundness of the bond between the electrodeposit and the die substrate and to detect penetration of the electroplated coating during the forging test.   After the wear evaluation had been carried out the die was cut into sections as illustrated in Fig.10 using an abrasive slitting wheel.   A section from the centre of the die which included part of the wear region, Figs 24a and b, was mounted face upwards in thermosetting plastic so that approximately 0.6cm of plastic remained above the surface of the sample.   The mounted specimen was clamped in a jig consisting of a parallel faced steel block approximately 1,8cm thick with a hole, the diameter of the mounted specimen, machined in the centre at an angle of 5° 44' to the vertical.   This angle resulted in a magnification of 10:1.   The sample was then surface ground to approximately

Central
Plateau

Wear
Ring

a

Perspex

b

Fig.24.   Taper section preparation.
   a)   Sample as cut from die
   b)   Sample in mount after grinding

the right position, Fig.24b, final metallographic preparation
being carried out in the usual manner.   All samples were etched
in 2% Nital.

The original technique as devised by Samuels[76]
included the use of a fine gauge wire attached by a thick electro-
deposit to the surface to be tapered.   During grinding and
polishing an elipse was produced on the wire and by measuring
the major and minor axes of this elipse and then dividing the
latter into the former the exact taper magnification could be
obtained.   This technique was used initially, the wires being
soft soldered to the sample and not attached by electrode position,
but the good reproducability of the taper using the jig was such
that it was discarded for subsequent work.   The inclusion of the
wire obviously gave a very exact measure of the taper magnification
produced on each sample but as the deposit thickness varied
slightly from die to die little could be gained from an exact
measure of crack depth.

8.4.2

Examination of worn die surfaces using the S.E.M.

Samples for S.E.M. examination were cut from the flat
dies as shown in Fig.10 in order to include the central plateau
region, the wear ring and a small part of the undamaged surface
outside the wear region.   The specimens were mounted on stubs in
the usual manner and examined directly.

9. DEVELOPMENT OF THE SODIUM HEPTONATE BATH FOR THE DEPOSITION OF COBALT-MOLYBDENUM AND COBALT-TUNGSTEN ALLOYS

9.1 Deposits Obtained from Previous Bath Formulations

Before commencing development of the cobalt-molybdenum and cobalt-tungsten alloy baths which are the subject of this work it was thought that deposits should be obtained from some of the previously formulated baths. This was considered to be particularly important in the case of the Prosser patent[69] as this was the only bath which had been used for the plating of dies. In producing deposits from several types of bath some knowledge could be gained as to the quality of electrodeposits which could be expected from these alloy systems.

Table II gives a list of baths used together with their relevant sources. The three main types of bath used, as can be seen from the Table, are those incorporating sodium citrate, Rochelle salt and citric acid.

9.1.1

Sodium citrate baths for depositing cobalt-molybdenum and cobalt-tungsten alloys

Hull cell test panels were produced using the cobalt-molybdenum bath proposed by Ernst et al[39]. A current of 3A was passed through the cell for 15 min. There was very little deposit obtained on the Hull cell panel, the majority of the surface becoming passive during plating. While operating this solution it was noticed that the current gradually decreased on plating,

TABLE II.   Cobalt Alloy Plating Baths Developed by Previous Workers

Cobalt-Molybdenum Alloys   Source

    Cobaltous Sulphate   90 g/ℓ)   D.W.Ernst, R.F.Amlie
    Sodium Molybdate   48 g/ℓ)   and M.L.Holt. [39]
    Sodium Citrate   105 g/ℓ)
        Temp. 25° C, pH 10.5, c.d. 10A/dm^2

    Cobaltous Sulphate   50 g/ℓ)   A.Brenner and
    Sodium Molybdate   125 g/ℓ)   G.E.Riddell. [59]
    Rochelle Salt   150 g/ℓ)
        Temp. 25° C, pH 2-3, c.d. 2-6A/dm^2

Cobalt-Tungsten Alloys

    Cobaltous Chloride   120 g/ℓ)   A.Brenner, P.S.Burkhead
    Sodium Tungstate   45 g/ℓ)   and E.Seegmiller. [50]
    Rochelle Salt   400 g/ℓ)
    Ammonium Chloride   50 g/ℓ)
        Temp. 95° C, pH 9.0, c.d. 2A/dm^2

    Cobaltous Sulphate   170 g/ℓ)   Ibid
    Sodium Tungstate   10 g/ℓ)
    Sodium Citrate   200 g/ℓ)
    Ammonium Chloride   50 g/ℓ)
        Temp. 95° C, pH 9.0, c.d. 2A/dm^2

Example 1.*

    Cobaltous Sulphate   60 g/ℓ)   I.C.I. (Australia) Ltd. [70]
    Sodium Tungstate   70 g/ℓ)
    Citric Acid (Monohydrate) 66 g/ℓ)
    Ammonium Sulphate   50 g/ℓ)
        Temp. 70° C, pH 7-8 (using NH$_3$ aq.), c.d. 10A/dm^2

Example 5.*

    Cobaltous Sulphate   40 g/ℓ)   Ibid
    Sodium Tungstate   100 g/ℓ)
    Citric Acid (Monohydrate)120 g/ℓ)
    Ammonium Chloride   50 g/ℓ)
        Temp. 60° C, pH 6.5 (using NaOH), c.d. 15A/dm^2

TABLE II. (Contd.)

Example 6.*

Cobaltous Sulphate	59 g/ℓ	)	Ibid
Sodium Tungstate	69.4 g/1ℓ	)	
Citric Acid	71.5 g/ ℓ	)	

Temp. 80° C, pH 6.5 (using NaOH), c.d. 20A/dm^2.

Operating Conditions used by Prosser.[69] :-

Temp. 55° C, pH $\sim$ 8.5, c.d. 5A/dm^2

* Cobalt anodes were used in place of platinised titanium
as stated in the patent specification.

presumably due to polarisation. The solution also had a very high internal resistance: it was only possible to apply 3A to the cell at the maximum available voltage of 12V. This resistance resulted in the bath temperature rising from 25-50°C while plating the Hull cell panel.

The bath suggested by Brenner et al[50] for the deposition cobalt-tungsten alloys was next investigated. Hull cell panels were not used to assess the plating characteristics in this case as a very high operating temperature of 95°C was required for the bath making impossible the use of the perspex Hull cell. Brass panels of size 5cm x 10cm were therefore plated in a glass beaker at a uniform current density of $2A/dm^2$. Deposits obtained from this bath were crack-free and had a satin appearance. They were brittle and cracked readily on slight bending of the substrate. The use of this bath presented difficulties as regards to the control of pH which was required to be pH 9.0 adjusted by the use of aqueous ammonia. As can be appreciated with a bath temperature of 95°C this was not easily achieved when long plating times were employed. The copious ammonia fumes produced from the bath during the plating operation would also become a serious hazard if large scale plating operations were carried out.

9.1.2

Rochelle salt baths for depositing cobalt-molybdenum and cobalt-tungsten alloys

Hull cell tests were carried out on the cobalt-molybdenum solution due to Brenner and Ridell[59]. A plating current of 1A was passed through the cell for 15 min. Copious gas evolution

was experienced at the cathode during plating and passivation occurred extensively. The other Rochelle salt type bath investigated was that proposed by Brenner et al[50] for the deposition of cobalt-tungsten alloys. Brass panels as mentioned previously were used as the cathode due to the high operating temperature of the bath. A uniform current density of $2A/dm^2$ was employed which produced a dull, severely cracked deposit.

9.1.3

Citric acid baths for depositing cobalt-tungsten alloys

The particular bath investigated was proposed for "Improvements in tools for working metals" by C.A. Prosser[69] in British Patent Specification No.1,243,205. The basic solution formulation had been taken from British Patent Specification No.959,498 which had been filed by I.C.I. (Australia) Ltd[70] for use in plating titanium fuel cell elements. In general the current density and bath temperature used in the Prosser specification were lower than those employed in the I.C.I. specification which the pH of the bath was higher (see Table II). The Prosser specification did not specify an exact bath formulation, it merely stated, "the plating solution being substantially as described in those examples of British Patent Specification No.959,498 referring to the deposition of cobalt-tungsten alloys." There were three such baths mentioned in the specification and they were thus all tried. Their exact composition and operating conditions are given in Table II. They will be referred to by their numbers as given in the Patent Specification No.959,498. The brass panels mentioned previously were used as cathodes.

Example 1

The deposit obtained after 1 hr. plating operating under
the I.C.I conditions had a matt grey appearance and was very
nodular.   The deposit was extremely brittle and flaked from
the substrate with minimal bending.   The scanning electromicro-
graphs shown in Fig.25a illustrate the very nodular surface
topography of the deposit.   Several flakes of the deposit were
analysed by wet chemical methods and found to contain 52% cobalt
and 48% tungsten.   During the plating operation the anode became
covered with an extremely thick, blue-white, powdery, deposit
which caused a drop in the plating current requiring a higher
applied voltage.   The extreme surface of this deposit was black
in colour.   This deposit did not redissolve in the plating solution.
The same solution formulation was then tried using the conditions
stated by Prosser.   After plating for 1 hour a deposit showing
very similar properties of brittleness and surface topography to
those exhibited by the I.C.I. deposit was produced (fig.25b).
A similar anode deposit was also obtained.   Chemical analysis
of this deposit gave a composition of 55% cobalt and 45% tungsten.

Example 5

Plating for 1 hour produced a bright but rough and
flaking deposit using the conditions stated by the I.C.I. patent.
The scanning electronmicrograph shown in Fig.26a was produced
from a flake of the deposit and chemical analysis of the deposit
showed that it contained 56% cobalt and 44% tungsten.   The
solution was very inefficient, considerable gassing of the cathode
occurred during plating, which caused the pH of the solution to

Aston University

Illustration removed for copyright restrictions

a)   I.C.I.[70] plating conditions x 300

Aston University

Illustration removed for copyright restrictions

b)   Prosser[69] plating conditions x 300

Fig.25.   Scanning electronmicrographs of cobalt-tungsten alloys obtained from patent bath.   Example 1.[70]

Aston University

Illustration removed for copyright restrictions

a) I.C.I.[70] plating conditions x 300

Aston University

Illustration removed for copyright restrictions

b) Prosser[69] plating conditions x 2000

Fig.26. Scanning electronmicrographs of cobalt-tungsten alloys obtained from patent bath. Example 5.[70]

rise. This increase in pH caused an anode deposit to be produced leading to a decrease in the plating current. An electrodeposit was then obtained from this solution using the conditions stated by Prosser. A very heavy precipitate was produced on adjusting the pH of the bath to pH 8.5 with sodium hydroxide solution which did not dissolve on heating. A very unsatisfactory, powdery deposit was obtained from this solution and plating was discontinued after 15 min. Scanning electronmicrographs of the deposit were obtained, as shown in Fig.26b, but no chemical analysis of the deposit was attempted.

Example 6

Deposits obtained from this solution, after 1 hours plating at the I.C.I. conditions, were dendritic and peeled from the substrate. High gas evolution occurred during the plating operation but no anode deposit was produced. Scanning electronmicrographs of the deposit were obtained and are shown in Fig.27a. The deposit was found to contain a lower tungsten concentration, 31%, than deposits obtained from the other two baths. A deposit was also obtained using the conditions stated by Prosser. This deposit was smooth and dark grey in colour with good adhesion to the substrate but was very thin. High gas evolution at the cathode had been noticed during plating indicating a low cathode current efficiency. A black abode deposit was produced during plating which caused a fall in plating current. Scanning electronmicrographs of the deposit were obtained (Fig.27b) but no chemical analysis of the deposit could be attempted since it was so thin.

From the examination of the various baths cited by the

a) I.C.I.[70] plating conditions x 500

b) Prosser[69] plating conditions x 6000

Fig.27. Scanning electronmicrographs of cobalt-tungsten alloys obtained from patent bath. Example 6.[70]

I.C.I. patent it appears that only Example 6 would produce a deposit sufficiently sound for the use envisaged in the Prosser patent. However it is unlikely that this was the bath used because the time involved in producing a suitable thickness of alloy deposit from such an inefficient solution would be impracticable. It is also considered that the anode film formed during plating would cause considerable problems if lengthy plating operations were carried out using this bath. Consequently if this alloy bath has been exploited on a commercial basis some modifications, not disclosed in the Prosser patent, must have been made to either the bath composition or operating conditions.

The overall conclusions gained from the examination of all of the above bath formulations is that each formulation suffered from one or more of the following defects:-

1. Low efficiency resulting in considerable gas evolution during plating and consequently thin deposits.

2. High stress and brittleness leading to spontaneous peeling from the substrate during plating.

3. Operating conditions which were impracticable for length plating operations.

4. Dendritic, nodular or powdery deposits which were unsuitable for the application under consideration.

5. Build up of an anode deposit during plating which caused a fall in the operating current.

9.2 The Sodium Heptonate Bath for Depositing Cobalt-Molybdenum and Cobalt-Tungsten Alloys

Since the survey of cobalt-molybdenum and cobalt-tungsten baths indicated that a deposit suitable for coating hot forging dies was unlikely to be obtained using previous formulations, a bath composition was therefore devised based on a nickel molybdenum alloy plating bath containing sodium heptonate as the complexing agent. This acid type bath, formulated by Dennis[77], was known to give satisfactory deposits containing up to 5% molybdenum. The cobalt-molybdenum bath was thus prepared by substituting cobalt salts for the nickel salts used in the nickel-molybdenum bath and the cobalt-tungsten bath by substituting both cobalt and tungsten salts for the nickel and molybdenum salts.

The exact formulation of the alloy baths was influenced by difficulties experienced when plating pure cobalt during evaluation of the cobalt-nickel series of alloys. The alloy bath used to deposit the cobalt-nickel alloys was based on a cobaltous sulphate concentration of 300g/l and this concentration was therefore used to deposit pure cobalt. Hull cell tests carried out with this solution indicated that the most satisfactory deposits were to be obtained at pH values between pH 3.0-5.0, B1, Fig.28. However dies plated on this bath at pH 4.0 and $4.0A/dm^2$ exhibited radial cracking of the electrodeposit at the edges and subsequent surface grinding resulted in the coating flaking from the steel substrate. In order to improve the quality of the deposit the cobaltous sulphate concentration of the solution was reduced to 150g/l,B3. Hull cell panels obtained from this bath,
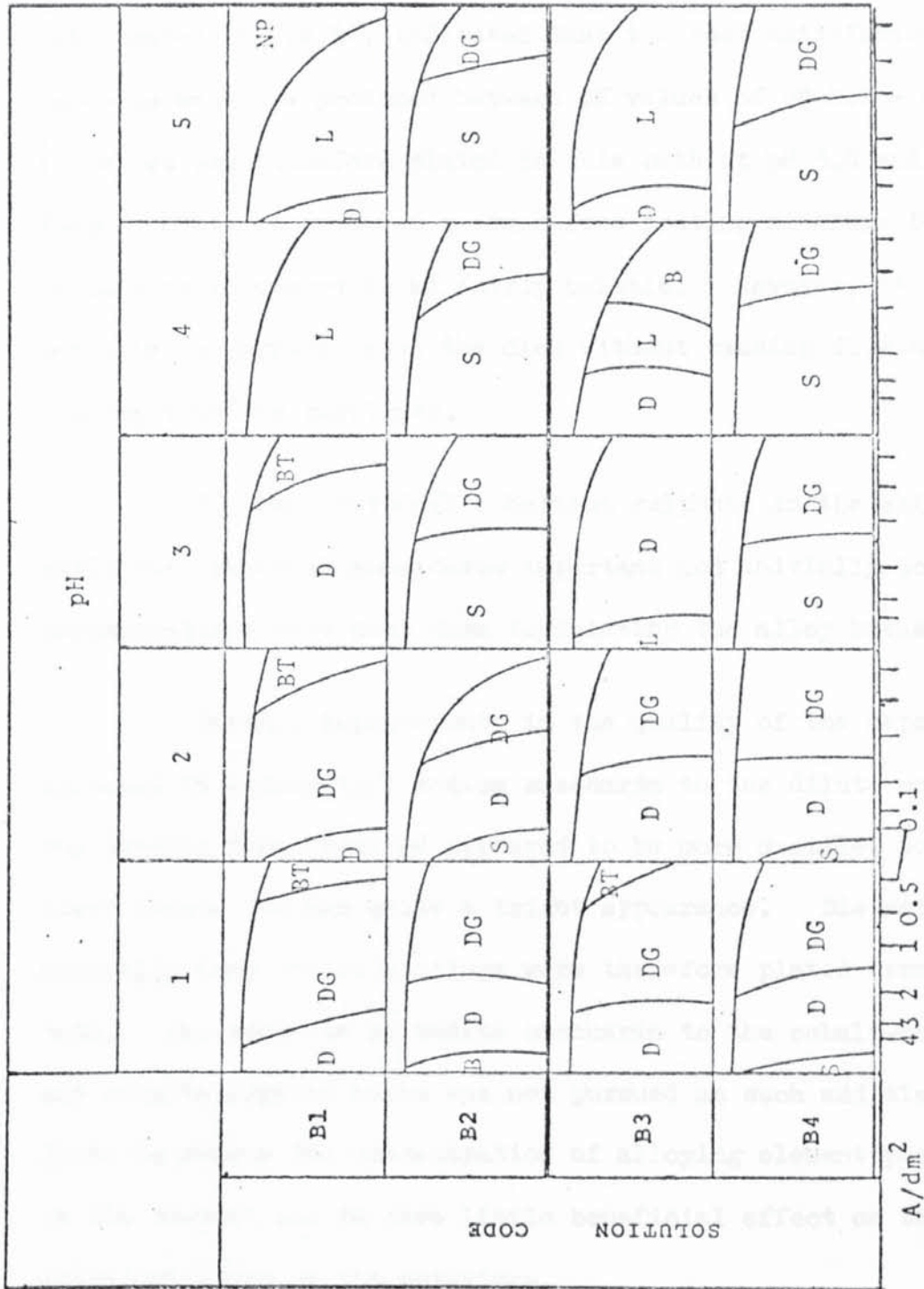
Fig.28. Appearance of Hull cell panels plated in solutions B1, B2, B3 and B4 at 55°C and various pH values.

CODE

B	Bright
BT	Bright but thin
D	Dull
DG	Dark Grey
G	Grey
L	Lustrous
NP	No Plate
P	Passive
S	Stressed and flaking
SC	Stressed and cracked

illustrated in Fig.28, indicated that the most satisfactory

deposits were now produced between pH values of pH 2.0 - 4.0.

A die set was therefore plated in this bath at pH 3.0 and $4.0A/dm^2$.

These conditions produced a crack-free coating although the

deposit still seemed to be fairly brittle.   However, it was

possible to surface grind the dies without causing flaking of the

coating from the substrate.

The use of 150g/l cobaltous sulphate in the alloy plating

baths was therefore considered important and initially both

concentrations were used when formulating the alloy baths.

Further improvements in the quality of the deposit were

achieved by adding 1g/l sodium saccharin to the dilute cobalt bath.

The deposit then obtained appeared to be more ductile, to have a

lower stress and had quite a bright appearance.   Die sets with

nominally pure cobalt coatings were therefore plated from this

bath.   The addition of sodium saccharin to the cobalt-molybdenum

and cobalt-tungsten baths was not pursued as such additions were

found to reduce the concentration of alloying element present

in the deposit and to have little beneficial effect on the plating

characteristics of the solutions.

9.2.1

Development of the sodium heptonate bath for the deposition

of cobalt-molybdenum alloys

Solutions containing both high and low cobaltous sulphate

concentrations were utilised initially having a concentration of

200g/l sodium heptonate, see Table III.   The Hull cell panels

TABLE III.   Cobalt-Molybdenum Solutions

Solution Code	BATH COMPOSITION g/ℓ				
	Cobaltous sulphate	Sodium Chloride	Boric Acid	Sodium Heptonate	Sodium Molybdate
B1	300	28	40	-	-
B2	300	28	40	200	-
M1	300	28	40	200	3.15
M2	300	28	40	200	6.30
M3	300	28	40	200	9.45
M4	300	28	40	200	12.60
M5	300	28	40	200	15.75
B3	150	28	40	-	-
B4	150	28	40	200	-
M6	150	28	40	200	3.15
M7	150	28	40	200	6.30
M8	150	28	40	200	9.45
M9	150	28	40	200	12.60
M10	150	28	40	200	15.75
M11	300	28	40	100	3.15
M12	300	28	40	100	6.30
M13	300	28	40	100	9.45
M14	300	28	40	100	12.60
M15	300	28	40	100	15.75
B5	150	28	40	100	-
M16	150	28	40	100	3.15
M17	150	28	40	100	6.30
M18	150	28	40	100	9.45
M19	150	28	40	100	12.60
M20	150	28	40	100	15.75
M21	150	28	40	100	18.90
M22	150	28	40	100	22.05

produced from these baths are illustrated in Figs.29 and 30.
These indicated that the characteristics of the two solutions
were similar above pH values of pH2; large stressed and flaking
areas of electrodeposit being present on all of the panels. At
pH values of pH2.0 and below there was a marked decrease in the
size of these areas, particularly on panels plated from the solutions
containing 150g/l cobaltous sulphate.

Although the above investigation indicated several baths
which gave satisfactory deposits, analysis of the alloys obtained
showed that only low concentrations of the alloying element were
present. In spite of this several dies coated with deposits from
certain of these baths exhibited reasonably good wear resistance
when subjected to the forging test. Since such low alloy contents
appeared to give encouraging results it was thought that deposits
containing higher percentages of the alloying element might produce
more wear resistant coatings.

The most obvious way of obtaining higher molybdenum contents
in the deposit was to raise the concentration of sodium molybdate
in the baths. This was not possible however because the Hull cell
tests indicated that very poor, cracked and flaking deposits were
obtained even at low pH values, when the sodium molybdate concentration
of the bath exceeded about 15g/l.

The other variable which could be altered, and one which
has the greatest influence on the composition of the deposit next
to the metal ion ratio of the bath, was the concentration of the
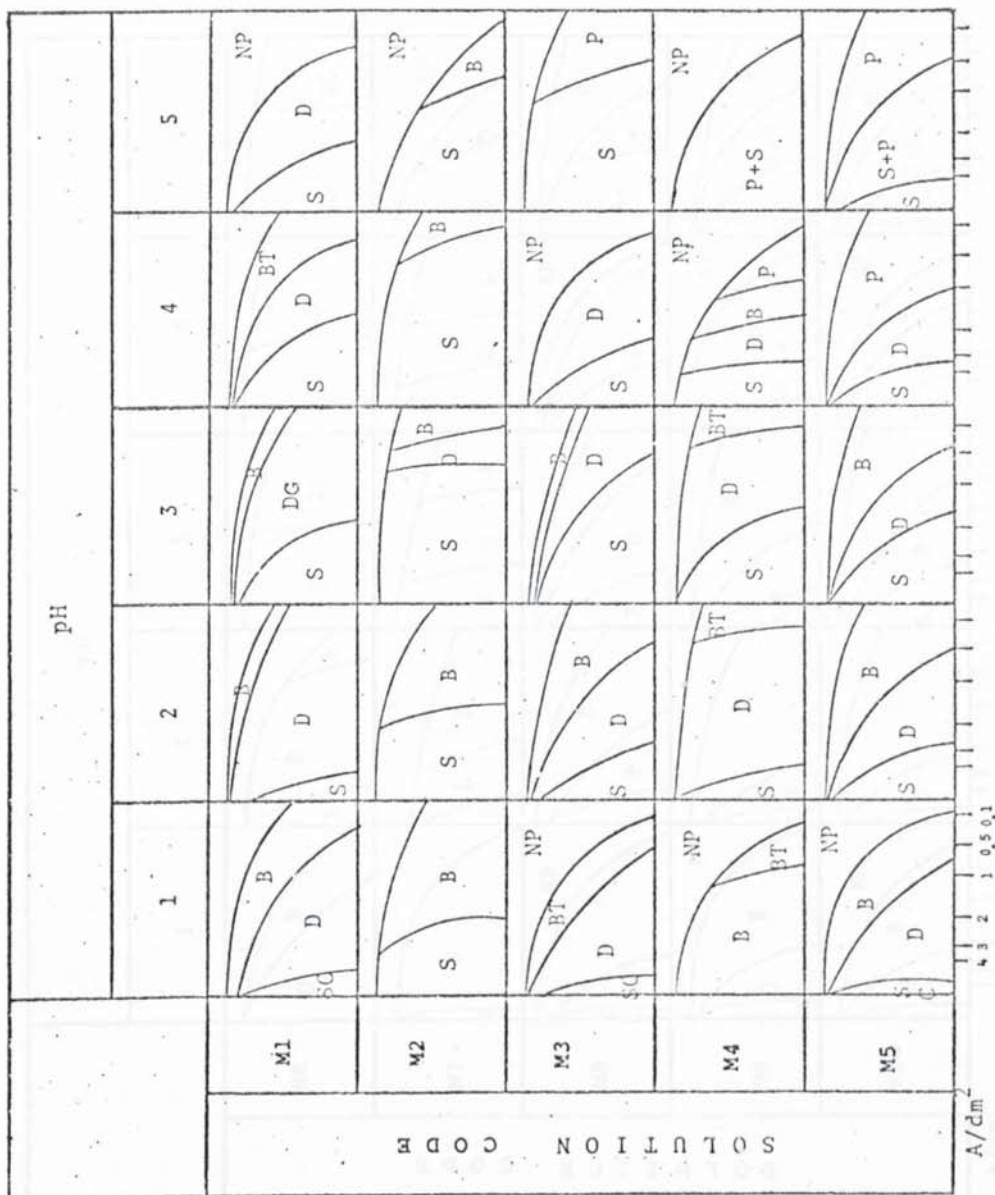
Fig.29. Appearance of Hull cell panels plated in solutions M1, M2, M3, M4 and M5 at 55°C and various pH values.
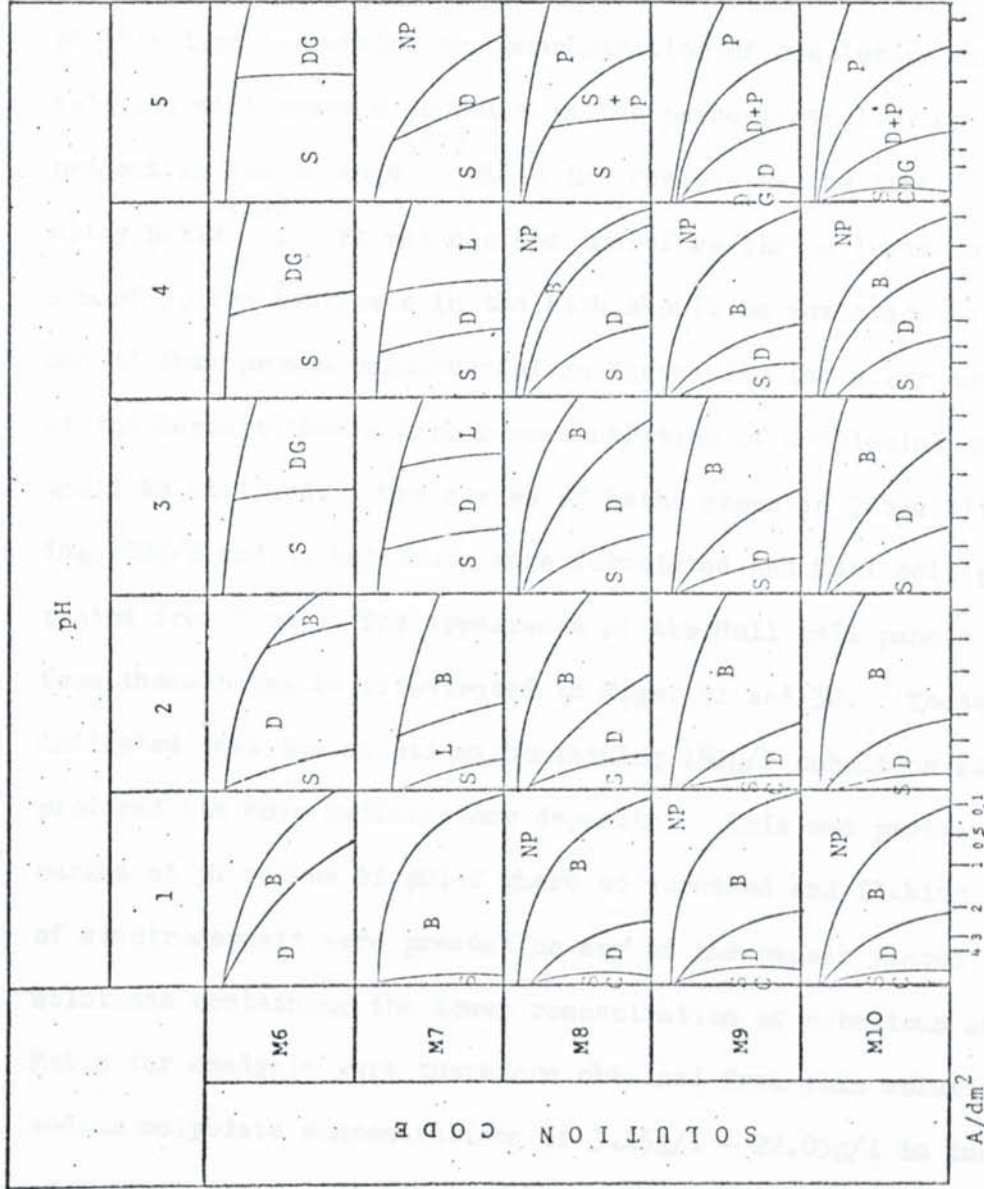
CODE

B	Bright
BT	Bright but thin
D	Dull
DG	Dark Grey
G	Grey
L	Lustrous
NP	No Plate
P	Passive
S	Stressed and flaking
SC	Stressed and cracked

Fig.30. Appearance of Hull cell panels plated in solutions M6, M7, M8, M9 and M10 at 55°C and various pH values.

CODE

B	Bright	
BT	Bright but thin	
D	Dull	
DG	Dark Grey	
G	Grey	
L	Lustrous	
NP	No Plate	
P	Passive	
S	Stressed and flaking	
SC	Stressed and cracked	

complexing agent. The role of complexing agents and their effects
on induced codeposition is not fully understood. In some baths
of this type increasing the concentration of complexing agent in
solution will cause a decrease in the percentage alloying element
present in the deposit [47] while the reverse may be true in other
alloy baths [39]. It was decided therefore that a lower concentrat-
ion of sodium heptonate in the bath should be investigated initially
and if this proved unsuccessful in increasing the alloy content
of the deposit then a higher concentration of complexing agent
would be utilised. The series of baths shown in Table III contain-
ing 100g/l sodium heptonate were formulated and Hull cell panels
plated from them. The appearance of the Hull cell panels obtained
from these baths is illustrated in Figs. 31 and 32. These
indicated that the solutions containing 150g/l cobaltous sulphate
produced the more satisfactory deposits. This was particularly
marked at pH values of pH1-2 where no stressed and flaking regions
of electrodeposit were present on any of the panels plated from
solutions containing the lower concentration of cobaltous sulphate.
Foils for analysis were therefore obtained from this solution at
sodium molybdate concentrations of 3.15g/l - 22.05g/l in increments
of 3.15g/l sodium molybdate. The plating conditions employed
were, current density 4.0 A/dm^2 and pH 1.5-2.0. The foils were
plated at two bath temperatures of 55-60°C and 70-75°C. The
higher bath temperature was employed as several baths of the induced
codeposition type investigated by Holt and co-workers [24,51] and
Brenner et al [50] had shown an increase in the amount of reluctant
metal in the electrodeposit with rise in temperature. The
composition of the foils obtained at both of these temperatures is
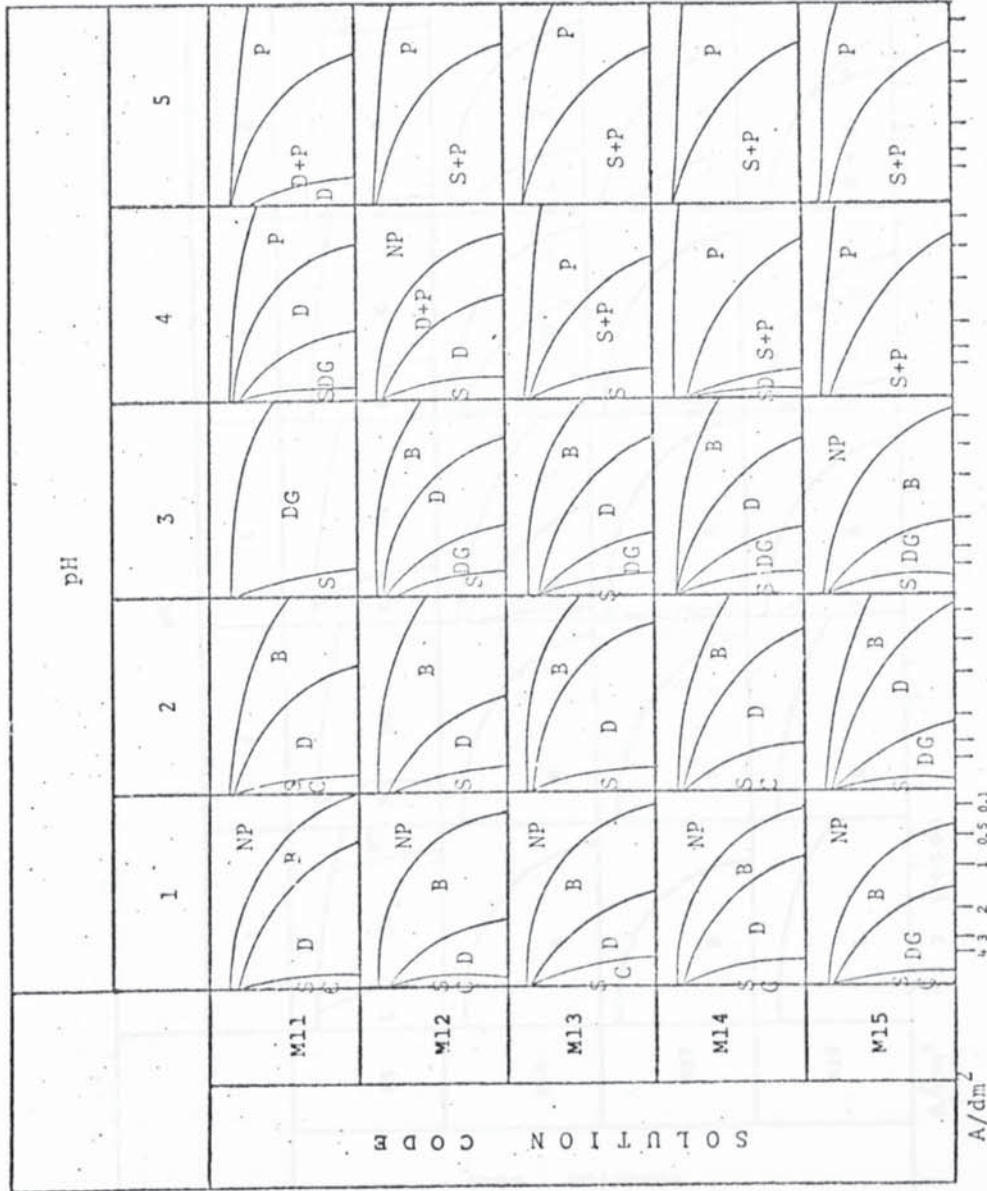
Fig.31. Appearance of Hull cell panels plated in solutions M11, M12, M13, M14 and M15 at 55°C and various pH values.
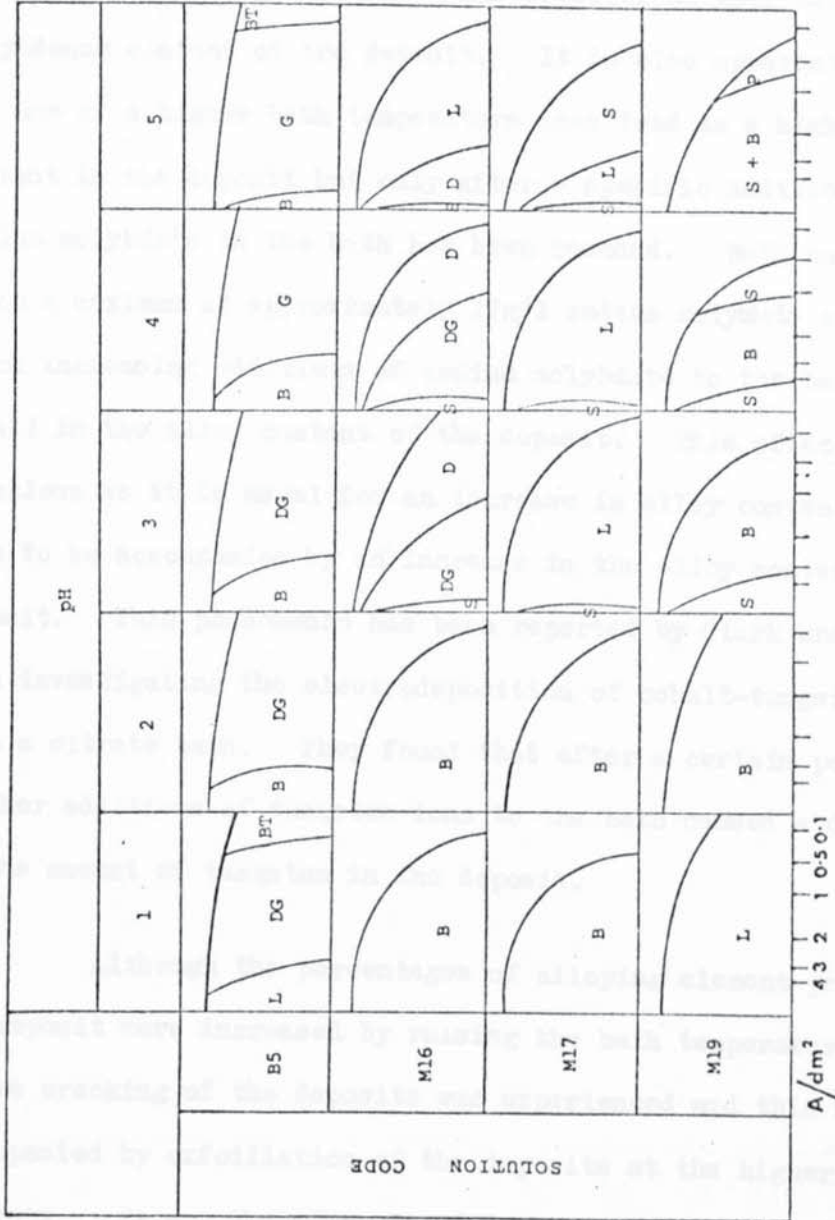
CODE

B	Bright
BT	Bright but thin
D	Dull
DG	Dark Grey
G	Grey
L	Lustrous
NP	No Plate
P	Passive
S	Stressed and flaking
SC	Stressed and cracked

Fig.32. Appearance of Hull cell panels plated in solutions B5, M16, M17 and M19 at 55°C and various pH values.

SOLUTION CODE

	pH				
	1	2	3	4	5
B5	L DG	B DG	B DG	B G	G BT
M16	B	B	DG D S	DG D L	D L
M17	B	B S	L B	L S B	S L S
M19	L	B S	S B	S B S	S+B P

A/dm² 4 3 2 1 0·5 0·1

CODE

Code	Meaning
B	Bright
BT	Bright but thin
D	Dull
DG	Dark Grey
G	Grey
L	Lustrous
NP	No Plate
P	Passive
S	Stressed and flaking
SC	Stressed and cracked

shown in Fig.33 and it can be seen that a lower concentration
of sodium heptonate in the bath has produced an increase in the
molybdenum content of the deposit.   It is also apparent that
the use of a higher bath temperature does lead to a higher alloy
content in the deposit but only after a specific addition of
sodium molybdate in the bath has been reached.   Both curves
reach a maximum at approximately 17g/1 sodium molybdate after
which increasing additions of sodium molybdate to the bath cause
a fall in the alloy content of the deposit.   This effect seems
anomalous as it is usual for an increase in alloy content of the
bath to be accompanies by an increase in the alloy content of the
deposit.   This phenomenon has been reported by Clark and Holt[47]
when investigating the electrodeposition of cobalt-tungsten alloys
from a citrate bath.   They found that after a certain point
further additions of tungsten ions to the bath caused a decrease
in the amount of tungsten in the deposit.

Although the percentages of alloying element present in
the deposit were increased by raising the bath temperature, quite
severe cracking of the deposits was experienced and this was
accompanied by exfoiliation of the deposits at the higher molybdenum
contents.   It was therefore decided that the lower temperature
bath was to be prefered for the present investigation as fairly
thick, sound deposits were essential for die plating.   It was
also apparent from these results that there was little point in
increasing the sodium molybdate content of the bath above 12.60g/1
as no increase in alloy content resulted.   The solutions chosen
for the plating of dies were therefore restricted to those containing
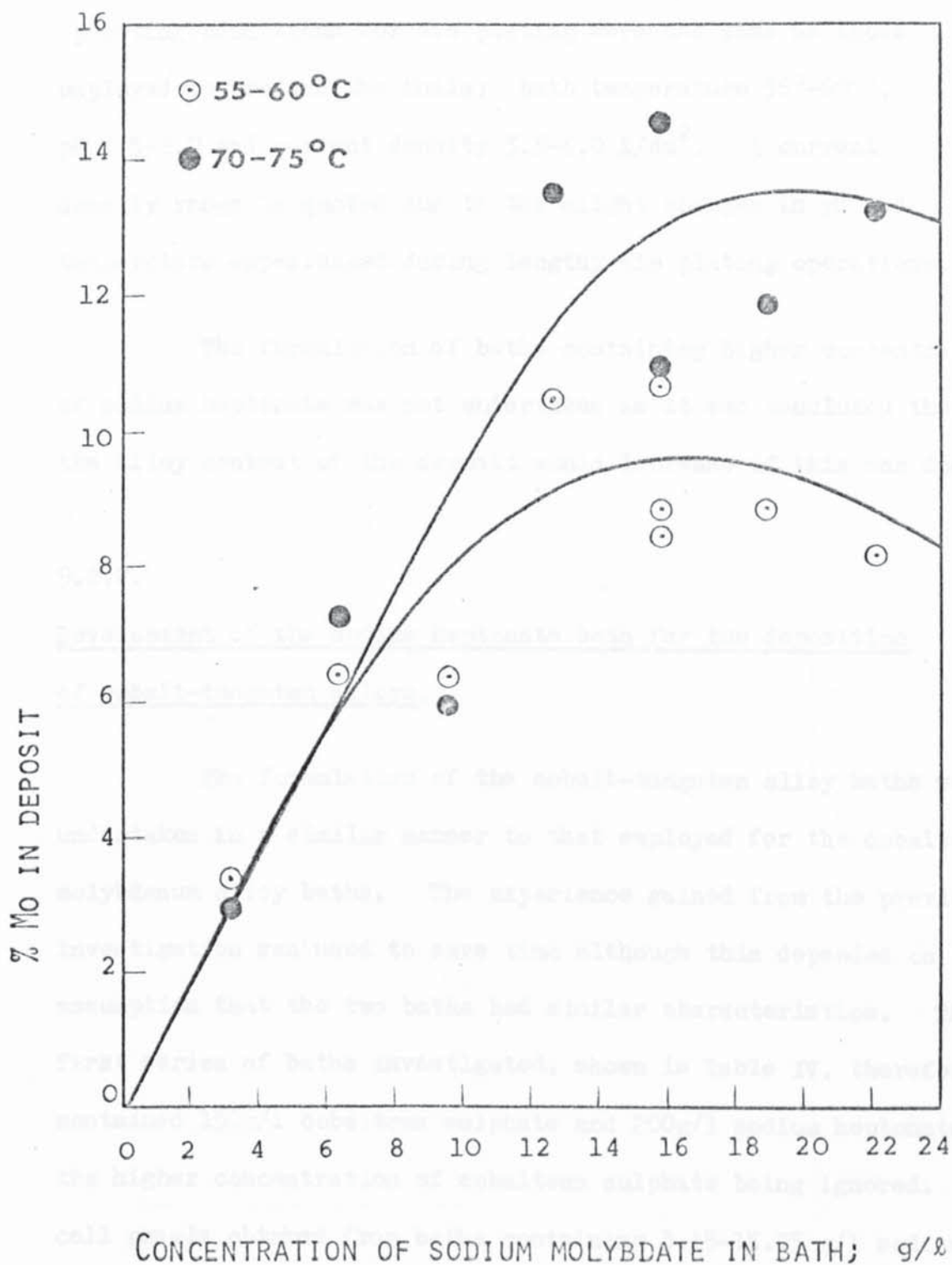
Fig.33. Relationship between the amount of sodium molybdate in solution and the percentage of molybdenum in the deposit.

sodium molybdate concentrations of between 3.15-12.60g/l. The operating conditions for die plating were the same as those employed to produce the foils; bath temperature 55°-60°C, pH 1.5-2.0 and current density 3.5-4.0 A/dm^2. A current density range is quoted due to the slight changes in pH and temperature experienced during lengthy die plating operations.

The formulation of baths containing higher concentrations of sodium heptonate was not undertaken as it was concluded that the alloy content of the deposit would decrease if this was done.

9.2.2.
Development of the sodium heptonate bath for the deposition of cobalt-tungsten alloys.

The formulation of the cobalt-tungsten alloy baths was undertaken in a similar manner to that employed for the cobalt-molybdenum alloy baths. The experience gained from the previous investigation was used to save time although this depended on the assumption that the two baths had similar characteristics. The first series of baths investigated, shown in Table IV, therefore contained 150g/l cobaltous sulphate and 200g/l sodium heptonate, the higher concentration of cobaltous sulphate being ignored. Hull cell panels obtained from baths containing 3.15-15.75 g/l sodium tungstate are illustrated in Fig.34. The panels indicated that very poor deposits were obtained above pH2.0, large stressed and flaking areas being present as with the cobalt-molybdenum alloys obtained from this bath composition. Foils for analysis were

TABLE IV. Cobalt-Tungsten Solutions

Solution Code	BATH COMPOSITION, g/ℓ				
	Cobaltous Sulphate	Sodium Chloride	Boric Acid	Sodium Heptonate	Sodium Tungstate
W1	150	28	40	200	3.15
W2	150	28	40	200	6.30
W3	150	28	40	200	9.45
W4	150	28	40	200	12.60
W5	150	28	40	200	15.75
W6	300	28	40	100	3.15
W7	300	28	40	100	6.30
W8	300	28	40	100	9.45
W9	300	28	40	100	12.60
W10	300	28	40	100	15.75
W11	150	28	40	100	15.75
W12	150	28	40	100	31.50
W13	150	28	40	100	47.25
W14	150	28	40	100	63.00
W15	150	28	40	100	78.75
W16	150	28	40	100	94.50
W17	150	28	40	200	47.25
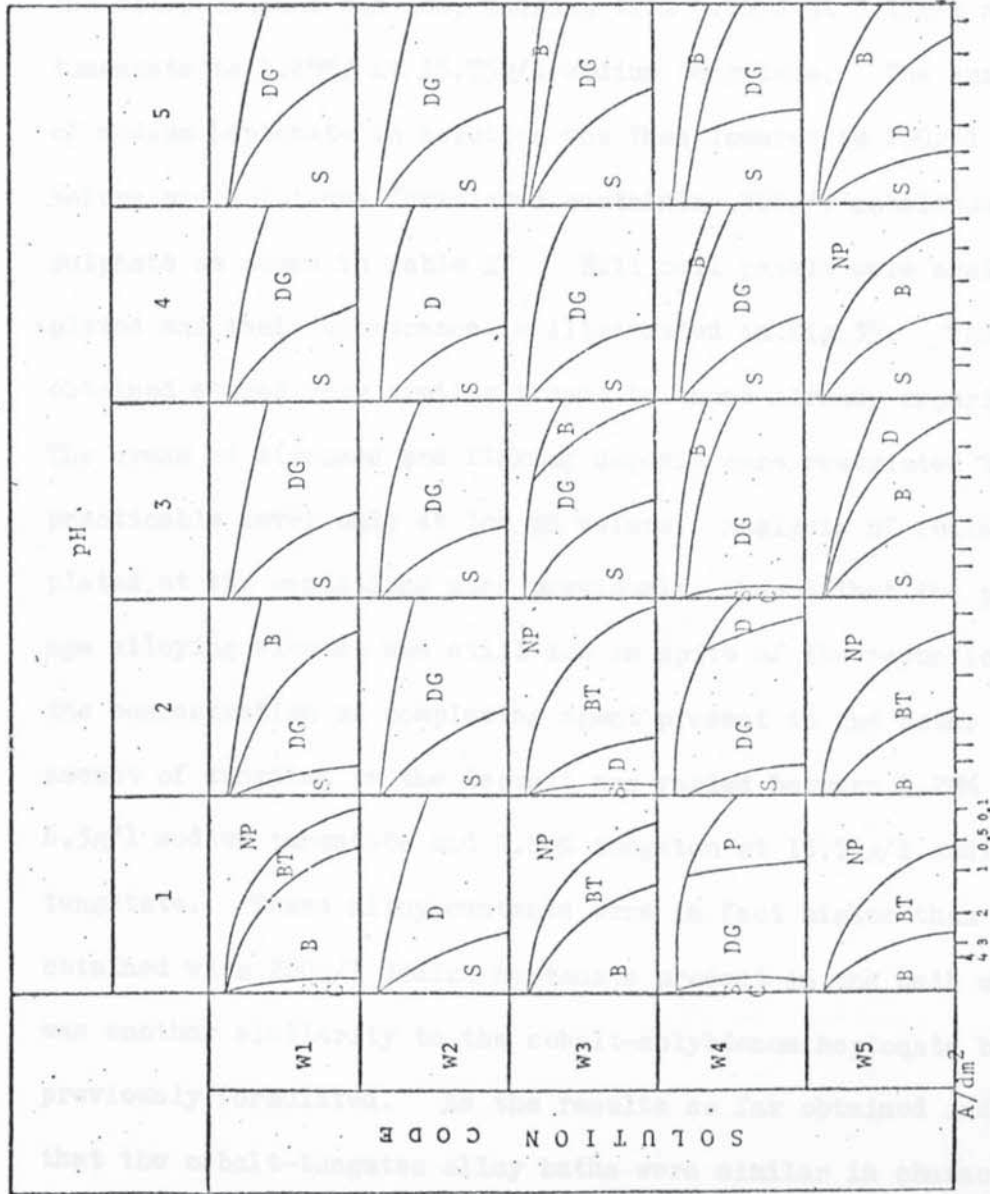
CODE

B — Bright
BT — Bright but thin
D — Dull
DG — Dark Grey
G — Grey
L — Lustrous
NP — No Plate
P — Passive
S — Stressed and flaking
SC — Stressed and cracked

Fig. 34. Appearance of Hull cell panels plated in solutions W1, W2, W3, W4 and W5 at 55°C and various pH values.

therefore plated at pH 1.5-2.0 and 3.5A/dm^2. This showed that
the alloy content was low, ranging from 0.66%W at 3.15g/l sodium
tungstate to 1.45%W at 15.75g/l sodium tungstate. The quantity
of sodium heptonate in solution was then lowered to 100g/l as
before and solutions formulated containing 300g/l cobaltous
sulphate as shown in Table IV. Hull cell panels were again
plated and their appearance is illustrated in Fig.35. The deposits
obtained showed very similar trends to those already experienced.
The areas of stressed and flaking deposit were restricted to a
practicable level only at low pH values. Analysis of foils,
plated at the conditions used previously, showed that the percent-
age alloying element was still low in spite of the reduction in
the concentration of complexing agent present in the bath. The
amount of tungsten in the deposit now varied between 1.28% at
6.3g/l sodium tungstate and 2.86% tungsten at 15.75g/l sodium
tungstate. These alloy contents were in fact higher than those
obtained with 200g/l sodium heptonate present in the bath which
was another similarity to the cobalt-molybdenum heptonate baths
previously formulated. As the results so far obtained indicated
that the cobalt-tungsten alloy baths were similar in character to
the cobalt-molybdenum baths several bath variables were changed
simultaneously and a series of foils plated at 4.0 A/dm^2, pH 1.5 -
2.0 and 55°C. The bath compositions employed are given in Table IV.
The solution used was basically the same as the cobalt-molybdenum
bath finalised for die plating in that it contained 150g/l cobaltous
sulphate and 100g/l sodium heptonate. The concentration of the
alloying element present in the bath however was considerably
increased and additions were made to the bath until very severe
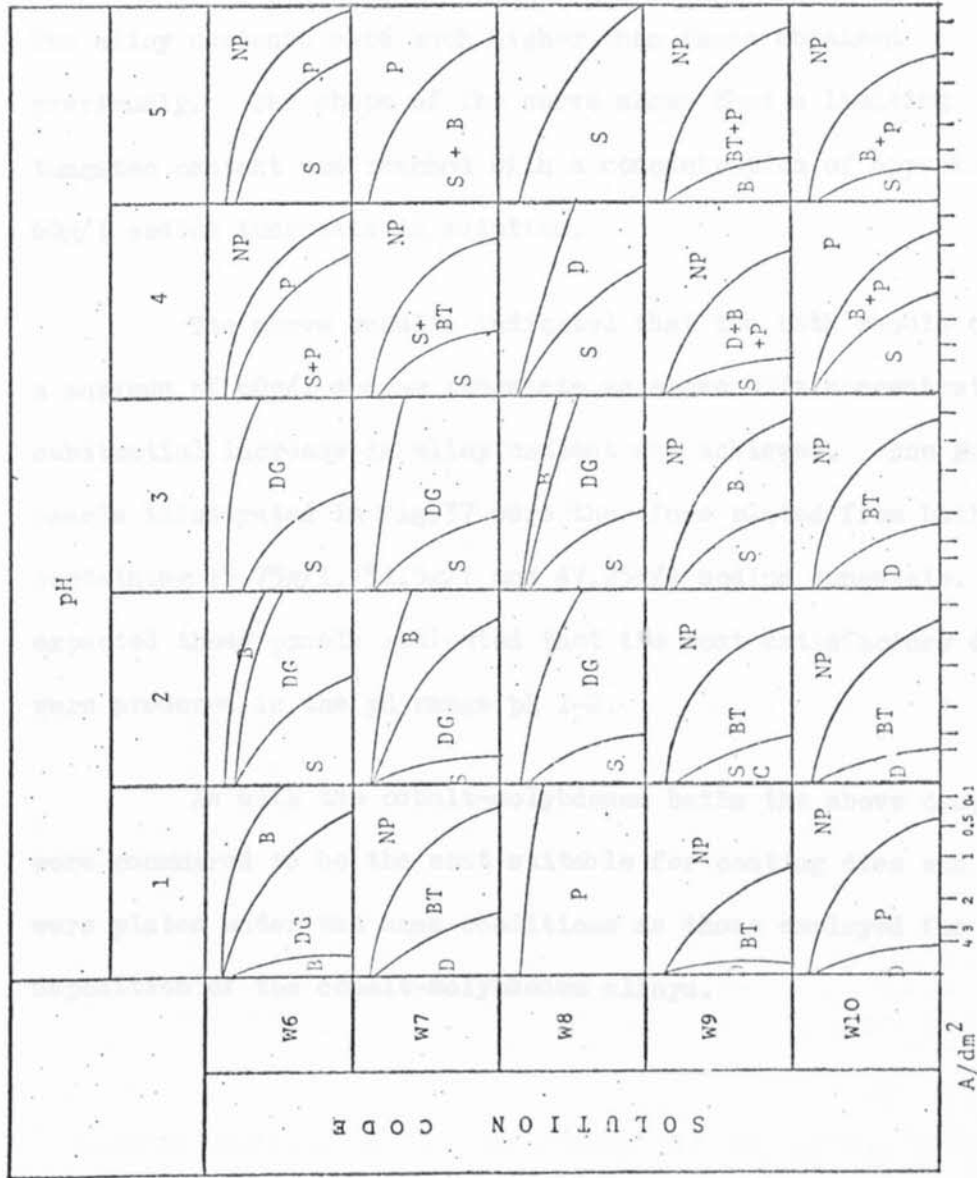
Fig.35. Appearance of Hull cell panels plated in solutions W6, W7, W8, W9 and W10 at 55°C and various pH values.

CODE

B   Bright

BT Bright but thin

D   Dull

DG Dark Grey

G   Grey

L   Lustrous

NP No Plate

P   Passive

S   Stressed and flaking

SC Stressed and cracked

cracking and flaking of the deposit was experienced. The
analysis of the foils obtained is shown graphically in Fig.36.
The alloy contents were much higher than those obtained
previously. The shape of the curve shows that a limiting
tungsten content was reached with a concentration of approximately
60g/l sodium tungstate in solution.

The above results indicated that the bath should contain
a maximum of 60g/l sodium tungstate as above this concentration no
substantial increase in alloy content was achieved. The Hull cell
panels illustrated in Fig.37 were therefore plated from baths
containing 15.75g/l, 31.5g/l and 47.25g/l sodium tungstate. As
expected these panels indicated that the most satisfactory deposits
were produced in the pH range pH 1-2.

As with the cobalt-molybdenum baths the above compositions
were considered to be the most suitable for coating dies and die sets
were plated under the same conditions as those employed for the
deposition of the cobalt-molybdenum alloys.
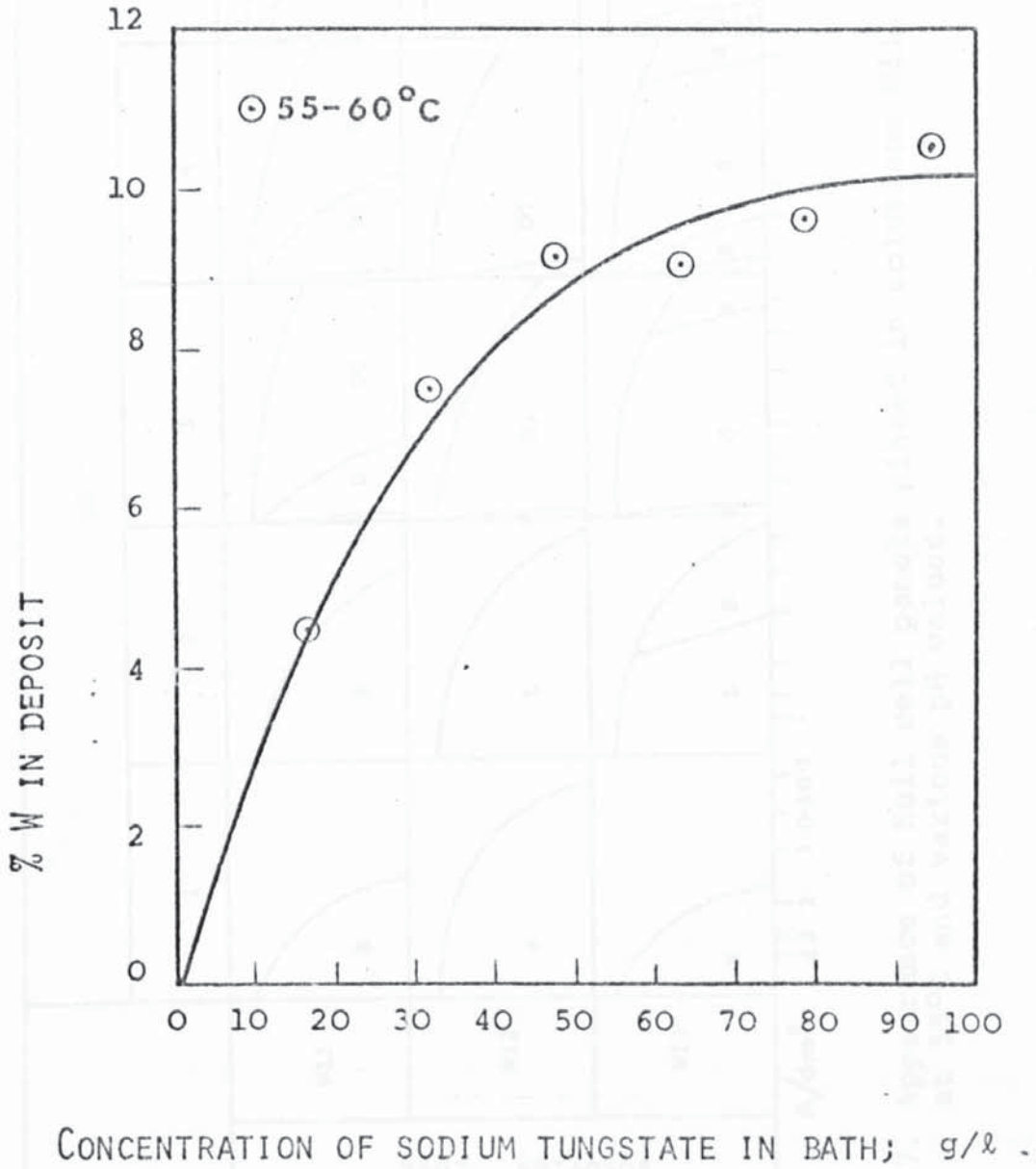
Fig.36. Relationship between the amount of sodium tungstate in solution and the percentage of tungsten in the deposit.
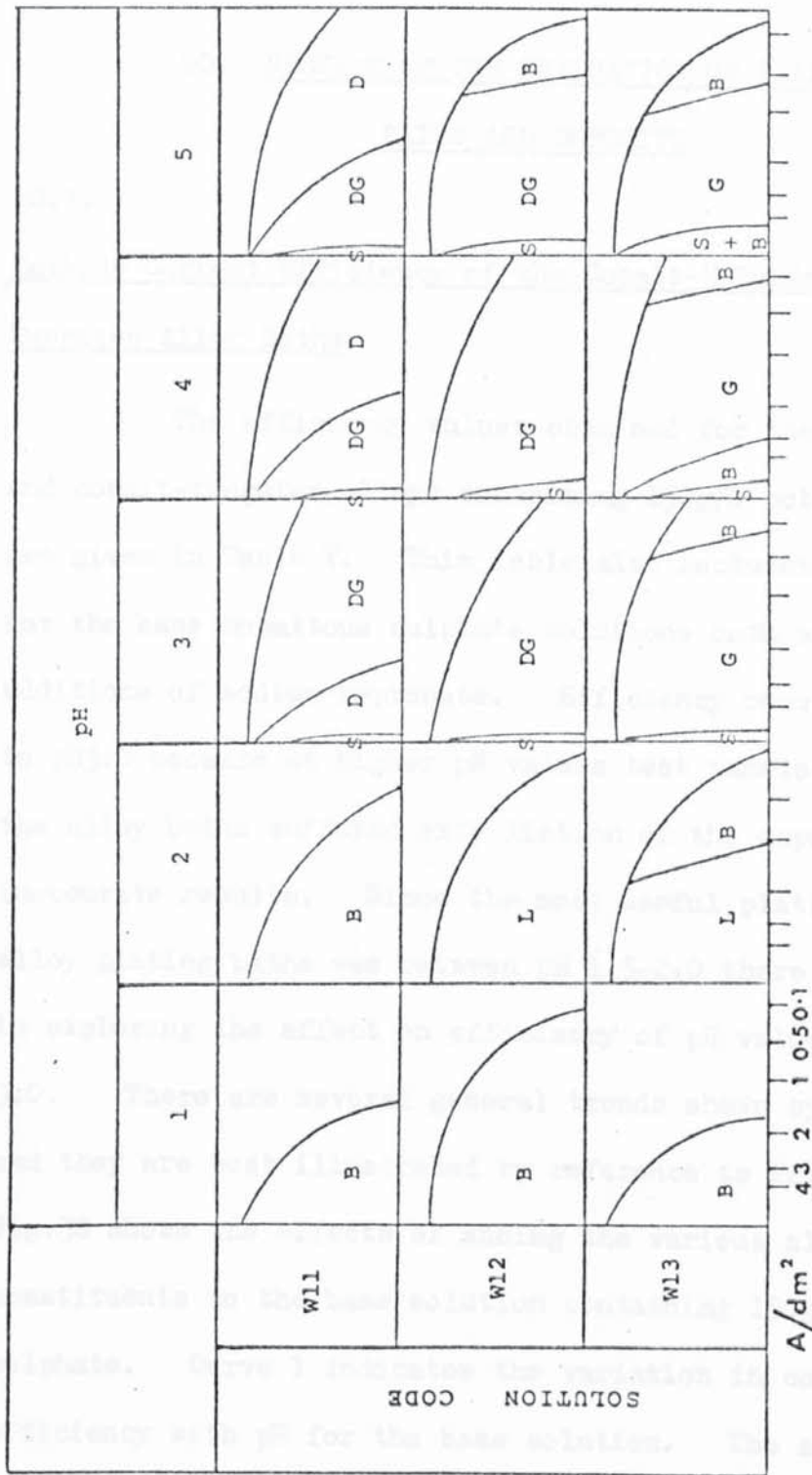
CODE

B	Bright
BT	Bright but thin
D	Dull
DG	Dark Grey
G	Grey
L	Lustrous
NP	No Plate
P	Passive
S	Stressed and flaking
SC	Stressed and cracked

pH

SOLUTION CODE	1	2	3	4	5
W11	B	B	S / D / DG	S / D / DG	S / D / DG
W12		L	DG	DG	S / DG / B
W13	B	L / B	B / S / G	B / S / G	S+B / G

A/dm² 43 2 1 0·5 0·1

Fig.37. Appearance of Hull cell panels plated in solutions W11, W12 and W13 at 55°C and various pH values.

10. RESULTS OF THE EVALUATION OF PLATING

BATHS AND DEPOSITS

10.1.

Cathode Current Efficiency of the Cobalt-Molybdenum and Cobalt-Tungsten Alloy Baths.

The efficiency values obtained for the cobalt-molybdenum and cobalt-tungsten alloys containing 150g/1 cobaltous sulphate are given in Table V. This table also includes efficiency values for the base cobaltous sulphate solutions both with and without additions of sodium heptonate. Efficiency results are only shown to pH3.0 because at higher pH values test panels plated in some of the alloy baths suffered exfo.liation of the deposit leading to inaccurate results. Since the most useful plating range of the alloy plating baths was between pH 1.5-2.0 there was little advantage in exploring the effect on efficiency of pH values in excess of 3.0. There are several general trends shown by these results and they are best illustrated by reference to Figs. 38 and 39. Fig.38 shows the effects of adding the various alloy bath constituents to the base solution containing 150g/1 cobaltous sulphate. Curve 1 indicates the variation in cathode current efficiency with pH for the base solution. The addition of 100g/1 sodium heptonate to the bath decreased the efficiency as illustrated by curve 2. The efficiency was depressed still further by the addition of either molybdate or tungstate ions. Curves 3 and 4 show examples of this phenomenon and relate to a sodium molybdate concentration of 12.6g/1 (5g/1 Mo) and a sodium tungstate concentration of 15.75g/1 (8.75g/1 W) respectively. The cobalt-tungsten bath

TABLE V. Efficiencies of Cobalt-Molybdenum and Cobalt-Tungsten
Electrodeposits

Solution Code	% Efficiency				
	pH1	pH2	pH3	pH4	pH5
B1	90	94	98	98	100
B2	78	85	93	95	96
B3	85	94	98	98	99
B4	63	82	98	90	97
B5	74	89	97	-	-
M6	61	75	81	80	85
M16	62	77	88	-	-
M17	53	68	87	-	-
M19	41	56	74	-	-
W11	40	58	91	-	-
W12	33	69	87	-	-
W13	41	61	85	-	-
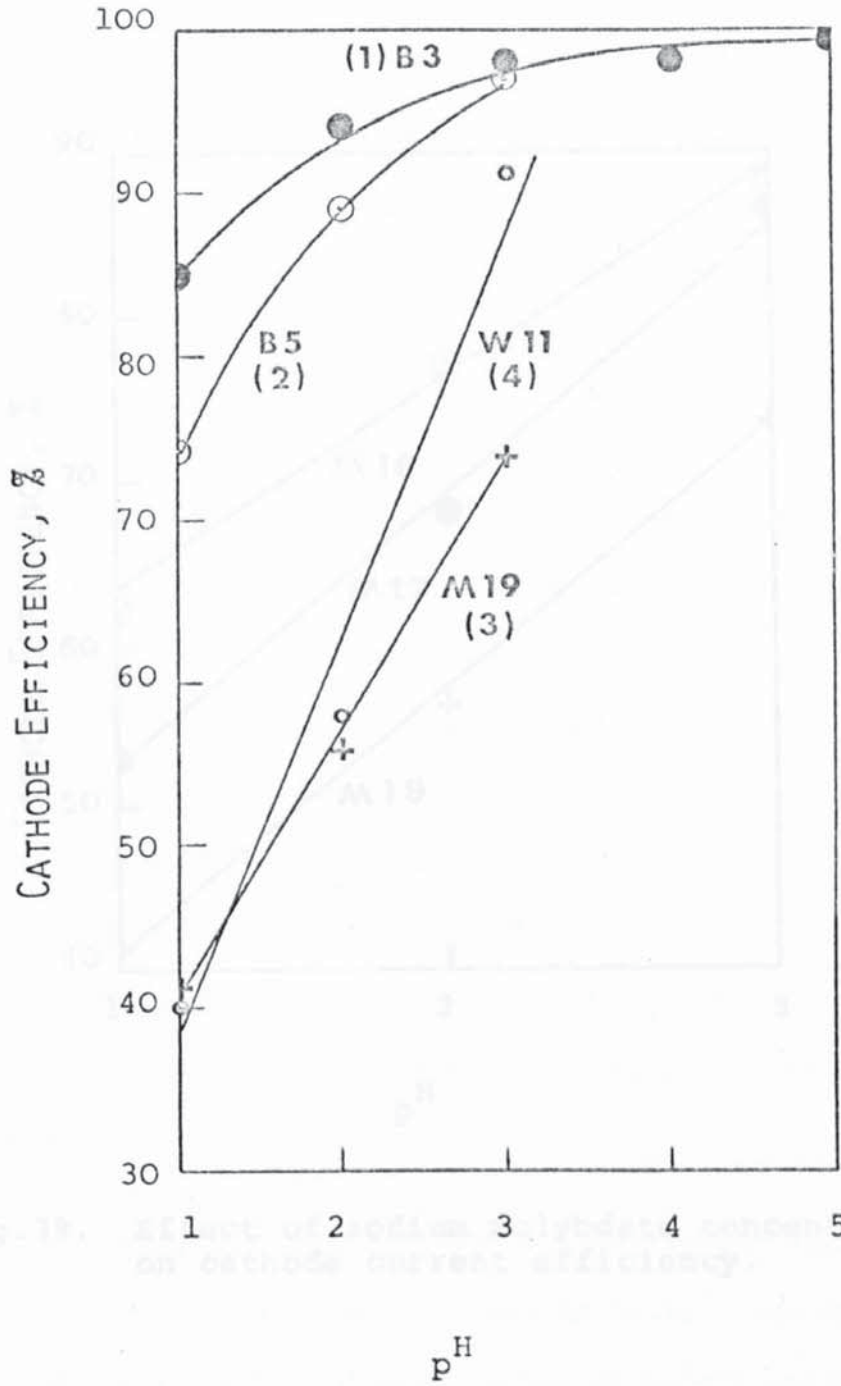
Fig.38. Effect of pH on cathode current efficiency.
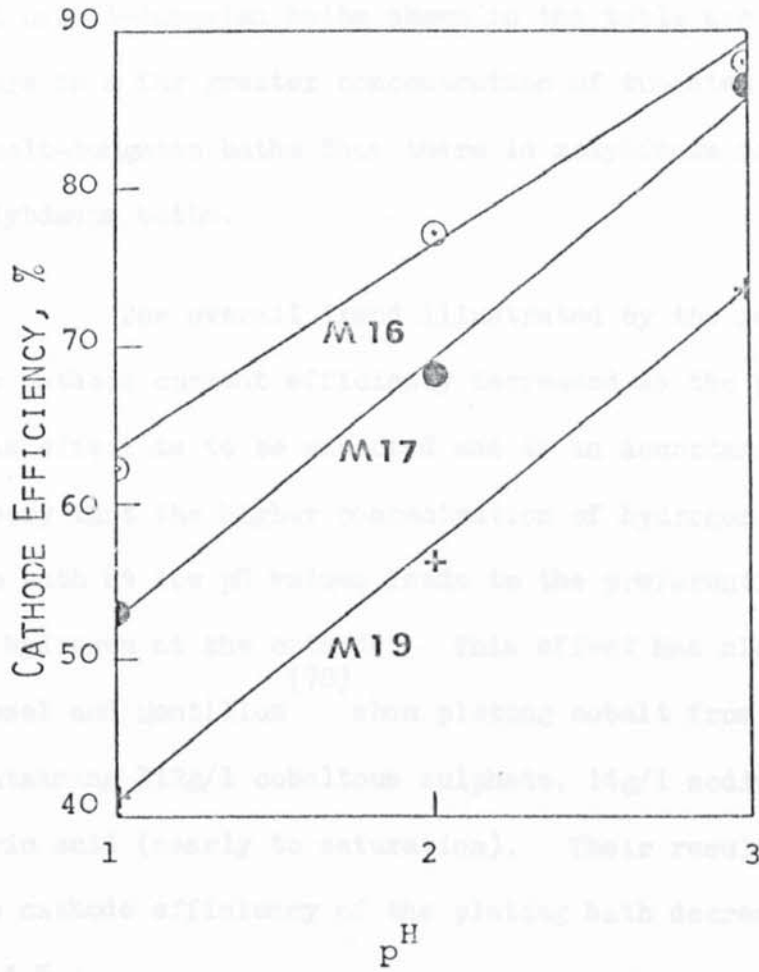
Fig.39. Effect of sodium molybdate concentration
on cathode current efficiency.

appears to have a greater efficiency than the cobalt-molybdenum bath at the higher pH values even though it contains a greater concentration of reluctant metal ions in solution. Further comparison between the efficiency of the other cobalt-molybdenum and cobalt-tungsten baths shown in the table are not valid since there is a far greater concentration of tungsten ions in the cobalt-tungsten baths than there is molybdenum ions in the cobalt-molybdenum baths.

The overall trend illustrated by the results is that the cathode current efficiency decreased as the pH was lowered. This effect is to be expected and is in accordance with accepted theory that the higher concentration of hydrogen ions present in the bath at low pH values leads to the preferential discharge of hydrogen at the cathode. This effect has also been noted by Cassel and Montillon[78] when plating cobalt from a solution containing 312g/l cobaltous sulphate. 14g/l sodium fluride and boric acid (nearly to saturation). Their results showed that the cathode efficiency of the plating bath decreased rapidly below pH 4.5.

Fig.39 shows the effect of increasing alloy content on the cathode efficiency of the plating bath. The curves illustrated are for the cobalt-molybdenum series of alloys and indicate that the efficiency of the bath decreased with increasing sodium molybdate concentration. This effect is not as conclusively shown with all of the cobalt-tungsten alloy baths but the trend is apparent at pH 3.0 (see Table V).

The results obtained for the base solutions with and without additions of sodium heptonate illustrate the effects of the complexing agent on the deposition potential of the cobalt. In general the addition of a complexing agent to an alloy bath will make the deposition potentials of the metals more negative (less noble) and tend to bring them closer together. The effect of adding the complexing agent to the base solution therefore would be to make the deposition potential of the cobalt more negative resulting in a decrease in the cathode current efficiency. This is seen to be correct when comparing the efficiency results obtained from solution B3 (no sodium heptonate) with those obtained from solution B5 (100g/l sodium heptonate) and solution B4 (200g/l sodium heptonate).

This effect becomes greater as the pH of the bath decreases and therefore is most probably accentuated by the general drop in efficiency associated with the fall in pH mentioned earlier.

10.2.

Internal Stress of the Cobalt-Molybdenum and Cobalt-Tungsten Electrodeposits.

Internal stress was determined for deposits plated from nine solutions, mainly the most successful ones, using the same plating conditions employed for the plating of dies i.e. pH 1.75, 55°C and 4A/dm². The results are reported at four deposit thicknesses in Table VI, each result being the average of two determinations.

Table VI. Variation of Mean Internal Stress with Deposit Thickness

Solution Code	Mean Stress, N/mm^2			
	1 μm	2 μm	5 μm	8 μm
B3	953	800	613	553
B4	975	895	840	963
B5	1005	940	913	1023
M16	1028	970	945	1048
M17	805	753	698	703
M19*	420	450	580	-
W11	585	597	665	835
W12	500	510	670	1050
W13	275	270	330	340

Plating conditions:- pH 1.75, 55°C, 4 A/dm^2, mild steel substrate

* Plated at 3 A/dm^2

The internal stress values obtained for the base solution B3
which contained no sodium heptonate or alloy additions illustrate
that a high mean stress was developed at an early stage.   A value
of $953N/mm^2$ was obtained at a thickness of 1 µm, but then decreased
gradually as the deposit thickness increased.   The addition of
sodium heptonate to this solution, giving solutions B4 (200g/1)
and B5 (100g/1), caused a marked change in the stress characteristics
of the deposits.   The values at a thickness of 1 µm were approximately
1000 N/mm^2 but minimum values occurred at a thickness of about 4 µm,
the stress values being in the region of 850-900 N/mm^2.

The addition of 3.15 and 6.3 g/1 sodium molybdate to
bath B5 resulted in little increase in the mean stress level but
examination of the plated test strips revealed that some cracking
had occurred.   The fact that lower stress values were obtained
for deposits plated from the solution containing the higher
concentration of sodium molybdate may be due to the development
of a higher crack density which effectively relieved the stress.
Sound deposits could not be plated onto the test strips from solution
M19 (12.6g/1 sodium molybdate) at $4A/dm^2$.   Exfoliation occurred
repeatedly although the mild steel strip was thoroughly cleaned in
a conventional manner.   The results reported in Table VI were
obtained at $3A/dm^2$.   The stress was much lower than that obtained for
M16 and M17 at $4A/dm^2$ and the deposit was crack-free since presumably
the tensile strength had not been exceeded.

The stress values obtained for the cobalt-tungsten
deposits exhibited a steady increase as the thickness increased.

The deposits were crack-free in the case of solutions W12 and W13 but W11 contained cracks similar to those occurring in the cobalt-molybdenum alloys. The results for W11 are surprising since no decrease in stress was associated with cracking. Stress appeared to take longer to build up in the case of the cobalt-tungsten alloys in comparison to the cobalt-molybdenum ones. In the later stress values of the order of 800-1000 N/mm^2 were observed in very thin coatings whereas comparable stress values were only reached at a thickness of about 8 µm with W11 and W12, and were not reached at all with W13 by the time the tests were halted at thicknesses somewhat in excess of 8 µm. The results obtained for solution W13 were most unexpected since this solution contained the highest sodium tungstate content (47.25 g/l). The mean stress was less than that developed in the case of the base solution, B3.

In general the results indicated that fairly high tensile stresses were developed in deposits plated from all these baths. On the mild steel substrates used in these tests cracking occurred in some instances and was usually more apparent than when similar coatings were plated onto dies. It has been reported previously that the nature and condition of the substrate can influence the cracking behaviour and the magnitude of internal stress developed in coatings.[79] Since most of these solutions have a cathode current efficiency of about 60-70%, at the conditions employed for testing, a considerable amount of hydrogen would be liberated and may influence the stress obtained if absorbed by the substrate, or coating. As mild steel was used as the basis metal in this

investigation the effect is not likely to be very large. (79) Macro

stress measurements of this type do not provide absolute values but

are to some extent determined by experimental conditions. It was

not possible to produce No.5 die steel in a form suitable for use

as a test piece and the pre-plating procedure was not the same for

dies as for the mild steel strips. Dies were given an anodic etch

prior to plating. Another important aspect is that agitation

cannot be used when employing the Hoar and Arrowsmith technique

of stress measurement and as outlined in section 10.6., the

character of these alloy deposits is influenced by the degree of

agitation. The composition of the coatings on the test strips

may bot be exactly the same as when plated on dies.

10.3.

Hardness of the Cobalt-Molybdenum and Cobalt-Tungsten Coatings Used on Dies.

The hardness values obtained from taper sections of the

dies plated with cobalt-nickel, cobalt-molybdenum and cobalt-

tungsten are given in Table VII. The hardness values used to

plot the relationship between coating hardness and percentage

alloying element in the deposit are those obtained from just

outside the wear ring region of the dies, (i.e. at 10 mm from the

centre of the wear ring). In this way the influence on the hard-

ness of working and high temperature heat treatments was reduced

to a minimum. The coating in this region had effectively been

subjected to a heat treatment of approximately $4\frac{1}{2}$ hrs. at 150°C.

TABLE VII. Hardness Survey Across Wear Regions of Flat Dies After Forging 1000 Billets

Code	Hardness HV, at 1 mm intervals from centre of die											Average hardness HV
	Centre	1	2	3	4	5	6	7	8	9	10	
N1 T	+	+	+	+	+	+	+	+	+	+	+	+
N1 B	376	383	354	370	366	380	376	383	380	409	429	382
N2 T	268	294	304	297	299	297	297	276	285	309	309	294
N2 B	309	299	279	297	306	*	*	297	292	279	283	293
N3 T	297	254	266	260	219	240	237	292	268	363	413	283
N3 B	333	314	322	287	-	245	297	405	508	473	473	366
N4 T	360	325	322	345	297	351	345	354	383	397	380	351
N4 B	446	441	380	339	302	283	*	*	287	297	297	341
N5 T	183	188	186	212	187	187	*	180	217	217	183	194
N5 B	233	233	161	199	206	195	206	187	189	188	206	200
N7 T	297	268	262	274	*	*	*	*	*	*	306	281
N7 B	297	274	297	304	*	*	*	*	272	272	287	286
N8 T	201	225	224	228	230	*	*	251	297	366	387	268
N8 B	209	258	254	247	240	240	*	230	264	292	292	253
N9 T	147	148	145	157	162	157	157	*	165	192	222	165
N9 B	144	151	155	151	158	158	163	181	163	169	203	163

TABLE VII Contd.

Code	Centre	1	2	3	4	5	6	7	8	9	10	Average hardness HV
				Hardness HV, at 1 mm intervals from centre of die								
B4 T	508	478	370	*	*	*	417	343	362	316	377	396
B4 B	274	376	342	311	401	397	*	*	*	*	370	353
B5 T	345	319	336	339	*	*	*	354	314	383	350	343
B5 B	+	+	+	+	+	+	+	+	+	+	+	+
M5 T	423	423	423	466	480	466	509	473	324	401	460	450
M6 B	396	453	412	435	473	473	501	423	396	396	433	436
M7 T	433	401	450	413	446	394	390	413	503	441	425	428
M7 B	503	488	459	478	450	336	508	420	468	473	464	459
M9 T	433	417	401	417	417	380	383	383	394	351	357	394
M9 B	483	464	464	441	413	417	420	357	373	380	373	417
M16 T	603	532	689	549	603	584	460	557	633	644	593	586
M16 B	487	447	473	516	473	487	453	473	494	435	466	473
M17 T	841	857	795	891	841	874	810	874	852	891	891	854
M17 B	965	841	874	927	841	841	857	985	927	810	810	880
M19 T	909	965	946	927	927	891	927	857	841	750	766	882
M19 B	501	584	593	549	501	603	549	584	584	575	603	566

TABLE VII Contd.

Code	Centre	1	2	3	4	5	6	7	8	9	10	Average hardness HV
			Hardness HV, at 1 mm intervals from centre of die									
W11T	417	373	394	420	417	409	420	409	390	387	420	406
W11B	488	459	425	498	429	376	446	450	459	429	387	441
W12T	536	536	459	483	498	525	578	503	503	454	473	495
W12B	634	752	734	689	762	772	698	689	724	665	698	710
W13T	715	689	707	689	803	707	762	707	657	649	642	702
W13B	1018	1003	1018	1018	988	907	920	907	953	824	803	940
W17T	574	459	464	488	417	488	464	503	464	450	405	465
W17B	446	441	437	409	446	488	454	441	405	373	390	430

T   Indicates top die.   B Indicates bottom die.   + Die not evaluated.

*   Indicates that a result could not be obtained because the coating had been severely eroded away.

Figs. 40 and 41 show the relationship between hardness and percentage alloying element for cobalt-nickel, cobalt-molybdenum and cobalt-tungsten respectively. The cobalt-nickel results include data from dies plated in both sulphate and sulphamate baths and that for cobalt-molybdenum and cobalt-tungsten are for dies plated from the 150g/l cobaltous sulphate baths containing 100g/l and 200g/l sodium heptonate. As can be seen these graphs are all straight-line relationships and regression analysis was carried out to find the lines of best fit. The curves plotted in Figs.41 for the cobalt-molybdenum and cobalt-tungsten alloys were found to be significant at the 0.1% level and that plotted in Fig.40 for cobalt-nickel was significant at the 1.0% level. The relationships shown by the graphs are as would be expected from the addition of the elements concerned to the pure cobalt. The addition of molybdenum and tungsten to the cobalt increases hardness of the deposit while the addition of nickel resulted in a decrease in hardness. The hardness values obtained for the cobalt-nickel coatings employed in this work are much lower than those reported by Belt et al [56] who found that a peak hardness of 525 H_v was reached with a nickel content of 65%. The hardness of the deposit containing 67% nickel in this work was only 341 H_v and there was no evidence of a peak of hardness in the region of this alloy content. It is possible that the use of a sulphate bath to deposit this alloy and not a sulphamate bath is the cause of this but it seems improbable that the type of bath used would influence the hardness of deposits having approximately the same composition to such a large extent.
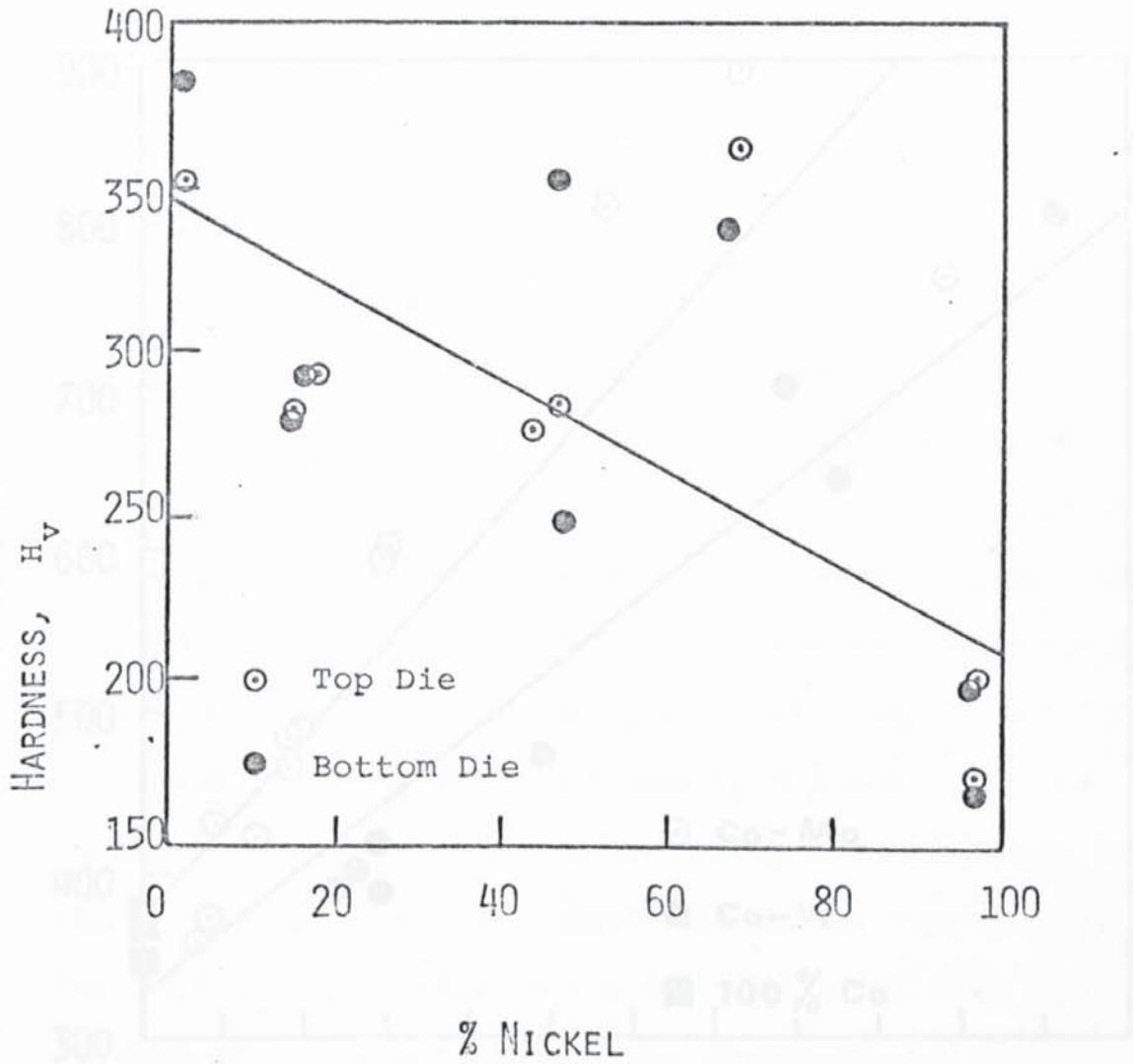
Fig.40. Relationship between the alloying
element content of Co-Ni electrodeposits
and their hardness.

Fig.41. Relationship between the alloying element content of Co-Mo and Co-W electrodeposits and their hardness.

Examination of the hardness values obtained across the
wear region reveals that two of the coated dies, M19 (top) and
W13 (bottom) show a marked difference in hardness between the
central plateau region of the die and the region just outside
the wear ring.   This effect could be explained by a precipitation
hardening process as both of the coatings contain the highest
alloy content obtained in each system (approximately 20%).
It would be expected that such a hardening process would be at
a maximum in the centre of the die as temperature measurements
have shown that the maximum surface temperature is reached in
this region.   However it is also possible that the difference
in hardness is caused by a variation in alloy content as it has
been shown above that hardness increases in direct proportion
with alloy content.   A variation in alloy content could easily
be obtained due to current density variations across the surface
of the die.   The lowest current density region would be the
centre of the die and this would gradually increase towards the
edges.   For alloys of the induced codeposition type it is often
the trend that an increase in current density will lead to a
decrease in the concentration of the reluctant metal in the deposit.
(34,35,57)
Therefore the centre of the die would be likely to contain the
highest percentage of alloying element and this would gradually
decrease towards the edges of the die.

10.4.

Hardness of the Cobalt-Molybdenum and Cobalt-Tungsten Alloy
Deposits in the As Plated and Heat-Treated Condition.

The deposits evaluated and their hardness after various
heat treatments are given in Table VIII and Table IX respectively.
The hardness results are the mean values of five impressions
taken from each sample. As can be seen the hardness of the
deposits differs widely from those obtained on the die coatings.
The heat treatment of the deposits has produced no definite trends
although the cobalt-molybdenum alloys M16 and M19 and the cobalt-
tungsten alloy W13 appear to have increased in hardness when
subjected to the 500°C heat treatment.

The low hardness values obtained for the cobalt-
molybdenum alloys are probably due to their low alloy content as
shown in Table VIII which would give soft coatings as indicated
in section 10.3. However the cobalt-tungsten alloys have far
lower hardnesses than their alloy content would suggest. It
would seem likely therefore that the structural difference observed
between the deposits plated onto brass plates and those plated
onto die steel is the main reason for the differences in hardness
observed. As stated in section 10.5 the deposits on brass
substrates all had columnar structures whereas the cobalt-tungsten
coatings plated onto dies had a lamellar structure. The relatively
large grain size associated with columnar structures could be
expected to be softer than the fine grain deposit usually present
with a lamellar deposit.

TABLE VIII.   Analysis of Coating Applied to Brass Panels

Solution Code	% Alloying Element in Deposit		
	Max.	Min.	Mean
M6	1.50 Mo	0.70 Mo	1.10 Mo
M16	4.45 Mo	1.80 Mo	3.13 Mo
M17	2.15 Mo	0.65 Mo	1.40 Mp
M19	3.60 Mo	1.50 Mo	2.55 Mo
W11	11.10 W	7.20 W	9.15 W
W12	17.50 W	11.70 W	14.60 W
W13	12.30 W	12.30 W	12.30 W

TABLE IX. Hardness of Coatings Applied to Brass Panels

Solution Code	Hardness of Deposit, H_v		
	As Plated	Heat-Treated 4½ hr at 150°C	Heat treated 15 min at 500°C
B3	263	258	284
B4	407	434	373
B5	418	432	380
M6	475	456	377
M16	316	327	425
M17	416	399	464
M19	313	323	510
W11	408	330	393
W12	369	303	356
W13	240	249	326

A hardness traverse across the thickness of several
deposits was carried out to determine if the variation in alloy
content observed on the analysis traces could be detected as a
change in hardness.   However no significant variation in hard-
ness was found.

It is clear that the results obtained from this
particular investigation are inconclusive and that more work is
required to determine the effects of heat treatment on the alloy
coatings.

10.5.

Structure of Deposits plated on Dies and Brass Test Panels.

The structure of pure cobalt, cobalt-molybdenum and
cobalt-tungsten alloys obtained from the heptonate bath were
examined.   The structure of all of the deposits plated onto
brass panels was columnar whether the deposit had been heat
treated or not.   A typical example of this type of structure
is shown in Fig.42a.   There was a tendency for several of the
alloy deposits which had been heat treated for 15 min. at 500°C
to show a more random structure but this effect was not definite.
Fig.42b shows a section through a nodule and illustrates that it
had resulted from the incorporation of an inclusion.   A few
nodules were detected in die coatings but did not appear to
adversely affect performance.

The pure cobalt coatings and those containing low
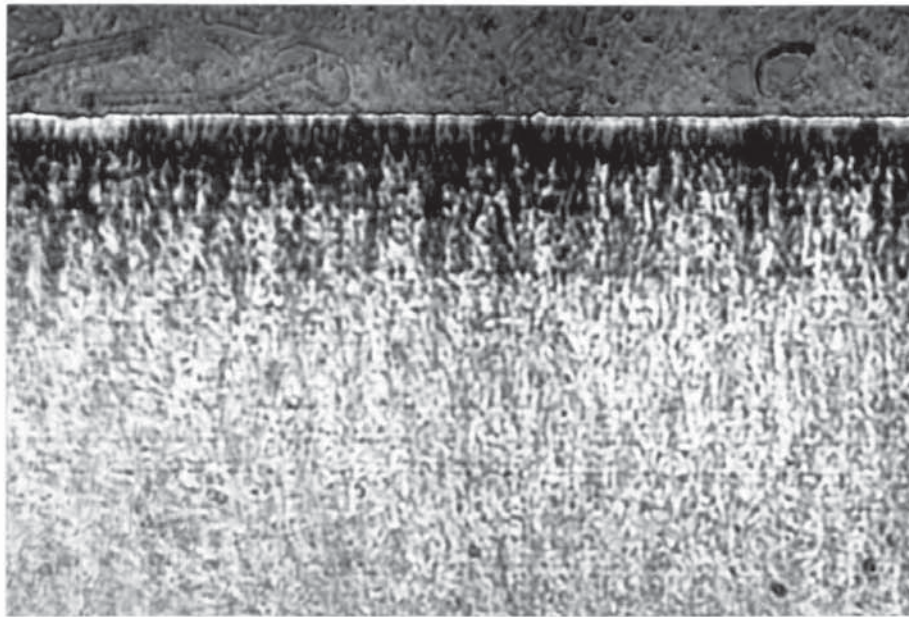
a) Typical collumnar structure x 750
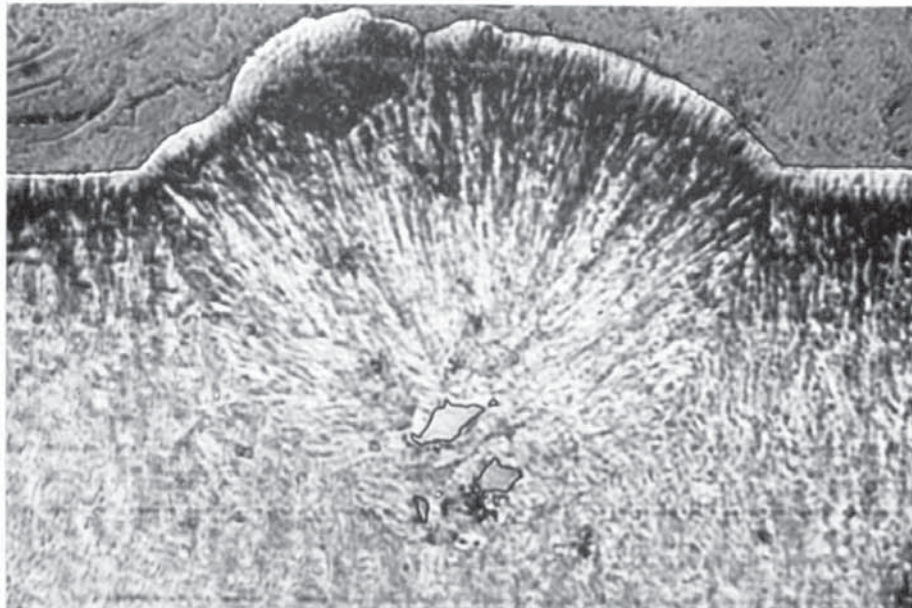
b) Section through a nodule x 750

Fig.42.   Structure of deposits plated on brass test panels
(cobalt deposit B4)

concentrations of alloying element plated onto dies, whether obtained from baths containing 100g/l or 200g/l sodium heptonate, had a columnar structure identical to that observed in deposits plated onto brass plates. The deposits of higher alloy content however exhibited a lamellar structure of varied fineness. This ranged from very narrow lamellae typical of bright nickel deposits to a very coarse, almost layered deposit. An example of the fine lamellar deposit obtained with bath M17 is shown in Fig.43a. Fig.43b shows the effect of a discontinuity, in this case the cavity originally occupied by an inclusion, on the lamellar nature of the deposit. There was no apparent pattern to the fineness of the layers but there was a slight tendency for the cobalt-molybdenum to have the finer structure. The coarse lamellae described above may not be a true structural effect as it has been shown[80] with nickel deposits that apparent lamination may be produced by the etchant used. This is substantiated by the fact that when fairly coarse layers were observed closely they were seen to be columnar in nature within each layer. Both the columnar structure and the lamellar structure have been observed by Brenner et al[50] when depositing cobalt-tungsten and iron-tungsten alloys respectively. It is interesting to note that the cobalt-tungsten alloys examined by Brenner et al[50] also showed signs of laminations within the columnar structure.

The fact that no laminations were observed in the deposits plated onto brass substrates is surprising but it is possible that the substrate had an effect on the structure of the deposit.[81] However caution must be exercised because the alloys plated onto
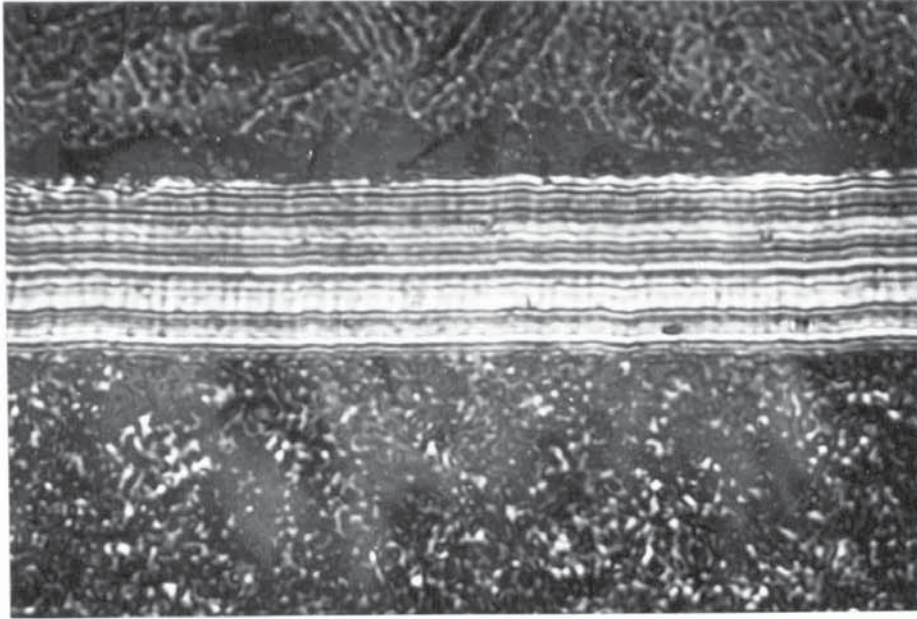
a) Typical lamellar structure x 1100
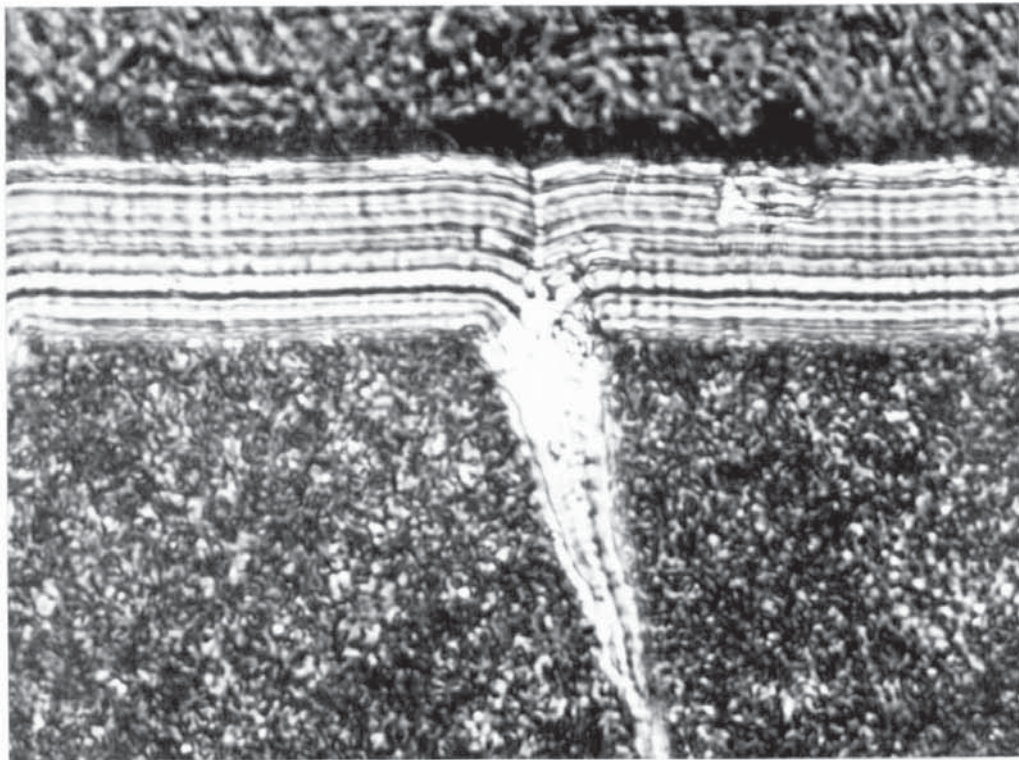
b) Section through an etched out inclusion
in the steel substrate x 1100

Fig.43.   Structure of deposits plated on dies
(cobalt-molybdenum alloy M17)

the brass panels, particularly the cobalt-molybdenum alloys, were found to contain lower concentrations of alloying element than the coatings applied to dies.   The different structures may therefore have been caused by the lower alloy content.

10.6.

Surface Topography of the Cobalt-Molybdenum and Cobalt-Tungsten Electrodeposits in the As Plated Condition.

The deposits examined were those listed in Table V. Some typical structures are shown in Figs. 44 and 45.   Since these relate to the centres of efficiency panels the current density would be somewhat less than $4A/dm^2$.   The 'spaghetti-like' structure was characteristic of alloys containing either molybdenum or tungsten and it became more pronounced as the alloying element content was increased.   This is illustrated clearly by Figs.44 which show that at the lower molybdenum content the 'spaghetti' structure had not begun to develop.   The structure shown in Fig.44a is very similar to that of pure cobalt deposits plated from the heptonate baths.   If the pH of any alloy solution was increased from pH1 - pH3 the 'spaghetti' became slightly finer.

The change in structure of the cobalt-tungsten alloys with increasing tungstate in solution is not as marked as with the cobalt-molybdenum alloys.   However Fig.45 shows an increase in fineness of the structure when increasing the sodium tungstate concentration of the bath from 15.75g/1 - 47.25g/1.
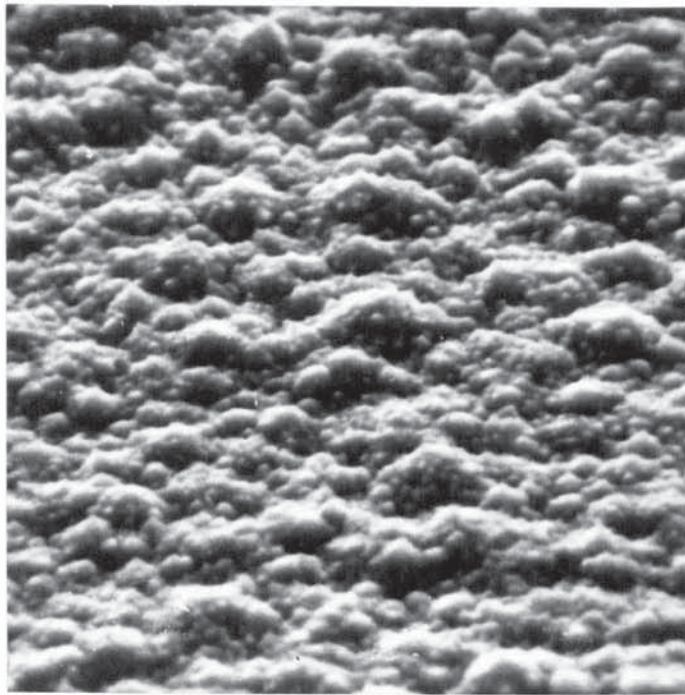
a) M16, x 5500
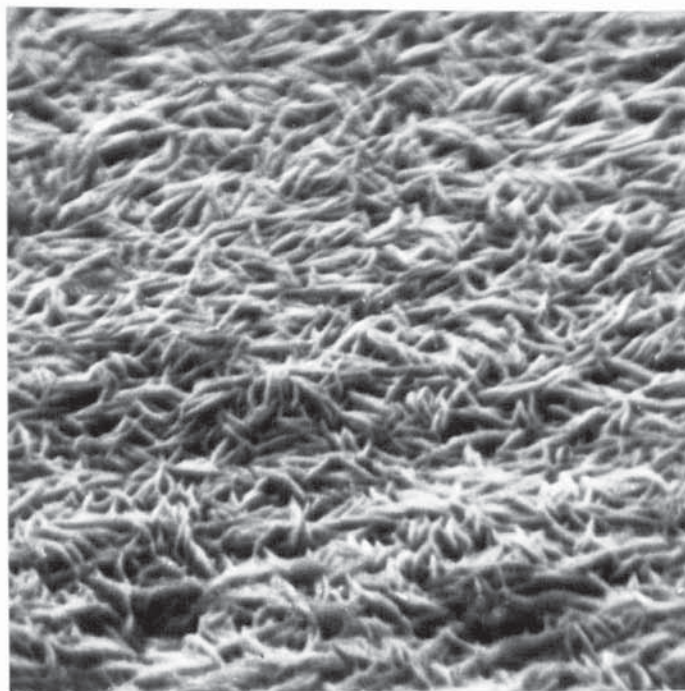
b) M19, x 5500

Fig.44. Scanning electronmicrographs showing the surface topography of cobalt-molybdenum deposits plated in solutions M16 and M19 at pH 15, 55° C and 4 A/dm^2
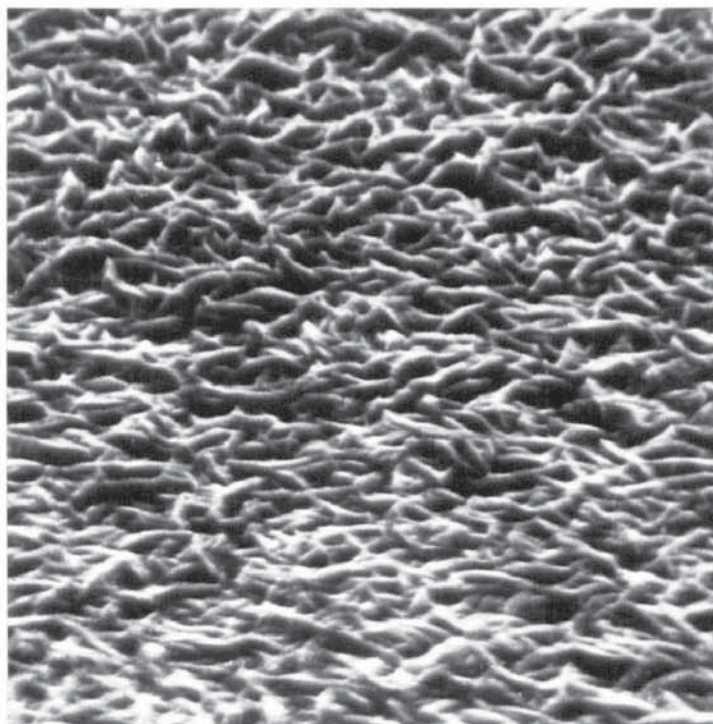
a) W11, x 5500
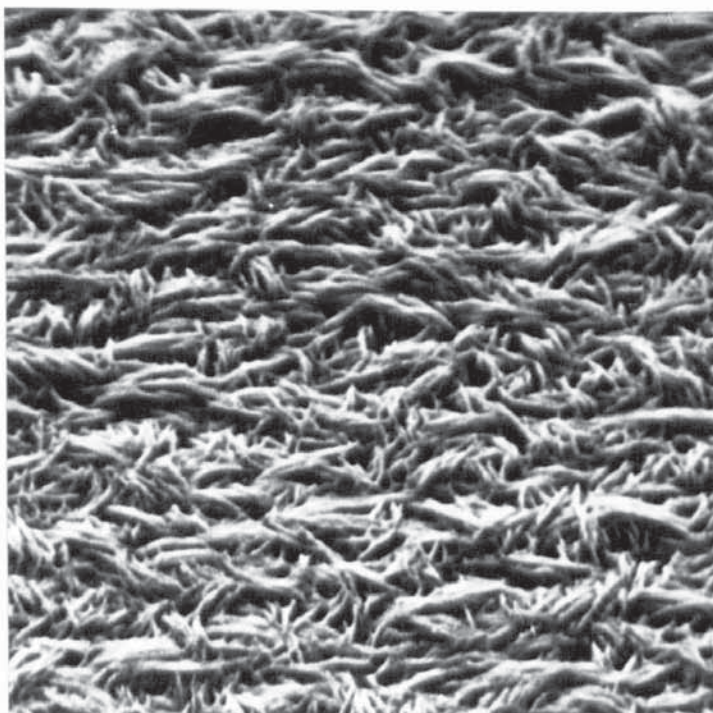
b) W13, x 5500

Fig.45. Scanning electronmicrographs showing the surface
topography of cobalt-tungsten deposits plated in
solutions W11 and W13 at pH 1.5, 55° C and 4A/dm^2.

To the naked eye, the deposits plated on efficiency panels and dies had a dull-lustrous appearance. However, results of Hull cell tests illustrated in Figs.32 and 37 indicate that at the plating conditions employed the deposit should have been bright. This difference in appearance is thought to be due to different degrees of agitation and the position of air inlet points in relation to the cathode. In the Hull cell the air bubbles swept up the face of the panels whereas in the case of efficiency panels and dies general agitation was provided in the centre of the beaker. Further evidence of this agitation effect was given by the fact that initially the air agitation for the die plating bath was placed directly beneath the die and this produced a variable surface appearance to the deposit. In some cases one edge was bright and the remainder of the die dull. The agitation was therefore repositioned between the anode and cathode with the result that the deposits obtained were dull-lustrous but uniform in surface appearance.

10.7.

Analysis of the Cobalt-Molybdenum and Cobalt-Tungsten Electrodeposits Using the E.P.M.A. and S.E.M.

The E.P.M.A. was used to produce analysis traces through the thickness of the deposits. It was found that the alloy content varied through the thickness of the deposit and that the distribution of alloying element appeared to be influenced by the type of metal substrate.

The coatings applied to dies were found to have a fairly random alloy distribution as illustrated by Fig.46 which shows the alloy distribution through the thickness of a cobalt-molybdenum and a cobalt-tungsten deposit. This figure also shows that in general the cobalt-molybdenum alloys had a more uneven distribution of alloying element than the cobalt-tungsten alloys. However the cobalt-molybdenum alloys did not necessarily give greater overall fluctuations in alloy content than the cobalt-tungsten alloys. The fluctuations in alloy content observed followed no general pattern; the alloys containing high concentrations of plate showing similar behaviour to those of lower alloy content. The analysis results obtained from the die coatings are given in Table X. The maximum and minimum alloy contents are given in this table together with the average alloy content. It should be noted that the average values are made use of throughout this work.

The alloy distribution through coatings deposited onto brass plates is illustrated in Fig.47. As can be seen the concentration of alloying element is a maximum at or near the brass coating interface and this decreases as the thickness of the coating increases. This effect is more marked with the cobalt-molybdenum alloys than with the cobalt-tungsten alloys. Heat treatment of the deposits at 150°C for 4½hrs. and 500°C for ¼ hr. did not alter this alloy distribution. The analysis of these deposits are given in Table VIII and again include the maximum, minimum and average values.

It is difficult to explain these differences in alloy

Steel

Surface
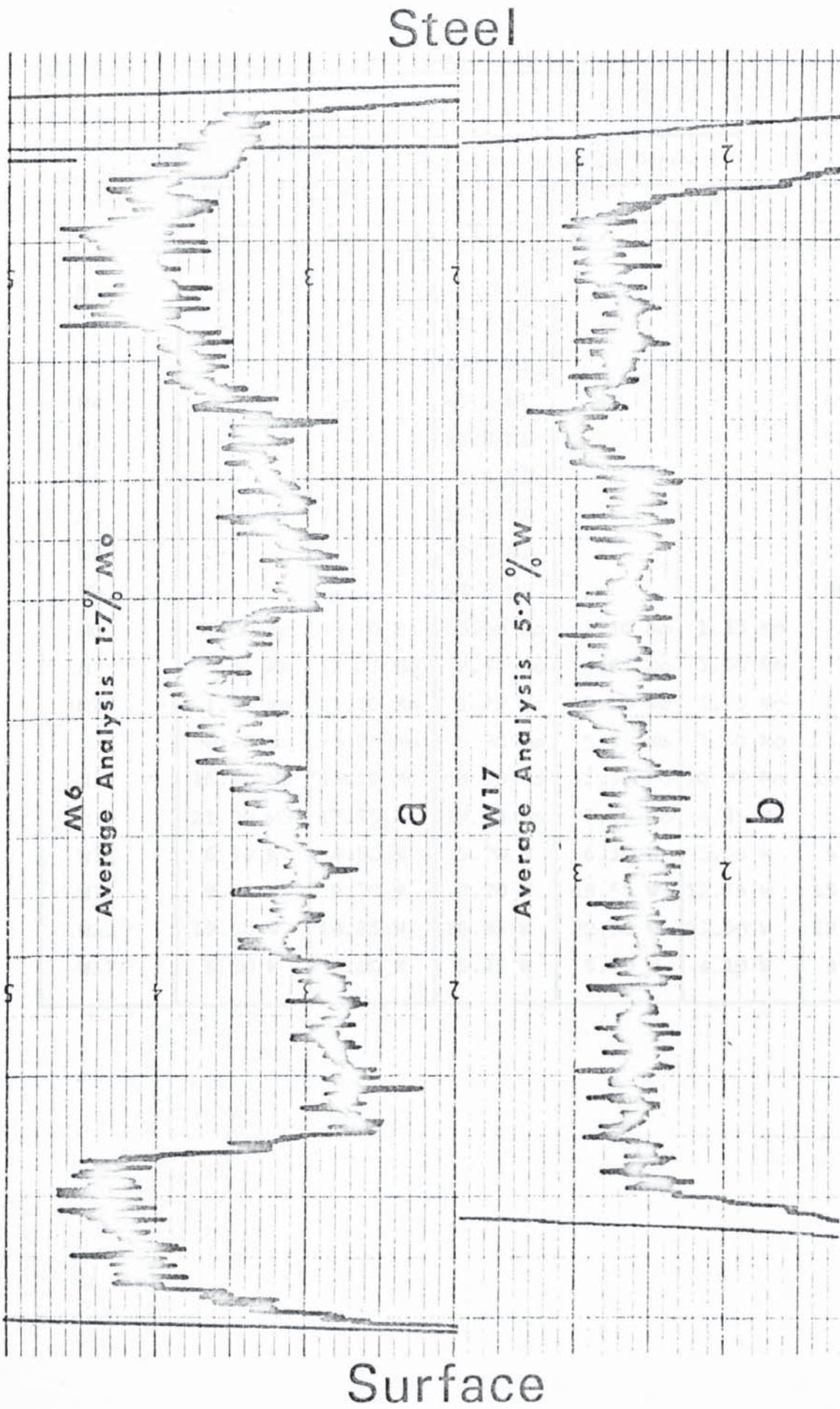
Fig. 46. Variation of molybdenum and tungsten concentrations over the cross-section of die coatings.

TABLE X.   Analysis of Coatings Applied to Dies

Solution Code	% Alloying Element in Deposit					
	Top Die			Bottom Die		
	Max	Min	Mean	Max	Min	Mean
N1	--	-	1.2 Ni	-	-	1.1 Ni
N2	-	-	17.7 Ni	-	-	16.9 Ni
N3	-	-	47.7 Ni	-	-	47.3 Ni
N4	-	-	68.5 Ni	-	-	66.9 Ni
N5	-	-	96.8 Ni	-	-	96.5 Ni
N6	--	-	1.5 Ni	-	-	2.1 Ni
N7	-	-	15.6 Ni	-	-	15.5 Ni
N8	-	-	43.3 Ni	-	-	47.1 Ni
N9	-	-	97.3 Ni	-	-	96.4 Ni
M6	4.00 Mo	3.00 Mo	3.50 Mo	2.10 Mo	1.25 Mo	1.68 Mo
M7	3.50 Mo	2.05 Mo	2.78 Mo	4.65 Mo	3.00 Mo	3.83 Mo
M9	1.50 Mo	1.00 Mo	1.25 Mo	2.00 Mo	1.25 Mo	1.63 Mo
M16	8.40 Mo	3.20 Mo	5.80 Mo	5.65 Mo	1.50 Mo	3.58 Mo
M17	16.20 Mo	13.10 Mo	14.65 Mo	12.55 Mo	10.07 Mo	11.31 Mo
M19	21.30 Mo	17.75 Mo	19.53 Mo	7.50 Mo	4.45 Mo	5.98 Mo
W11	6.60 W	4.80 W	5.70 W	6.10 W	5.50 W	5.80 W
W12	9.85 W	9.70 W	9.78 W	18.55 W	12.65 W	15.60 W
W13	19.55 W	14.15 W	16.85 W	22.50 W	21.90 W	22.20 W
W17	5.50 W	5.00 W	5.25 W	5.70 W	4.10 W	4.90 W

Fig.47. Variation of molybdenum and tungsten concentrations over the cross-section of coatings deposited on brass panels.

distribution within the coatings particularly as the deposits obtained on brass sheets were plated from the same solutions as were used to plate the die sets. A possible explanation of the two types of distribution found on the brass and steel substrates concerns the degree of agitation employed when plating the two specimens. The brass plates, being much higher than the steel dies, were plated under less severe agitation conditions. This would allow the cathode film to thicken causing a change in the deposition rate of the metals due to the formation of a more shallow concentration gradient across the film. The concentration of metal ions at the cathode/metal interface would decrease with time due to a longer time being required for diffusion through the thickening cathode film. This would lead to a decreasing concentration of alloying element in the deposit. The higher rate of agitation employed for the plating of dies would reduce the thickness of the cathode layer thus ensuring that depletion of metal ions did not occur. Therefore a gradual decrease in alloy content would not take place during plating. However this mechanism does not explain the random variations in alloy content experienced with the die coatings. These fluctuations are more likely to have been caused by variations in plating conditions during the lengthy die plating operations. The changes in pH and solution level (concentration), which were inevitable when operating a bath of only 2 litres capacity, were rectified at approximately $1\frac{1}{2}$ hr. intervals during plating. The change in plating conditions during these periods, particularly the rise in pH, would be likely to give the type of compositional changes experienced. The same

difficulties were encountered when plating the brass panels as long plating times were employed to obtain these deposits also but it is thought that the presence of a thick cathode diffusion layer postulated above would even out these fluctuations.

Although an attempt was made to correlate the variations in alloy content with the lamellar structures of the deposits no definite relationship appeared to exist as in most cases the individual lamellae were much narrower than the fluctuations recorded on the analysis traces. However it should be noted that the cobalt-molybdenum alloys which produced some of the best examples of lamellar deposits also exhibited some of the most uneven analysis traces.

The analysis of the deposits plated on brass panels shows that the cobalt-molybdenum alloys had low alloy contents compared to coatings plated on dies. This could be accounted for by the fact that the solutions used to plate dies were also used when plating the brass panels. Therefore the total plating time for the two litres of solution was of the order of 14 amp./hrs. which may have depleted the alloy content of the solution. An attempt was made to adjust the concentration of molybdenum in the bath between the plating operations by small additions of sodium molybdate. However their effect on restoring the molybdenum content of the bath is doubtful as the anticipated alloy contents of the deposits obtained from these baths was much lower than the alloy contents actually obtained. The depletion of alloying element would not be as marked with the cobalt-tungsten alloys due to the

greater proportion of tungsten was present in the solution. This is thought to be an alloy analysis of the cobalt-tungsten deposit and not a measure of the composition of the electrodeposited reduction.

The deposits are surface reasonably constant at any one composite since it present in any S.E.M. indicated in the alloy analysis showed that the higher the the alloy content of the the surface. On this in this is what could not be found in the system is on the surface of the deposit. When the there was considered discernable drop to lower to lower concentrations obtained electrolytic was present in the site of the deposit. this is demonstrated qualitatively by Fig.48 the the phase the x-ray spectrum produced by a nodule and that produced by the matrix of the same deposit.

10.8.

10.8.1.

Surface Temperature Measurement.

The maximum temperature reached in the centre of the die as recorded by the nuclear thermocouple was found to vary between 500°C and 820°C. The data obtained from the subsurface thermocouple is shown in Fig.49. The curve plotted is an extrapolation to the surface temperature and although it is difficult to make an accurate assessment by this means the surface temperature
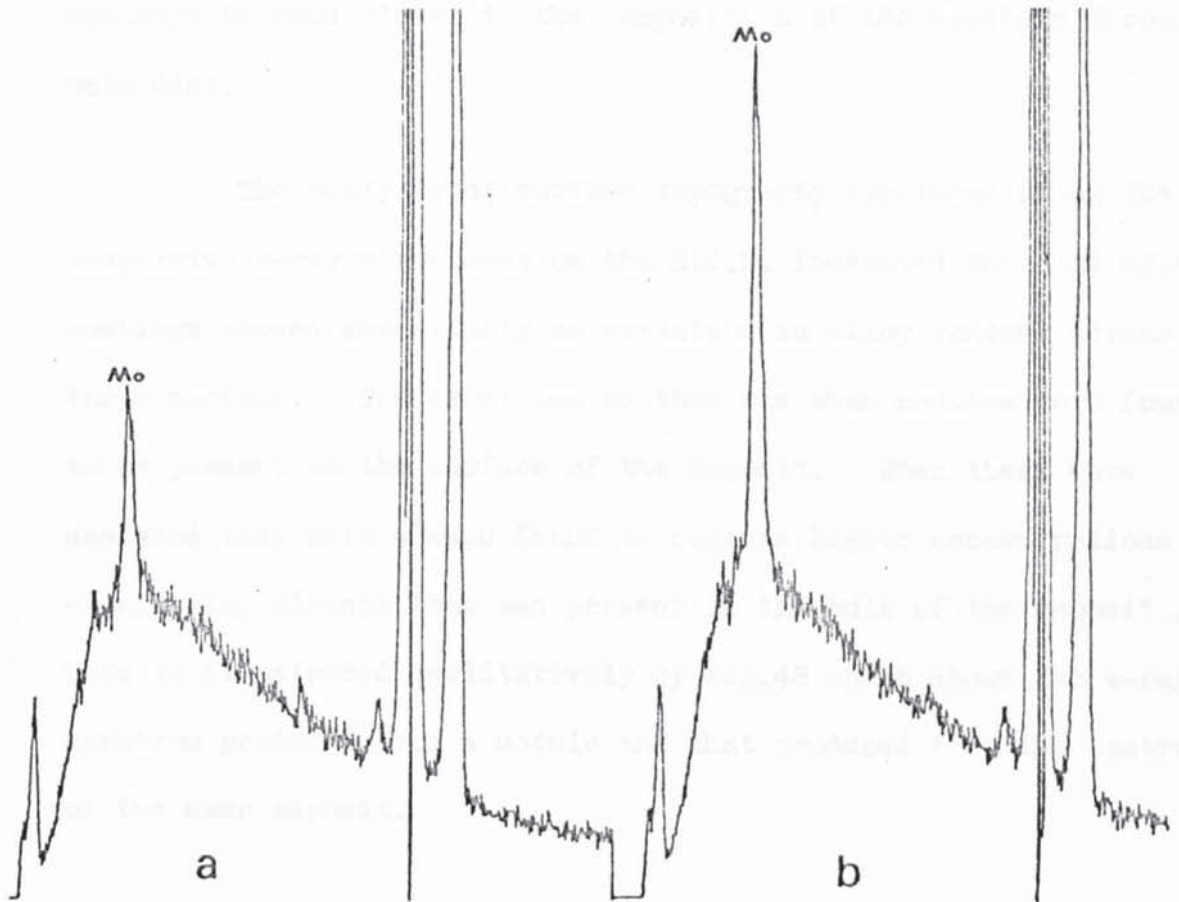

Fig.48.   S.E.M. analysis of cobalt-molybdenum alloy
           obtained from bath M19 at 55°C, pH 1.0 and
           4.0 A/dm² showing:-

           a)   Molybdenum content of the areas between
                nodules
           b)   Molybdenum content of a nodule

greater concentration of tungsten ions present in the solution.
This is seen to be so as the alloy contents of the cobalt-tungsten
coatings is much closer to the composition of the coatings deposited
onto dies.

The analysis of surface topography specimens using the
dispersive x-ray attachment on the S.E.M. indicated that the alloy
coatings showed essentially no variation in alloy content across
their surface. The exception to this was when nodules were found
to be present on the surface of the deposit. When these were
analysed they were always found to contain higher concentrations
of alloying element than was present in the bulk of the deposit.
This is illustrated qualitatively by Fig.48 which shows the x-ray
spectrum produced from a nodule and that produced from the matrix
of the same deposit.

10.8.

Thermal Fatigue of Alloy Coatings.

10.8.1 .

Surface Temperature measurement.

The maximum temperature reached in the centre of the
die as recorded by the surface thermocouple was found to vary
between 500° and 520°C. The data obtained from the subsurface
thermocouple is shown in Fig.49. The curve plotted is an
extrapolation to the surface temperature and although it is difficult
to make an accurate assessment by this means the surface temperature
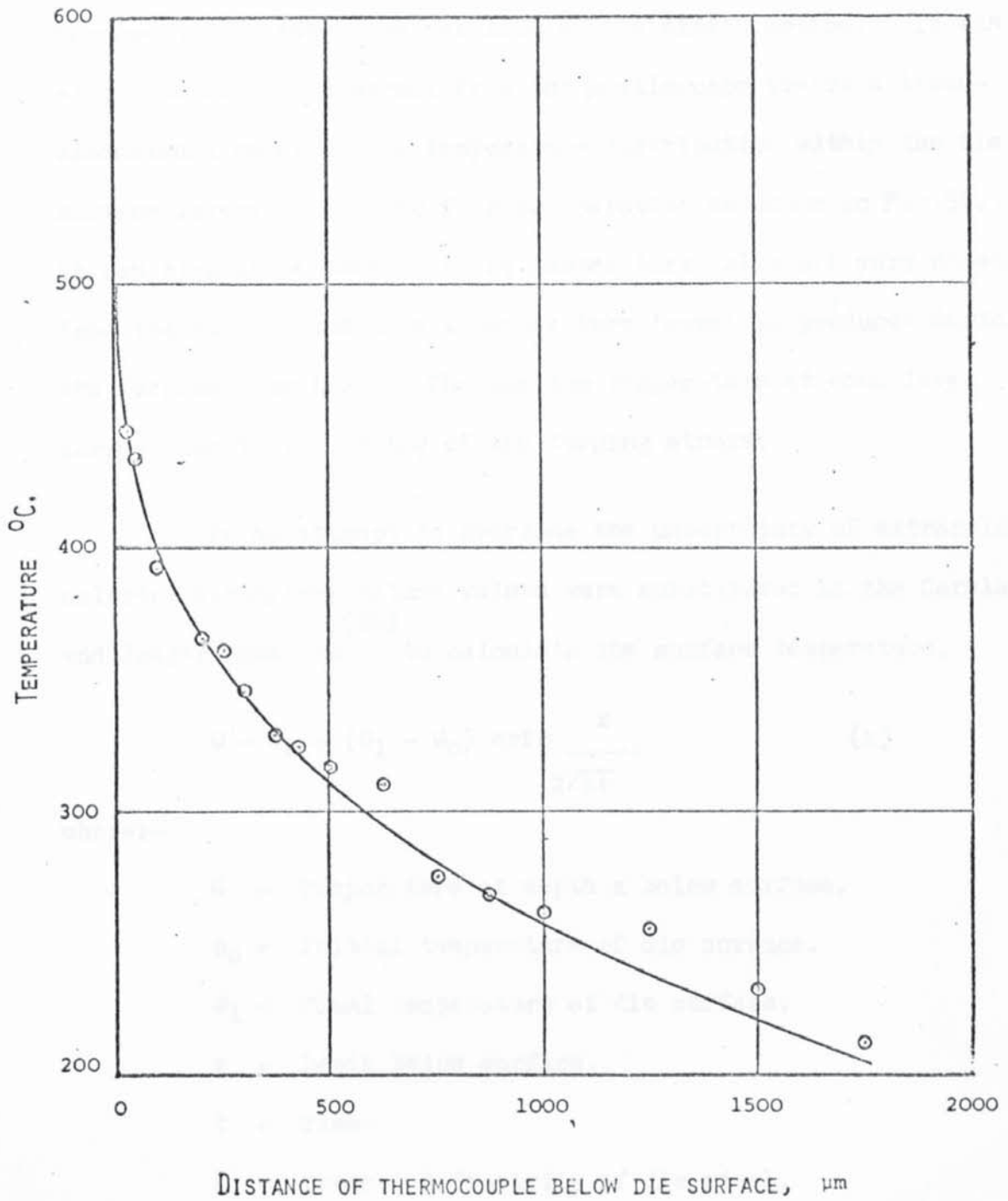
Fig.49. Temperature gradient in the surface layers of the die during forging.

appears to be in the range 480-500°C. This is in fairly close agreement with the value obtained by the direct method. It was also possible to construct from the oscilloscope traces a three-dimensional model of the temperature distribution within the die surface layers during the forging operation as shown in Fig.50. It can clearly be seen that the temperature falls off very steeply from the surface and that a temperature 'wave' is produced during the forging operation. The maximum temperature at each level corresponds to the bottom of the forging stroke.

In an attempt to overcome the uncertainty of extrapolation selected depth/temperature values were substituted in the Carslaw and Jaeger equation [82] to calculate the surface temperature.

$$\theta = \theta_0 + (\theta_1 - \theta_0) \operatorname{erfc} \frac{x}{2\sqrt{Kt}} \qquad (x)$$

where:-

θ = Temperature at depth x below surface.

θ_0 = Initial temperature of die surface.

θ_1 = Final temperature of die surface.

x = Depth below surface.

t = Time.

K = Thermal diffusivity of die steel.

The calculation was carried out by computer analysis using a programme which had already been developed for other heat flow problems concerned with metal casting. [83] The surface temperature calculated in this manner was only 420°C. The reason
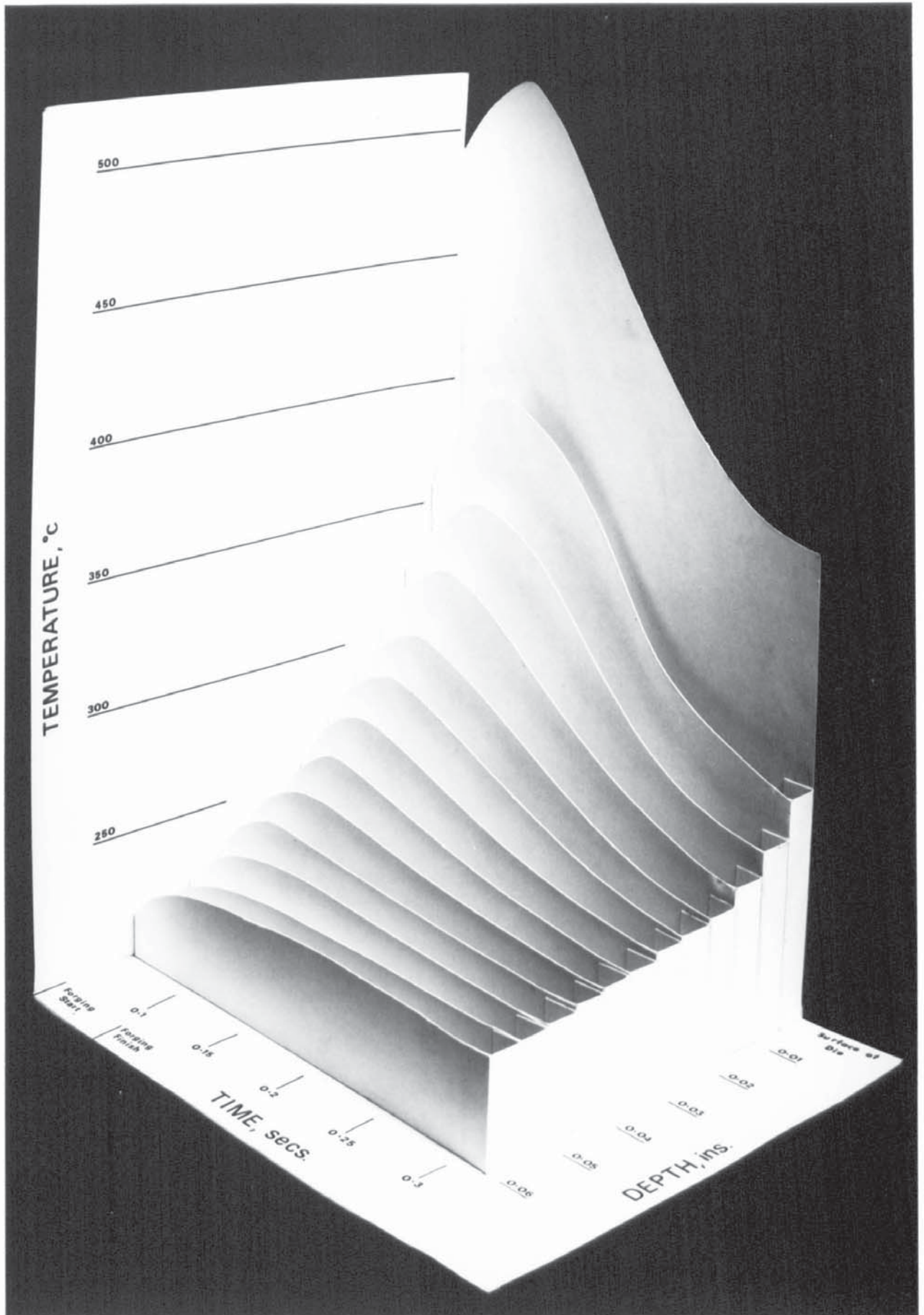
Fig.50. Three-dimensional model of the temperature distribution within the die surface layers during forging.

for this discrepancy was seen easily when the heat distribution curve, assuming a surface temperature of 420°C, was calculated and plotted. This showed a marked divergence from the experimental data both near to the surface and at depths greater than approximately 500 μm. This divergence can be attributed almost certainly to the limitations imposed by the Carslow and Jaeger equation (x).[82] The assumptions made by the above authors are that:-

    i)   semi-infinite plane conditions exist,

    ii)   temperature rise is instantaneous,

    iii)   thermal properties do not vary with temperature.

These conditions are not satisfied in the forging operation, the temperature rise is not instantaneous and the thermal diffusivity of the die steel is not known accurately particularly over the temperature range concerned. Two other factors which are also present under hot forging conditions are similarly not taken into account in this model. These are the transient nature of the die/billet contact time and the impedence of heat flow by oxide films. An equation developed by Demidov[84] is designed to take these factors into consideration and it is possible that a better correlation between the direct and indirect surface temperature measurements would be obtained if the results were analysed using this method. However it was thought that for the purpose of this investigation a surface temperature of 500°C could be assumed with some confidence. This temperature was therefore employed for the thermal cycling tests, the results of which are given below.

10.8.2.

Results of thermal cycling of alloy coatings.

     The conditions chosen for the thermal cycling test
were 1000 cycles through the temperature range measured on the
die surface during forging.   An air blast was used as the cooling
medium.   The temperature profile of the cycle used is shown in
Fig.51 together with the temperature cycle recorded on the surface
of the die during the forging operation.   As can be seen the
shapes of the temperature cycles are very similar, and good
simulation of the conditions occurring at the die surface has
been achieved on the surface of the thermal cycling specimen.

     The unplated Electem specimens were prepared with
inclusions in both the transverse and longitudinal directions but
as neither showed any cracks after the 1000 cycle test the specimens
used for plating all had the inclusions aligned in the longitudinal
direction.

     The results of the thermal cycling tests are given in
Table XI.   As mentioned above none of the unplated specimens
suffered cracking and this was also true of the cobalt-nickel
coatings deposited from the sulphamate bath.   With the exception
of W13 the cobalt-molybdenum and cobalt-tungsten coatings were all
cracked in the as plated condition.   In the case of the cobalt-
molybdenum coatings these cracks propagated slightly into the
steel substrate during the thermal cycling test as shown in Fig.52
but this did not occur with the cobalt-tungsten alloys.   The
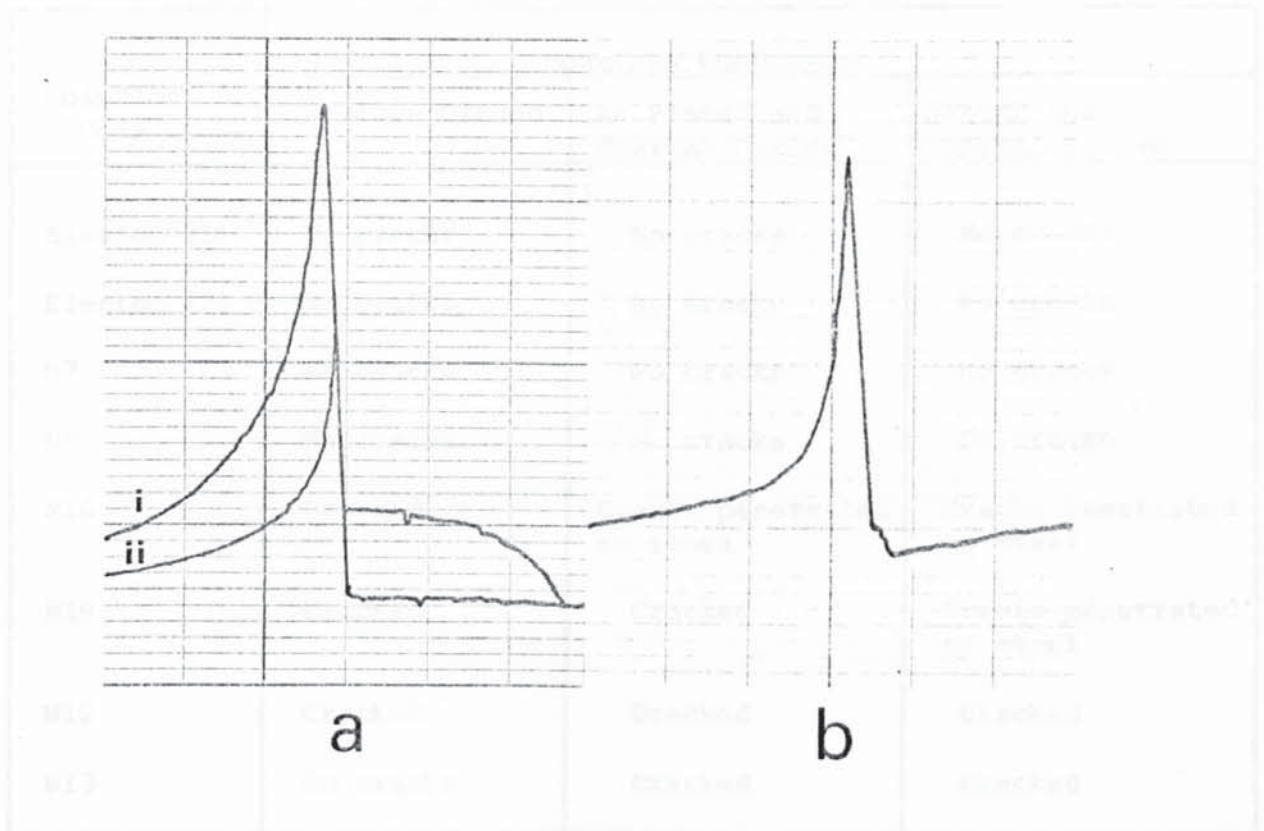
Fig.51.   Temperature profiles obtained on:-

a)   Die surface during forging operation
      i.   Central plateau
      ii. Wear ring

b)   Surface of thermal cycling specimens

TABLE XI.   Results of Thermal Fatigue Tests

Solution Code	Specimen Condition		
	Surface Ground	As Plated and Thermal Cycled	Ground and Thermal Cycled
Electem (L)	No cracks	No cracks	No cracks
Electem (T)	No cracks	No cracks	No cracks
N7	No cracks	No cracks	No cracks
N8	No cracks	No cracks	No cracks
M16	Cracked	Cracks penetrated to steel	Cracks penetrated to steel
M19	Cracked	Cracked	Cracks penetrated to steel
W12	Cracked	Cracked	Cracked
W13	No cracks	Cracked	Cracked

L.   Inclusions in longitudinal direction

T.   Inclusions in transverse direction
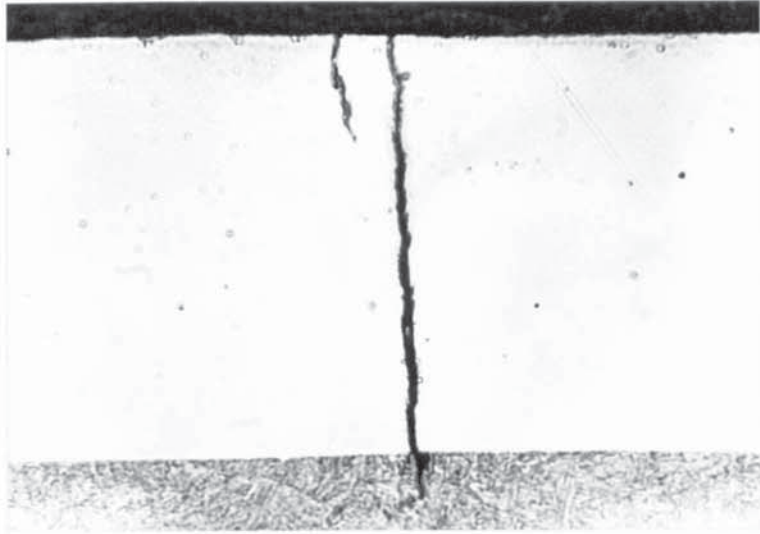
Fig.52. Thermal fatigue specimen showing propagation of cracks into steel substrate cobalt-molybdenum alloy M16 x 250 1000 cycles.

frequency of cracking increased when thermal cycling cobalt-molybdenum alloys but the cobalt-tungsten alloys produced varied results. W12 had approximately the same number of cracks before and after testing but W13 cracked as a result of thermal cycling.

The cracks in plated specimens after thermal cycling were quite different from those observed in the central plateau regions of dies. They appeared to be much wider and contained large quantities of oxide. This oxide build up was particularly severe with the cobalt-tungsten coatings where the deposit was seen to be lifting from the substrate due to lateral spread of the oxide at the base of the cracks. All cracks observed in the thermal cycling specimens were at 90° to the substrate whereas the cracks observed in die coatings occurred at various angles. Similar results were produced on thermal cycling whether or not the specimens were ground after plating.

Since cracks were not produced in unplated specimens by thermal cycling alone it appears that the conditions encountered are less severe than in the forging test where cracks did appear in the central plateau region of flat dies. Even in the case of plated dies when cracks were present in the coatings to act as stress raisers before thermal cycling, the cracks penetrated only very short distances into the die steel specimens by the end of the test. This work illustrates that either the repeated impact loading effect is responsible for cracking of die surfaces or that the combined effect of thermal cycling and impact is responsible for cracking. Thermal cycling alone either did not produce cracks

or the cracks were not of the same type as those encountered in dies.

The observation of cracked cobalt-molybdenum and cobalt-tungsten deposits in the as plated condition appears to confirm that the mechanism for cracking of the dies plated with these coatings, given in section 11.3.1., is probably correct.

11. RESULTS OF DIE WEAR TESTS

11.1.

Flat Die Wear Tests.

11.1.1.

Unplated No.5 die steel.

Unplated Electem No.5 die sets were forged to establish a control against which the performance of the plated dies could be compared. Firmly adherent scale built up on both top and bottom dies during the forging test and this could be removed only by the electrolytic process described in section 8.2.1.

The wear volumes obtained are given in Table XII for comparison with those obtained on the coated dies.

11.1.2.

Cobalt-nickel alloys.

The cobalt-nickel solutions used for the coating of flat die sets together with their plating conditions are given in Table XIII. The wear results obtained from these coatings after the 1000 billet forging test are shown in Table XII.

The mean wear volumes obtained from both top and bottom dies are shown plotted against the % nickel in the deposit in Fig.53. The curve obtained shows that wear of the coating decreases with increasing nickel content in the deposit. This trend is the same for alloys deposited from both the sulphate and the sulphamate baths. There is no indication of an increase in wear resistance at

TABLE XII. Wear Volume of Flat Dies after Forging 1000 Billets

Solution Code	Coating Thickness μm	Wear Volume x10^{-3} cm^3			Appearance after Plating	Appearance after Forging
		Top Die	Bottom Die	Mean		
Unplated Electem	-	4.70	4.04	4.37	-	S
N1	75	15.05	15.70	15.38	G	P, AS
N2	75	8.00	9.52	8.76	G	As
N3	75	5.78	10.32	8.05	G	P, AS
N4	75	7.55	6.24	6.89	G	P, AS
N5	75	2.66	1.89	2.28	G	AS
N6	75	10.70	11.50	11.10	G	P, AS
N7	75	14.90	17.50	16.20	G	P, AS
N8	75	10.52	3.61	7.07	G	P, AS
N9	75	4.77	2.36	3.57	G	P, AS
B4	100	11.45	12.10	11.78	HF	S
B5	75	8.20	+	8.20	SF	S
M6	100	5.15	6.70	5.92	F	N
M7	75	6.70	3.20	4.95	HF	N
M9	75	9.04	7.45	8.25	HF	N
M16	70	1.00	0.67	0.84	G	N
M17	25	0.66	0.44	0.56	SF	N
M19	25	0.41	0.57	0.49	SF	N
W11	75	6.56	3.98	5.27	HF	N
W12	75	1.03	0.46	0.75	G	N
W13	40	0.75	0.43	0.59	G	N
W17	75	7.26	4.71	5.99	HF	N

+ Die not evaluated

Plating Code

G   =   Good

SF =   Slight Edge Flaking

F   =   Edge Flaking

HF =   Heavy Edge Flaking

Forging Code

N = No scale except for small loosely adherent areas on bottom die.

S = Scale which is removed by electrolytic cleaning.

AS = Strongly adherent scale which is not removed by cleaning.

P = Plate penetration during test.

TABLE XIII. Cobalt-Nickel Solutions

Cobalt-Nickel Sulphate Solutions

Solution Code	COMPOSITION g/ℓ						pH	Current Density A/dm²	Temp. °C
	Cobalt Sulphate	Nickel Sulphate	Cobalt Chloride	Sodium Chloride	Boric Acid	Sodium Saccharin			
N1	140	–	23	–	15	–	3.0	4.0	55
N2	120	300	–	28	40	–	4.0	4.0	55
N3	25	300	–	28	40	–	4.0	4.0	55
N4	19	300	–	28	40	–	4.0	4.0	55
N5	–	300	–	28	40	–	4.5	4.0	55
N6	140	–	23	–	15	1	3.0	4.0	55

Cobalt-Nickel Sulphamate Solutions

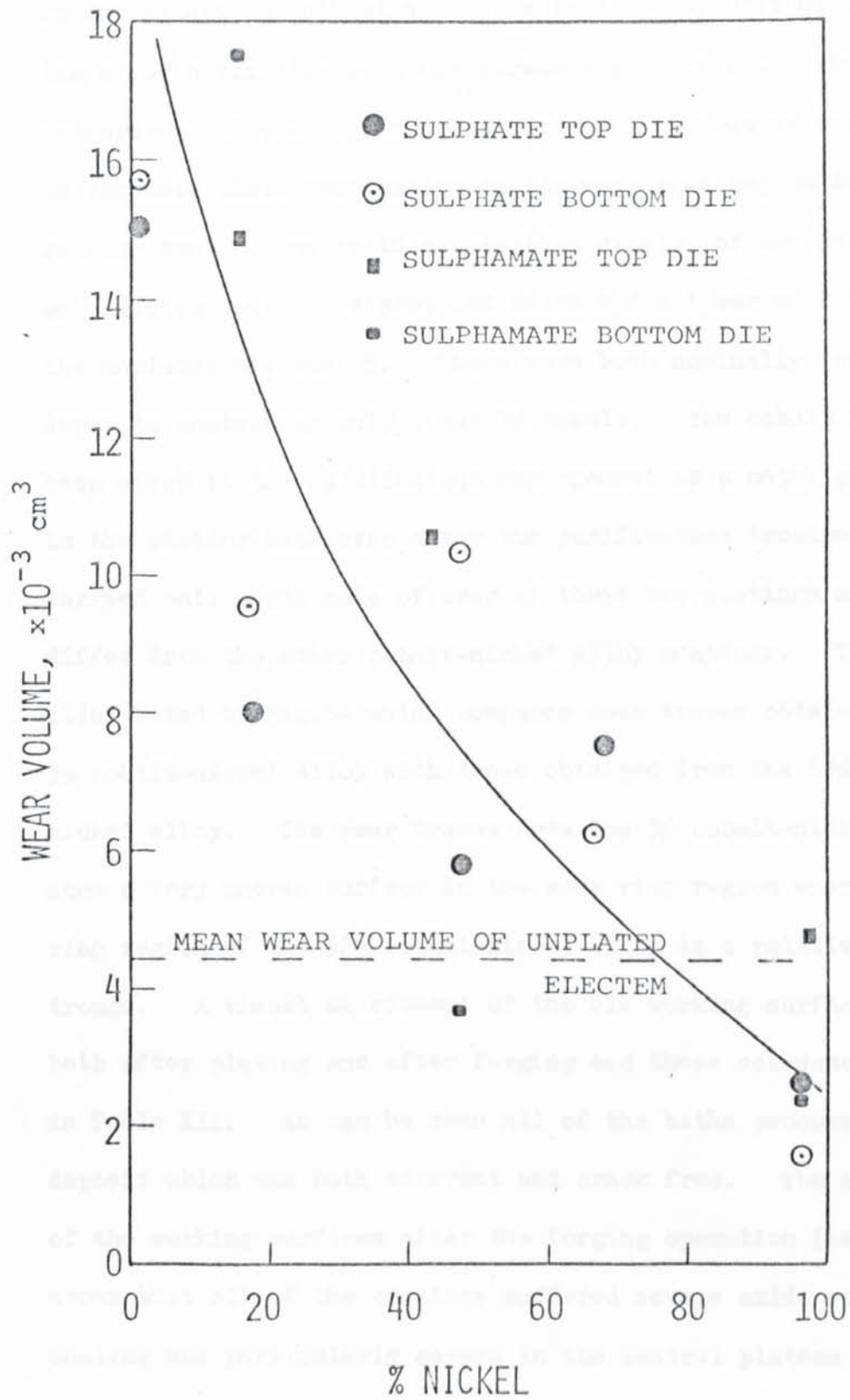| Solution Code	COMPOSITION g/ℓ				pH	Current Density A/dm²	Temp. °C
	Cobalt Sulphamate	Nickel Sulphamate	Nickel Chloride	Boric Acid			
N7	140	600	10	40	4.0	4.0	60
N8	28.7	600	10	40	4.0	4.0	60
N9	–	600	10	40	4.0	4.0	60

Fig.53.   Relationship between the nickel content
of Co-Ni coatings and their degree of
wear after forging 1000 billets.

approximately 65% nickel which was reported by Belt et al [1] as
the alloy having the best hot hardness properties.   The general
performance of the coatings was very poor as most suffered partial
or complete plate penetration in the wear ring region during the
forging test.   Due to this very high erosion of the coatings
only two coatings were produced which had a lower wear volume than
the unplated Electem 5.   These were both nominally 'pure' nickel
deposits containing only about 3% cobalt.   The cobalt had not
been added to the solution but was present as a metal contaminant
in the plating bath even after the purification treatment had been
carried out.   The mode of wear of these two coatings appeared to
differ from the other cobalt-nickel alloy coatings.   This is
illustrated by Fig.54 which compares wear traces obtained from the
3% cobalt-nickel alloy with those obtained from the 52% cobalt-
nickel alloy.   The wear traces from the 3% cobalt-nickel alloy
show a very uneven surface in the wear ring region whereas the wear
ring region of the 52% cobalt-nickel alloy is a relatively smooth
trough.   A visual assessment of the die working surface was made
both after plating and after forging and these assessments are given
in Table XII.   As can be seen all of the baths produced a good
deposit which was both adherent and crack free.   The assessment
of the working surfaces after the forging operation (before descaling),
shows that all of the coatings suffered severe oxide scaling.   This
scaling was particularly severe in the central plateau region of the
die and could not be removed completely by the electrolytic cleaning
operation as was the case with the unplated Electem dies.   The
majority of this oxide was introduced to the die surface from the
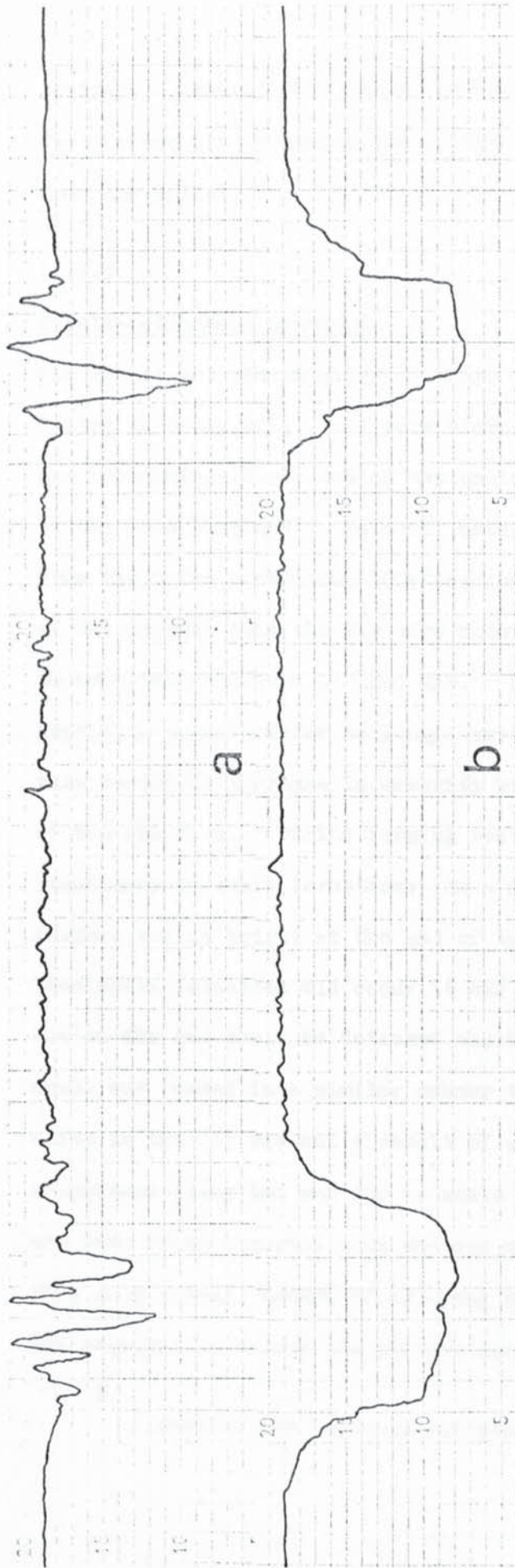hot billets and only a small proportion was due to oxidation of the

Fig.54. Talylin wear traces obtained on:-

a) Die plated with nickel from solution (N9)

b) Die plated with cobalt-nickel alloy (N3)

Vertical magnification x 500

coating.   However it appeared that the slight oxidation of the die surface was forming a low melting point 'slag' with the oxide from the billet.

11.1.3.

Cobalt-molybdenum coatings.

The cobalt-molybdenum alloy coatings evaluated on flat dies are listed in Table XII;   they were plated from two basic solutions, one containing 100g/1 sodium heptonate and the other containig 200g/1 of the same compound.   In most instances sound deposits were obtained from the baths containing 100g/ℓ sodium heptonate.   Slight flaking of the deposit from the die edge occurred on two die sets, that is those using solutions M17 and M19.   On increasing the sodium heptonate concentration to 200g/1 severe edge cracking resulted and this tended to increase in severity with increasing molybdate content of the solution.   During forging tests all coatings exhibited good resistance to scale formation;   in a number of cases the working surface was as bright at the end of the test as at the beginning. When scale formation did occur it was confined to the centre of the bottom die and could be detached easily with the finger nail.   The scale was formed in a similar manner to that on the cobalt-nickel alloy in that it was not a result of oxidation of the cobalt-molybdenum alloy but was due to scale flaking from the billets and then being impacted onto the die surface.   It should be emphasised that only a small amount of alloying element, of the order of 1-2%, was required to reduce the surface scale to a negligible proportion.

None of the coatings suffered plate penetration during the

forging test. The wear results given in Table XII show that the three solutions containing 100g/1 sodium heptonate produced the most wear resistant coatings, those plated using baths M17 and M19 giving wear results comparable with chromium.

The graph shown in Fig.55 is a plot of wear volume obtained against % molybdenum in the deposit for coatings obtained from baths containing both 100 and 200g/1 sodium heptonate. The graph shows that a significant increase in performance of the coating is achieved when a molybdenum content of approximately 4% has been exceeded. The wear volumes obtained for alloy coatings containing higher concentrations of molybdenum than this are approximately 12% of those obtained for unplated Electem. The individual points for top and bottom dies are plotted as in some cases the composition of the top and bottom die was not the same even though the sets had been plated in similar solutions. In most instances this difference was not too great but there was one outstanding exception in the case of the bath having the highest molybdenum content (M19). This variation was probably due to the small scale of operation ($2\frac{1}{2}$ litres plating bath was employed) and the fairly long plating time of 6-8 hours that was required to provide the 25-75 μm thick coatings.

11.1.4.

Cobalt-tungsten coatings

Cobalt-tungsten alloys were deposited from solutions of similar base formulation to those used for cobalt-molybdenum. The plating characteristics (shown in Table XII) were also similar to those
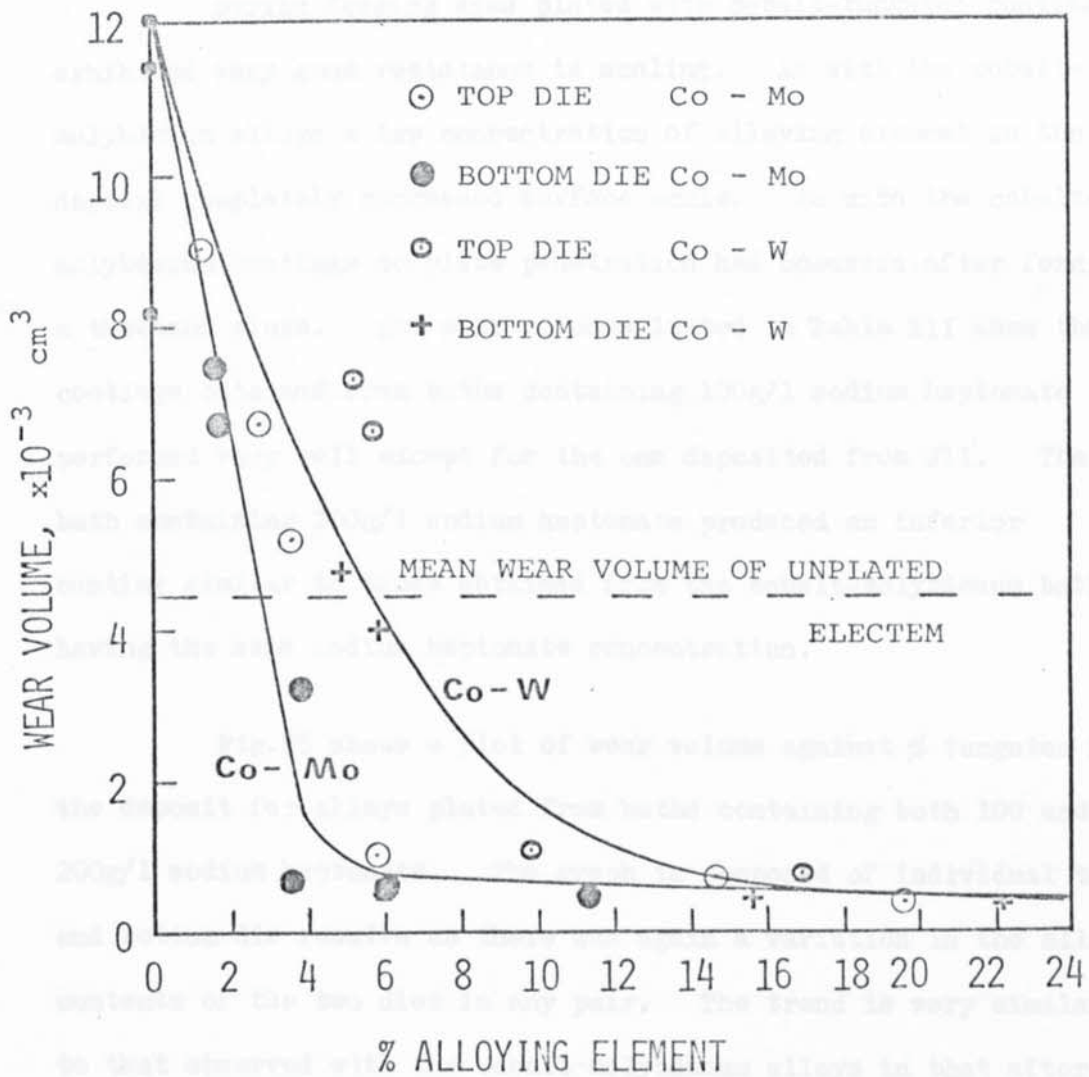
Fig.55. Relationship between the alloying element content of Co-Mo and Co-W coatings and their degree of wear after forging 1000 billets.

of the cobalt-molybdenum baths in that the ones containing 100g/1
sodium heptonate produced sound deposits with edge flaking occurring
only in the case of the coating plated from the bath containing
15.75g/1 sodium tungstate.

During forging dies plated with cobalt-tungsten coatings
exhibited very good resistance to scaling. As with the cobalt-
molybdenum alloys a low concentration of alloying element in the
deposit completely supressed surface scale. As with the cobalt-
molybdenum coatings no plate penetration had occurred after forging
a thousand slugs. The wear volumes listed in Table XII show that
coatings obtained from baths containing 100g/1 sodium heptonate
performed very well except for the one deposited from W11. The
bath containing 200g/1 sodium heptonate produced an inferior
coating similar to those obtained from the cobalt-molybdenum baths
having the same sodium heptonate concentration.

Fig.55 shows a plot of wear volume against % tungsten in
the deposit for alloys plated from baths containing both 100 and
200g/1 sodium heptonate. The graph is composed of individual top
and bottom die results as there was again a variation in the alloy
contents of the two dies in any pair. The trend is very similar
to that observed with the cobalt-molybdenum alloys in that after a
particular concentration of tungsten in the deposit has been exceeded
(8%) the coatings become much more wear resistant. The wear
volumes obtained for coatings having tungsten contents in excess of
8% are very similar to those obtained for alloys containing greater
than 4% molybdenum.

The wear results obtained for the cobalt-tungsten
coatings show that wear resistance is increased with increasing
tungsten content of the deposit for coatings obtained from baths
containing both 200g/l and 100g/l sodium heptonate.   The wear
resistant cobalt-molybdenum coatings however were only obtained
from the baths containing 100g/l sodium heptonate.   It is thought
that this effect is due to the fact that coatings were not produced
from the cobalt-molybdenum bath containing 100g/l sodium heptonate
with a sufficiently low molybdenum content to give poor wear
resistance and not to the fact that the bath contained the lower
sodium heptonate concentration.

11.2.

Shaped Die Wear Tests.

11.2.1.

Shape number 4.

Die shape number 4 was plated with the five coatings that
performed most satisfactorily on flat dies.   The results obtained
after the series of forging tests showed that, in terms of deformation,
all dies whether plated or not suffered a similar amount of deformation.
The plated dies were slightly worse than the unplated Electem.   It
is not surprising that the results are similar since the thin
electrodeposited coatings could not be expected to alter significantly
the behavior of the bulk die steel when subjected to fairly severe
deformation.   The detailed results are shown in Table XIV for
unplated Electem and for the die plated with an alloy coating
deposited from bath M19.   Unfortunately, two of the dies (M17 and W12)

TABLE XIV. Wear Results on Die Shape No.4.

| Solution Code | Deformation and Erosion after Forging | | | | |
	50 Forgings	100 Forgings	200 Forgings	300 Forgings	
Unplated Electem	6.86	9.4	11.0	12.2	Deformation x 10^{-2} mm
M19	6.10	9.90	14.0	13.3	
Unplated Electem	17.4	25.8	18.0	42.0	Erosion x10^{-3} mm^2
M17	1.9	1.6	2.8	5.2	
M19	7.7	6.4	4.1	1.6	
W13	5.2	6.4	4.8	2.6	

TABLE XV. Order of Merit on Visual Assessment of Dies after Forging and Descaling

| Solution Code | Number of Billets Forged | | | | |
	50	100	200	300	
Unplated Electem	4	4	4	4	Die Shape No.4.
M16		Adhesion failure			
M17	1	1	1	1	
M19	2	2	2	2	
W12		Adhesion failure			
W13	3	3	2	2	
Unplated Electem	6	6	6	6	Die Shape No.6.
M16	1	1	1	1	
M17	4	3	4	5	
M19	1	3	3	2	
W12	1	2	2	2	
W13	4	5	4	4	

could not be tested fully as adhesion failures developed between the coating and the substrate at an early stage. Similar failures occurred when repeat tests were carried out. This was due almost certainly to the severe deformation at the edge of the recess in the die and to the fact that the first few forgings stuck in the die cavity requiring considerable force to remove them.

Although erosion measurements were difficult to obtain from the wear traces, as the wear areas were very small, results are included in Table XIV and show that in all cases the plated dies performed better than the unplated Electern. The erosive wear of the plated dies shows a tendency for the wear area to decrease as the number of forging operations carried out is increased. This effect was most probably associated with the deformation of the die steel occurring at the edge of the die cavity which compensated for the low erosive wear of the coating. A visual assessment of the dies was made at intervals during the forging test and the order of performance is listed in Table XV. This shows that, except where adhesion failures occurred, the plated dies were superior to the unplated one at all stages of testing.

11.2.2.

Shape number 5 and 6.

Although it was decided that shape 5 would not be used due to the lengthy machining operations for its manufacture an unplated Electem die of this configuration was tested over the

series of forging operations. This was done as a literature
search had revealed that a small industrial die of this shape
had been used by Sveriges Mekanforbund [85] for die wear testing
and it was thought that a comparison with this work would be
valuable. One of the wear measuring techniques employed by
Sveriges Mekanforbund was to measure the height change in the
flash land during a series of forging operations. Therefore
such data was extracted from the wear traces obtained on die
shape 5. The results obtained by Sveriges Mekanforbund for a
die of similar hardness to that used in this work and those
obtained from die shape 5 are shown in Fig.56a and b. The
trends of both graphs are similar; both dies undergo deformation
initially which is followed by erosion as the number of forgings
increases. Fig.56c is the same information obtained for die
shape number 6 and again a similar trend is indicated. It
was concluded from these results that although die shape 5 was
slightly closer in wear behavior to the industrial die, the use
of the shape 6 was still a good simulation of industrial conditions
and so could be used with some confidence to assess the behavior
of alloy coatings.

In order to establish a control for die shape 6, against
which the performance of the coatings could be measured, three
unplated Electem dies were tested and their mean wear results
used for comparison. The Talyrond traces obtained from this
shape were more suitable for measuring erosion at the flash land
region than the Talylin traces obtained from shape 4 since they
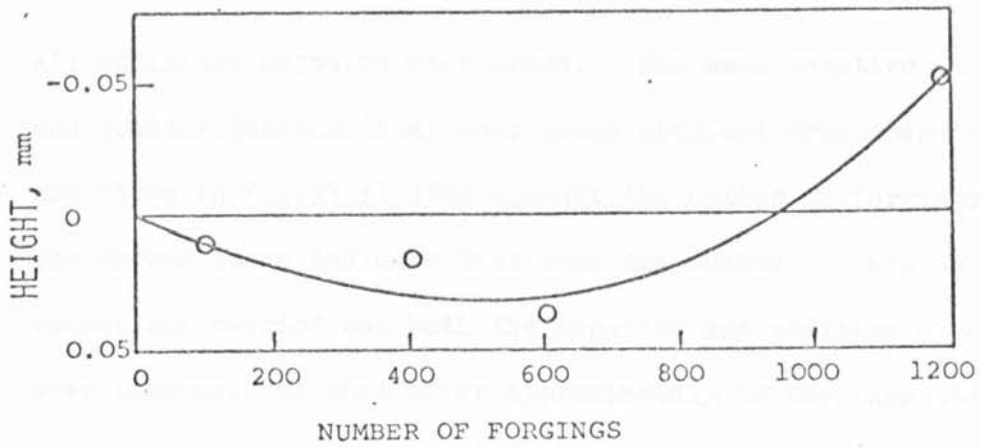
a) Data from Sveriges Mekanförbund.[85]
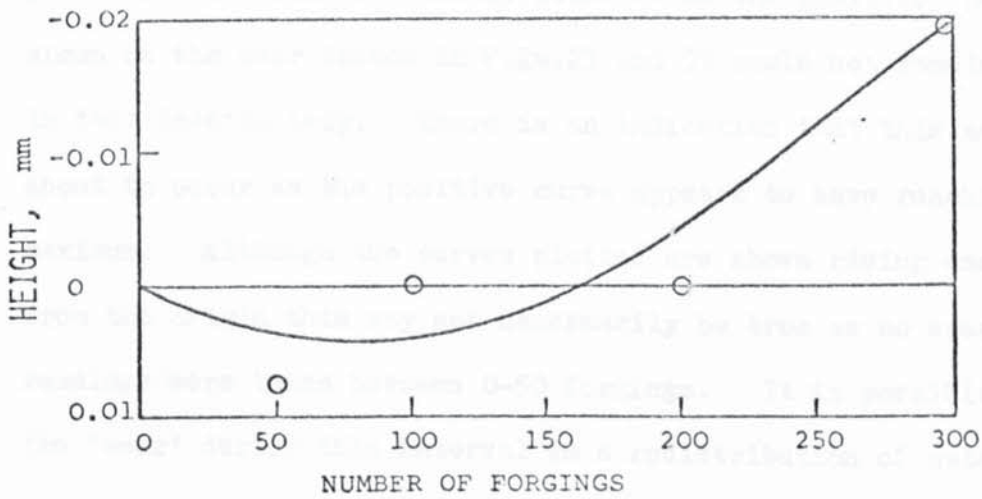
b) Data from die shape 5.
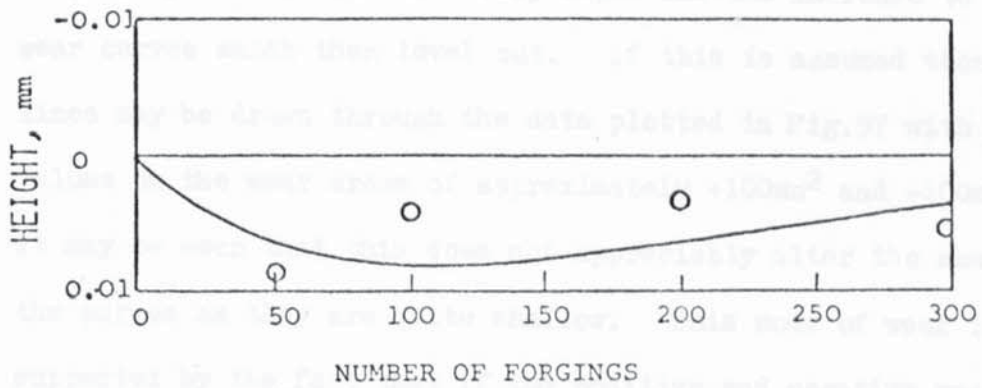
c) Data from die shape 6.

Fig.56. Graphs showing dimensional changes on shaped dies.

all exhibited negative wear areas.   The mean negative (erosion)
and positive(deformation) wear areas obtained from these dies
are shown in Fig.57 plotted against the number of forgings.
The curves shown indicate that over the number of forging
operations carried out both the negative and positive areas of
wear increase but that after approximately 50 forgings the
negative wear area (erosion) is the dominating factor.   It would
be expected that if the number of forgings were increased the
positive area would eventually decrease as the positive 'peaks'
shown on the wear traces in Figs.23 and 59 could not remain
in tact indefinitely.   There is an indication that this may be
about to occur as the positive curve appears to have reached a
maximum.   Although the curves plotted are shown rising smoothly
from the origin this may not necessarily be true as no wear
readings were taken between 0-50 forgings.   It is possible that
the 'wear' during this interval is a redistribution of metal
giving the peaks and troughs of the wear traces but resulting in
no actual loss of metal.   This may occur during the first few
forging operations giving a very rapid initial increase to both
wear curves which then level out.   If this is assumed then straight
lines may be drawn through the data plotted in Fig.57 with intercept
values on the wear areas of approximately $+100mm^2$ and $-100mm^2$.
It may be seen that this does not appreciably alter the shape of
the curves as they are quite shallow.   This mode of wear is
supported by the fact that if the positive and negative wear areas
for the first fifty forgings are added together a small positive
wear area is obtained indicating no loss of metal up to this point.
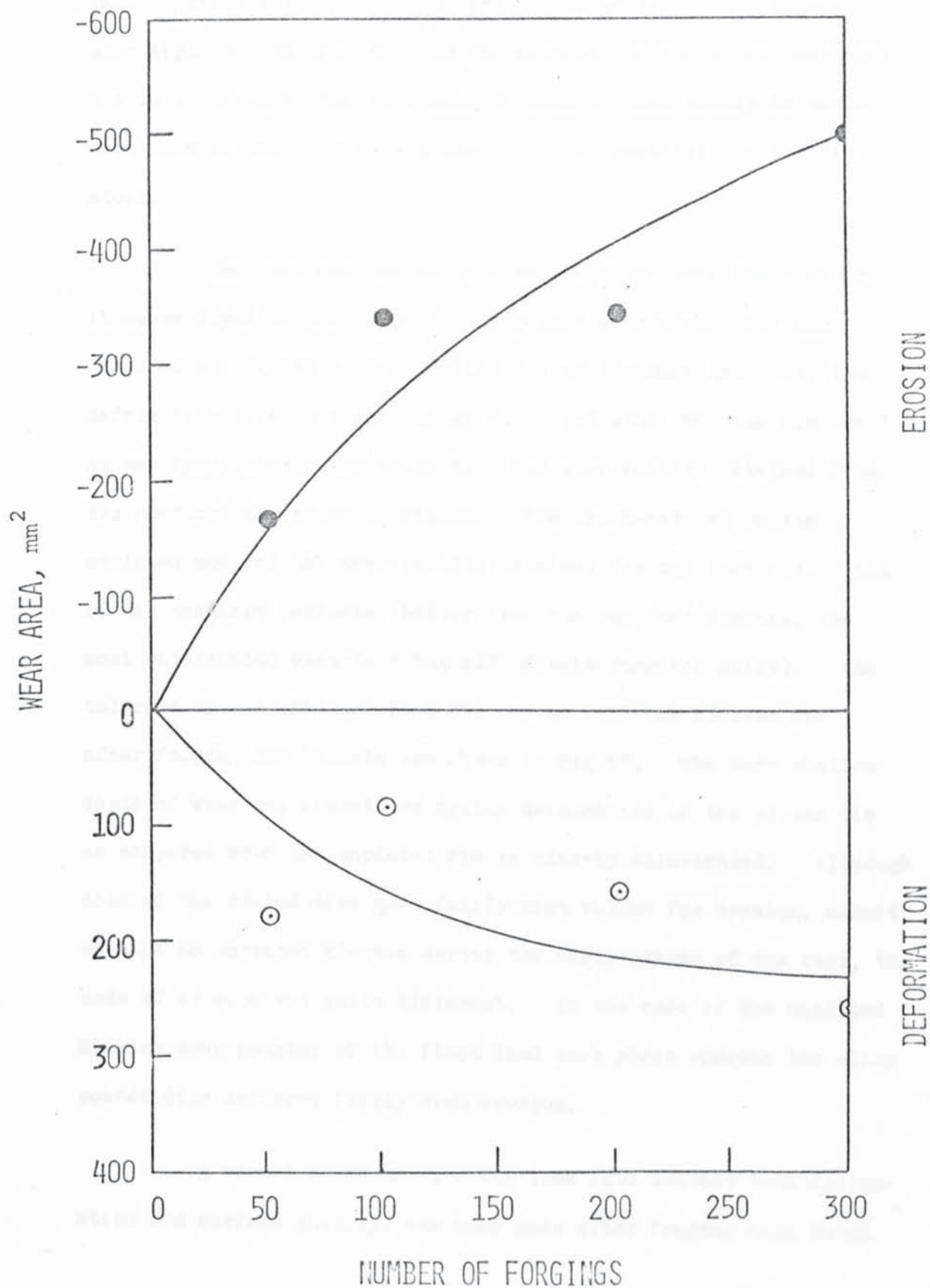Beyond fifty forgings addition of positive and negative areas results

Fig.57. Erosion and deformation of a shaped
unplated Electem die.

in a negative value indicating true metal loss. These remarks
also apply to the wear rate graphs plotted for the alloy coatings
but it is thought that this mode of wear is less likely to occur
with them as they are much harder and less ductile than the die
steel.

The coatings tested on this die shape were the same as
those employed on die shape 4. Negative wear areas only were
measured as erosion of the coating was of the most interest, the
deformation effects being mainly dependent upon the bulk die steel
as was found when using shape 4. The wear results obtained from
the coatings are shown in Fig.58. The cross-hatched region
encloses most of the wear results obtained for the coatings. All
of the coatings performed better than the unplated Electem, the
most outstanding example being W12 (Cobalt-tungsten alloy). The
talyrond traces obtained from W12 and an unplated Electem die
after forging 300 billets are shown in Fig.59. The very shallow
depth of wear and almost negligible deformation of the plated die
as compared with the unplated die is clearly illustrated. Although
some of the plated dies gave fairly high values for erosion, almost
as high as unplated Electem during the early stages of the test, the
mode of erosion was quite different. In the case of the unplated
Electem deep gouging of the flash land took place whereas the alloy
coated dies suffered fairly even erosion.

A visual assessment, which took into account both deform-
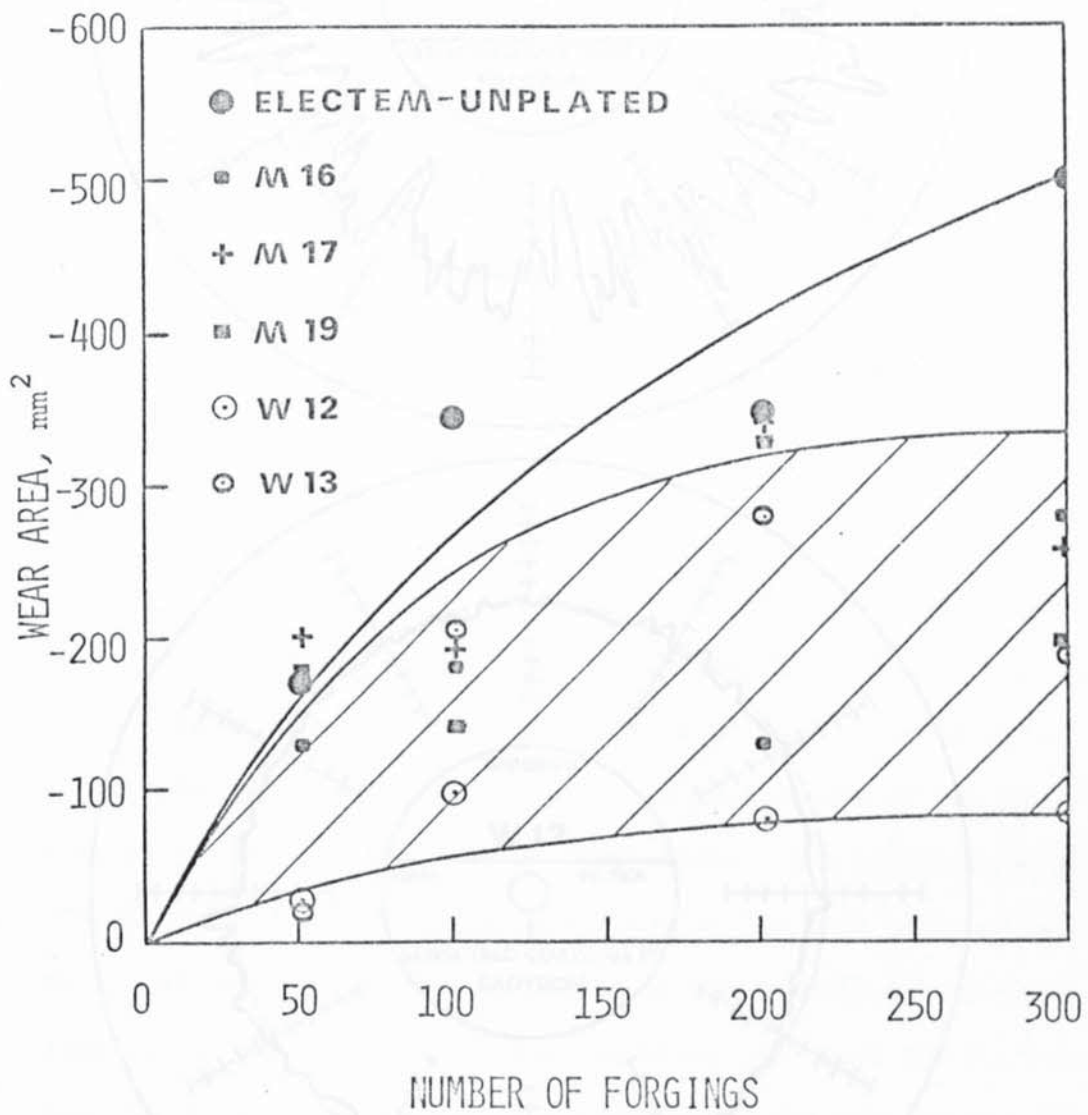ation and surface quality, was also made after forging each batch

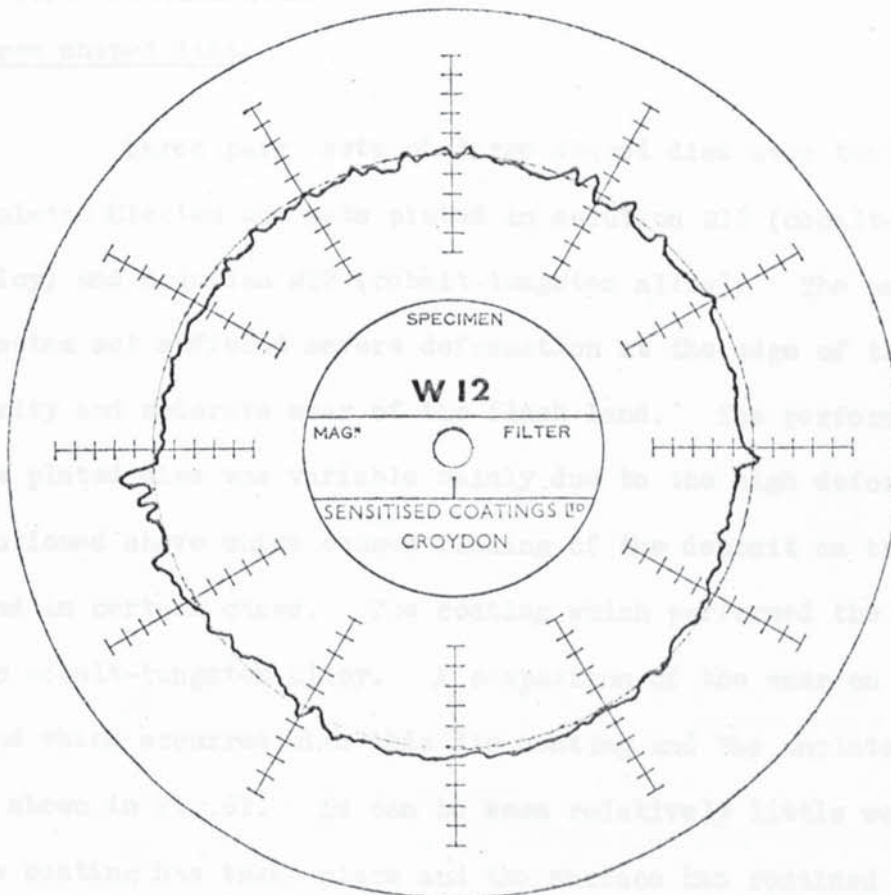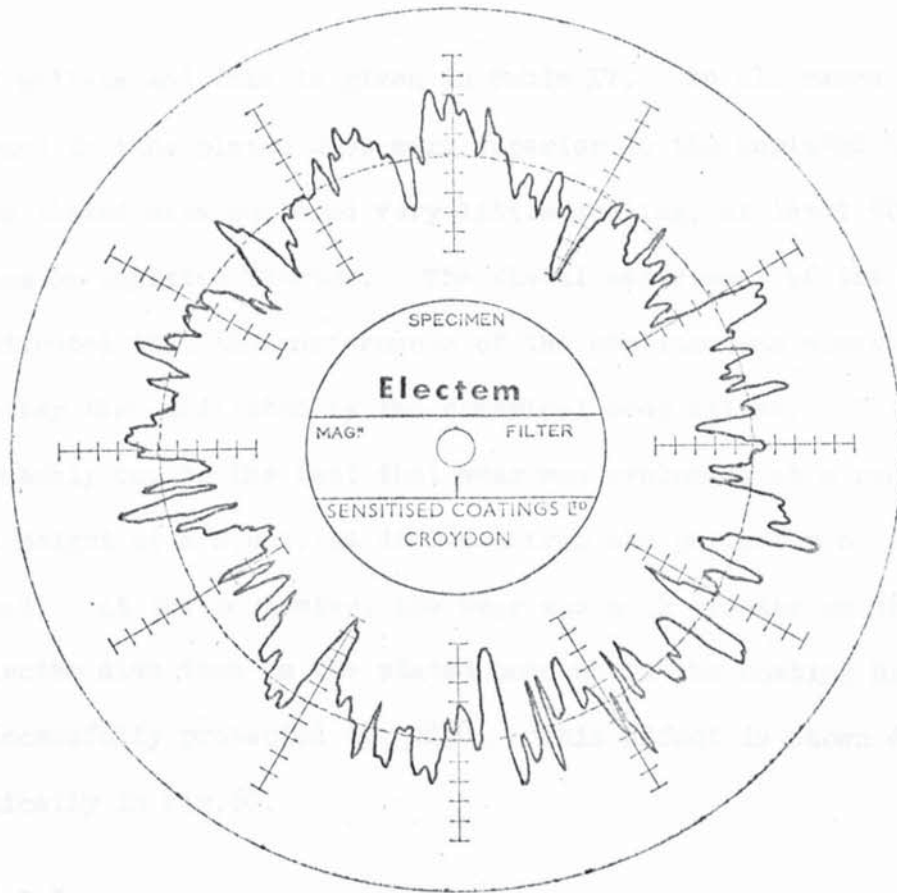Fig.58. Wear rate graph for various cobalt alloy deposits plated on die shape No.6.

Fig.59. Talyrond traces obtained for unplated electem and
a die plated with a cobalt-tungsten alloy (W12) after
forging 300 billets.
Vertical magnification x 1000

of billets and this is given in Table XV.   In all cases it was
found that the plated dies were superior to the unplated Electem.
The plated dies suffered very little scaling, at least 50% less
than on unplated Electem.   The visual assessment of the dies
indicated that the performance of the coatings was somewhat
better than indicated by the numerical wear values.   This was
probably due to the fact that wear was evaluated as a reduction
in height at a specified distance from the perimeter of the flash
land.   At the perimeter, the wear was much greater on the unplated
Electem dies than on the plated ones where the coating had
successfully protected the edge.....This effect is shown diagram-
atically in Fig.60.

11.2.3.

Large shaped dies.

        Three pair sets of large shaped dies were tested,
unplated Electem and sets plated in solution M16 (cobalt-molybdenum
alloy) and solution 712 (cobalt-tungsten alloy).   The unplated
Electem set suffered severe deformation at the edge of the die
cavity and moderate wear of the flash land.   The performance of
the plated dies was variable mainly due to the high deformation
mentioned above which caused flaking of the deposit on the flash
land in certain cases.   The coating which performed the best was
the cobalt-tungsten alloy.   A comparison of the wear on the flash
land which occurred with this die coating and the unplated Electem
is shown in Fig.61.   As can be seen relatively little wear of
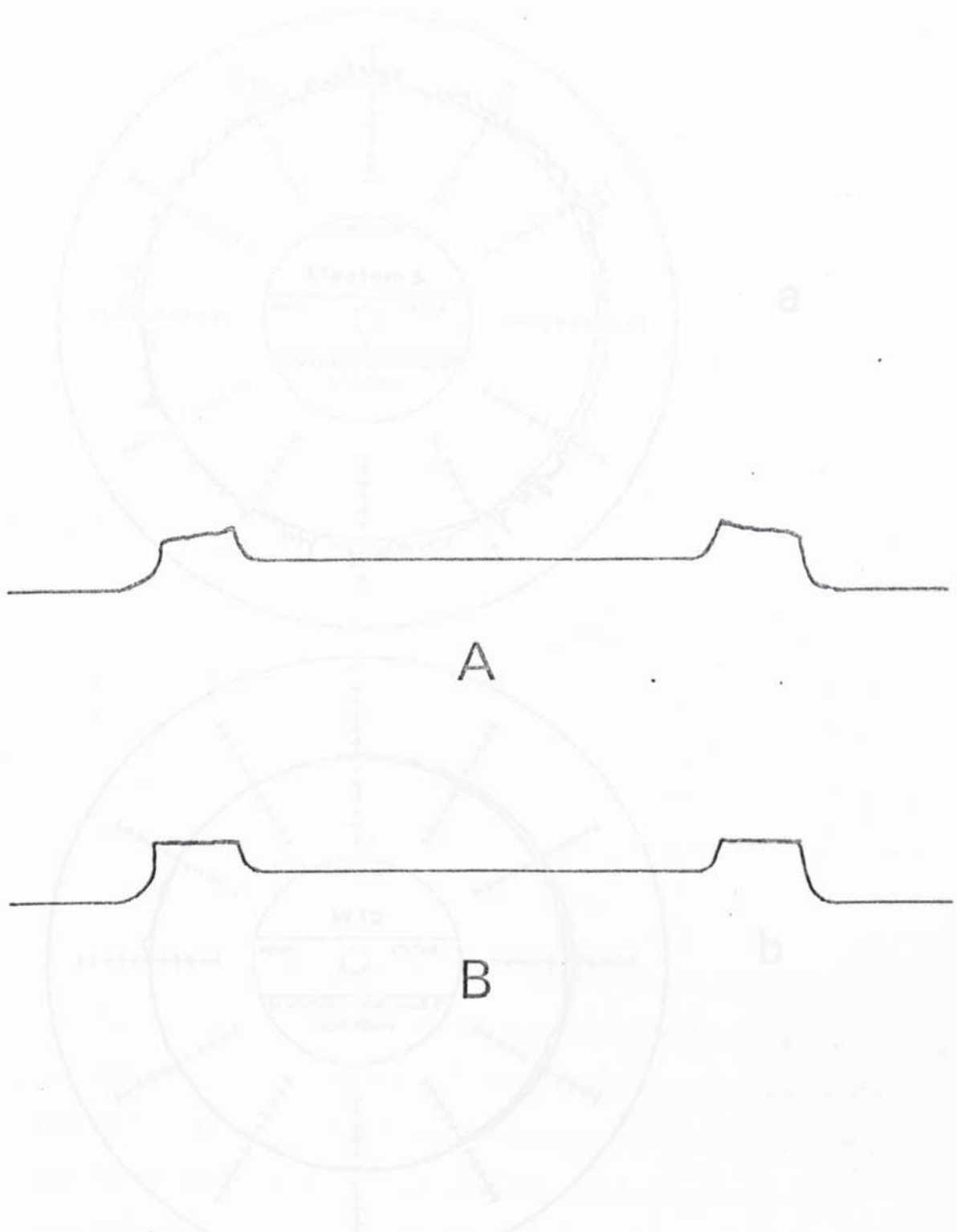the coating has taken place and the surface has remained quite

Fig.60. Sketch showing the mode of wear on die
         shape No.6.   Magnification approximately x 5.

         A) Unplated Electem
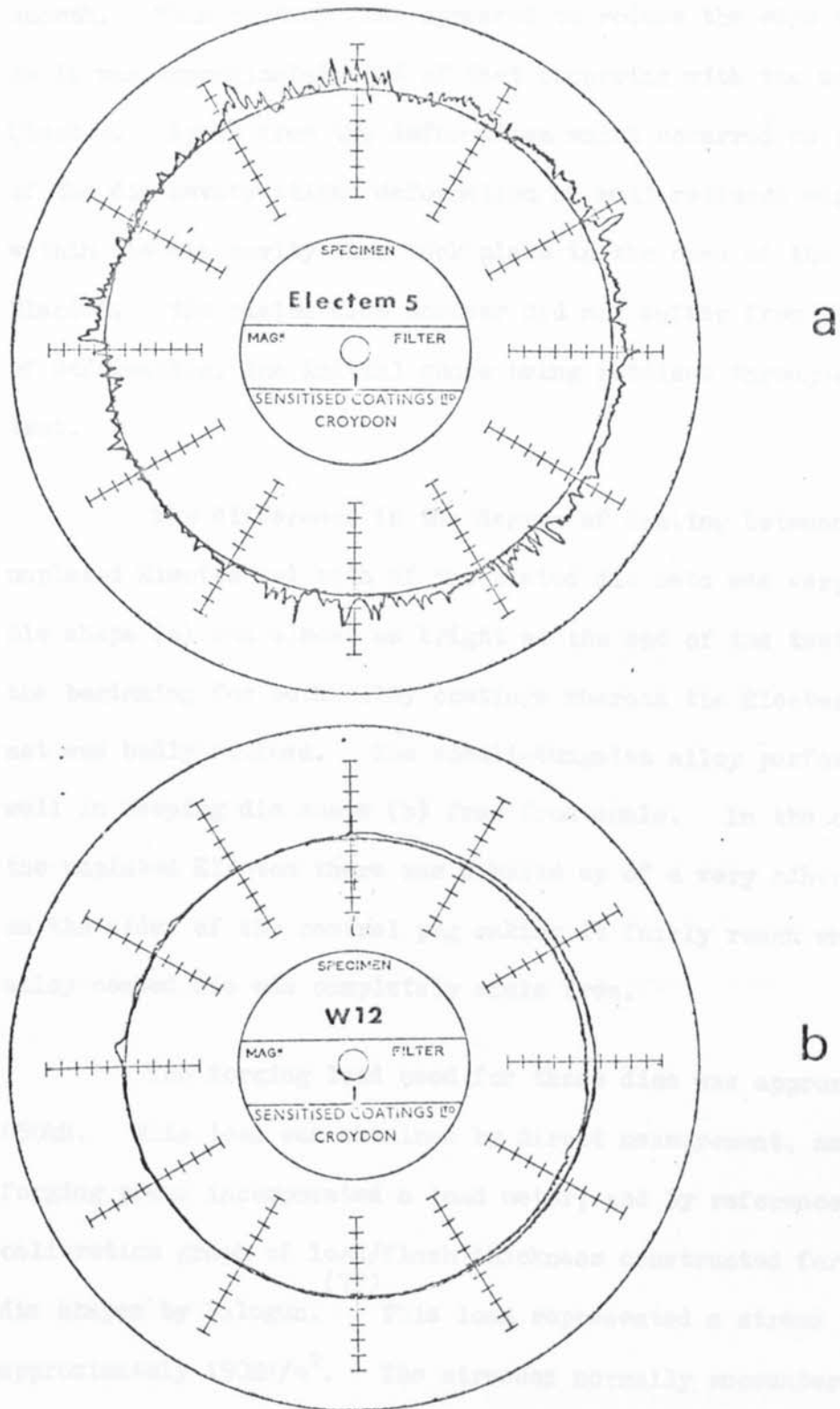   B) Die plated with coating from bath M16.

Fig.61. Talyrond traces obtained on large dies
(shape B) after forging 50 billets.
a) Unplated Electem No.5.
b) Die plated in bath W12.

smooth. This coating also appeared to reduce the edge deformation as it was approximately 50% of that occurring with the unplated Electem. Apart from the deformation which occurred on the edges of the die cavity slight deformation of well radiused edges within the die cavity also took place in the case of the unplated Electem. The plated dies however did not suffer from this type of deformation, the initial shape being retained throughout the test.

The difference in the degree of scaling between the unplated Electem and both of the plated die sets was very marked. Die shape (a) was almost as bright at the end of the test as at the beginning for both alloy coatings whereas the Electerm die set was badly stained. The cobalt-tungsten alloy performed very well in keeping die shape (b) free from scale. In the case of the unplated Electem there was a build up of a very adherent oxide on the sides of the central peg making it fairly rough whereas the alloy coated die was completely scale free.

The forging load used for these dies was approximately 650kN. This load was obtained by direct measurement, as the forging press incorporated a load meter, and by reference to the calibration graph of load/flash thickness constructed for these die shapes by Balogun.[75] This load represented a stress of approximately 190MN/m^2. The stresses normally encountered on industrial dies vary from the centre of the forging, where the stress is highest, to the flash gap where the stress is lowest.[86] The stress at the flash gap remains fairly constant with variation

in shape and size of the forging as shown by Foster [86] and it therefore may be assumed that the stress at the flash gap of the large dies was similar to that obtained on industrial ones. This was also indicated by the examination of Balogun's [75] dies which exhibited most of the wear mechanisms encountered on industrial dies.

The abnormally high wear of the large dies after forging only a small number of billets may be attributed to the fact that it is usual practice to use 5% chromium steel in forging presses and No.5 die steel for drop forging hammers. This is because forging conditions in the press are more severe than those on the drop hammer due to the longer billet/die contact time which leads to higher temperatures. The wear tests carried out with the large Electem 5 dies on the forging press were therefore considerably accelerated. The results obtained from the plated dies suggests that if the 5% chromium steel had been plated then the performance of the coatings may have been improved as this steel has a much greater resistance to deformation.
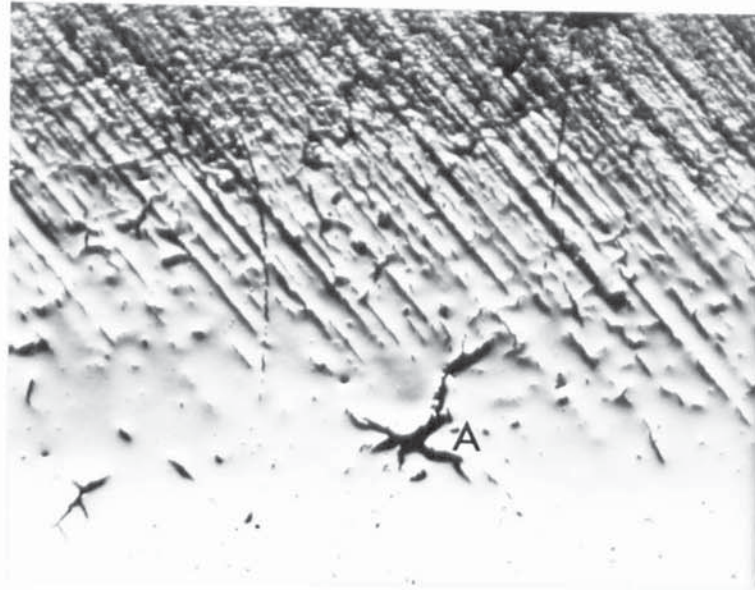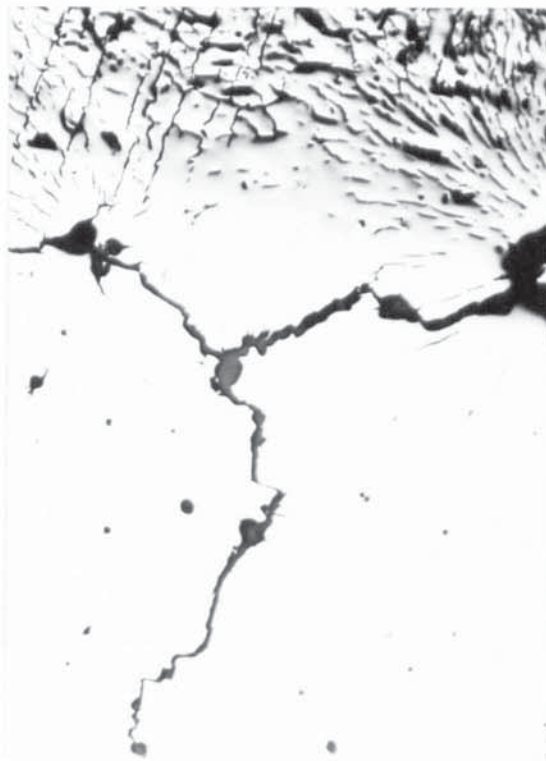
11.3.

Taper Sections of Flat Dies

11.3.1.

Unplated No.5 die steel.

The micrographs shown in Fig.62 illustrate the extent and type of cracking experienced after forging 1000 billets. In Fig.62a it appears that some of the cracks are associated with the original

a

b

Fig.62. Taper sections of unplated Electem 5 showing cracks
in central plateau region.
1000 billets forged x 1000

grinding marks since many of them are aligned in the same direction. Fig.62b shows the most severe type of cracking experienced and as can be seen the crack pattern follows the inclusions present in the steel.

The cracking of the dies was found to be associated with the central plateau region of the die only and was not present in the wear ring region. This does not necessarily mean that cracking did notoccur in the wear ring region but that development of the cracks was impeded in some way. It has been suggested[87] that erosion of the metal in this region polishes away newly initiated cracks before propagation into the bulk of the die is possible.

11.3.2.

Cobalt-nickel alloys.

Although most of these alloy coatings were penetrated in the wear ring regions after 1000 billets had been forged, it was evident that the degree of cracking, which again only occurred in the central plateau region, varied with composition and type of bath used to produce the deposit. The taper section illustrated in Fig.63 shows the central plateau region of a die plated using the cobalt-sulphate bath containing sodium saccharin (N6). This shows severe oxidation of the surface which was typical of the cobalt-nickel alloys and in this particular case it also illustrates that neither coating nor die steel had cracked. From the appearance of the surface layers shown in this figure and in Fig.64b it is not surprising that the cathodic pickling procedure was unsuccessful
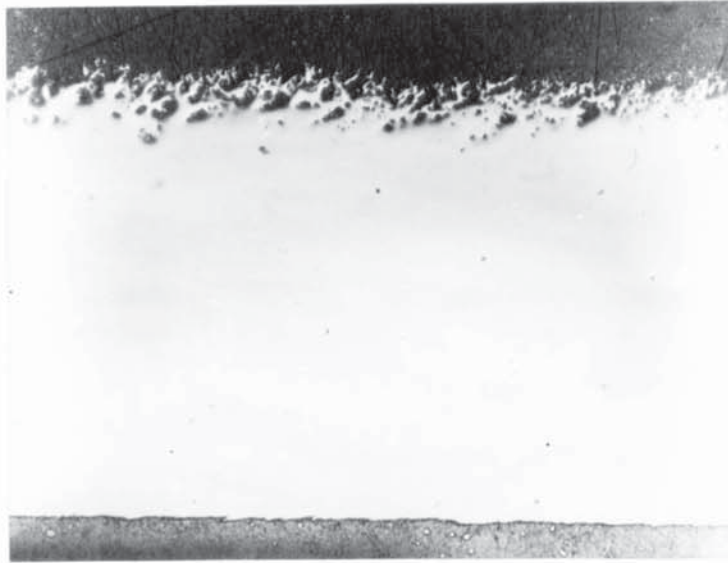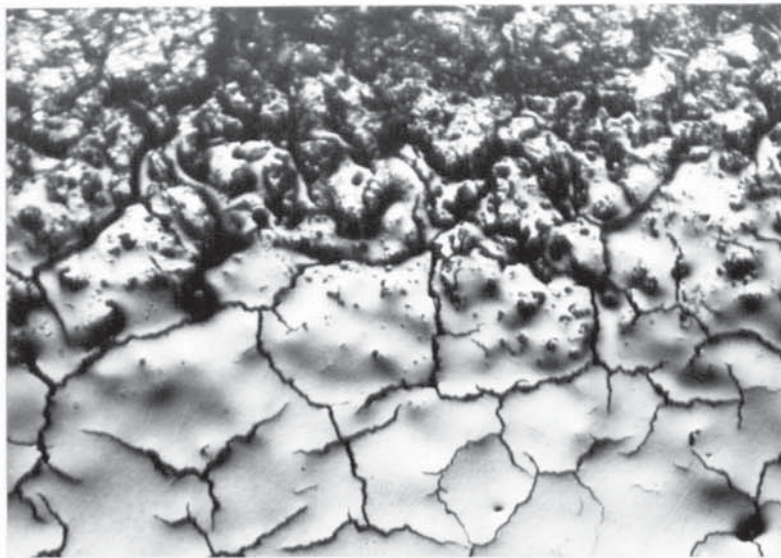
Fig.63. Taper section of die plated with cobalt-nickel
alloy (N6) showing surface oxidation of central
plateau region.
1000 billets forged x 1000

a)   Cracking in central plateau region.

b)   Surface oxidation.
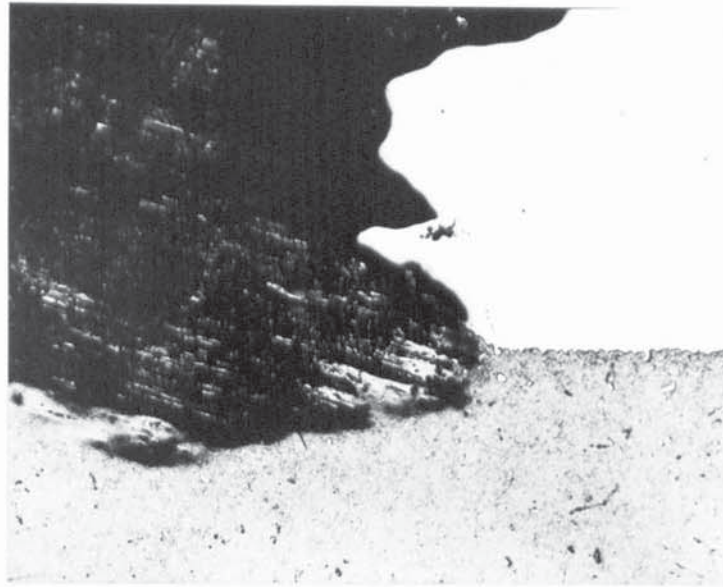
Fig.64.   Taper sections of die plated with cobalt-nickel
          alloy (N3).
          1000 billets forged.   x 1000

in removing scale from such coatings. The other die of the above set and the dies plated with the nominally pure cobalt coating. from bath N1 showed a considerable variation in the amount of cracking present in the central plateau region.

When a sulphate bath (N2) resulting in the deposition of an alloy containing 17% nickel and a sulphamate bath (N7) giving a coating containing 15.5% nickel were employed, cracking of the die steel was not experienced in the central plateau region in either case although slight cracking could be detected in the coating. The edge of the central plateau region of a die plated in the latter alloy is shown in Fig.65a. This illustrates that although complete penetration of the coating has taken place no cracking is present in the die steel or the coating. The severe deformation of the coating at the outer edge of the wear ring is illustrated in Fig.65b and again no cracks are seen to be present in the coating.

The alloy containing 48% nickel, deposited from the sulphate bath (N3), exhibited severe cracking in the central plateau region, the cracks propagated into the steel substrate on both top and bottom dies as shown in Fig.64a. However an alloy coating of similar composition, 45% nickel, plated from the sulphamate bath (N8) showed very little cracking in the centre of the bottom die and none at all in the top one.

Fig.66 shows the central plateau region of the die steel/ coating interface of the die set plated with 68% nickel from the

a) Penetration of coating at edge of central plateau region
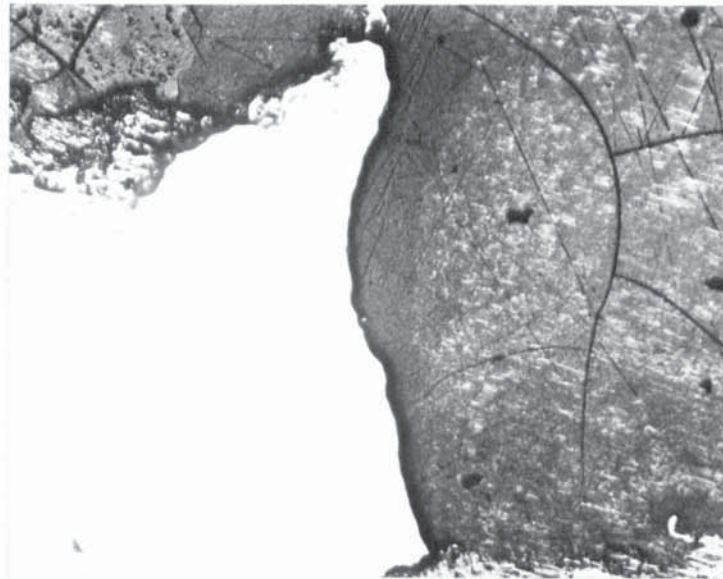
b) Deformation of coating at outer edge of wear ring

Fig.65. Taper sections of die plated with cobalt-nickel alloy (N7)
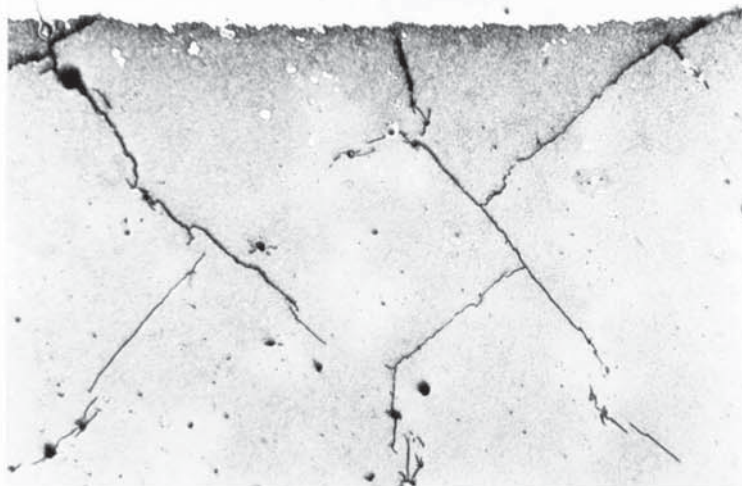1000 billets forged. x 1000

Fig.66.   Taper section of die plated with cobalt-nickel
          alloy (N4) showing cracks in the central plateau
          region associated with inclusions in the steel.
          1000 billets forged.   x 1000

sulphate bath (N4). The die steel and coating are cracked and it appears that many of the cracks are associated with inclusions in the steel.

Taper sections prepared from the die sets plated with nominally pure nickel from the sulphamate bath (N9) showed that very little cracking of the coating had occurred in the central plateau region and consequently the underlying die steel was crack free. However cracking did take place in both coating and die steel on the die sets plated from the nominally pure nickel sulphate bath (N5).

In general it seems that the sulphamate baths are slightly superior to the sulphate baths in reducing the extent of cracking. The coatings which appear to produce the fewest cracks are those containing low nickel concentrations. The exception to this was found to be the nominally pure nickel deposit obtained from the sulphamate bath (N9).

11.3.3.

Cobalt-molybdenum and cobalt-tungsten alloys

Examination of the taper sections prepared from all of the cobalt-molybdenum and cobalt-tungsten coatings after forging showed that cracks had penetrated from the coatings into the die steel. This was particularly severe in the central plateau region of the die but unlike the unplated Electem and the cobalt-nickel coatings, cracks were also present to some extent in the wear ring.

Typical areas of the central plateau region of both cobalt-molybdenum and cobalt-tungsten alloys showing cracking of the coating and steel are shown in Fig.67. The cracks in the steel are again seen to be associated with inclusions but they are finer than those present in the unplated electern (compare with Fig.62b). There was a slight tendency for the cobalt-tungsten alloys having good resistance to erosion to experience finer cracking than those having inferior wear resistance.

The presence of cracking in the wear ring region may be due to the coating being cracked as deposited therefore providing stress raisers. This would mean that the previously suggested mechanism for the lack of cracks in the wear ring region of the unplated Electem and the cobalt-nickel alloy coatings would not be possible as relatively deep cracks would be present from the start of the test.

If certain of the taper sections are examined (Figs.66a and 67a) it will be observed that there are white spots present just below the coating/die steel interface. These spots are due to pores produced during the pre-electroplating sequence being filled by electrodeposit. Electron proble microanalysis has indicated that the pores were formed due to inclusions, mainly manganese sulphate, being removed by the anodic etch as indicated by the series of x-ray photographs shown in Fig.68. It is interesting to note that when deposits in pores or deep grooves were analysed, very little molybdenum could be detected. Presumably the rate of replenishment of molybdenum ions in these regions was
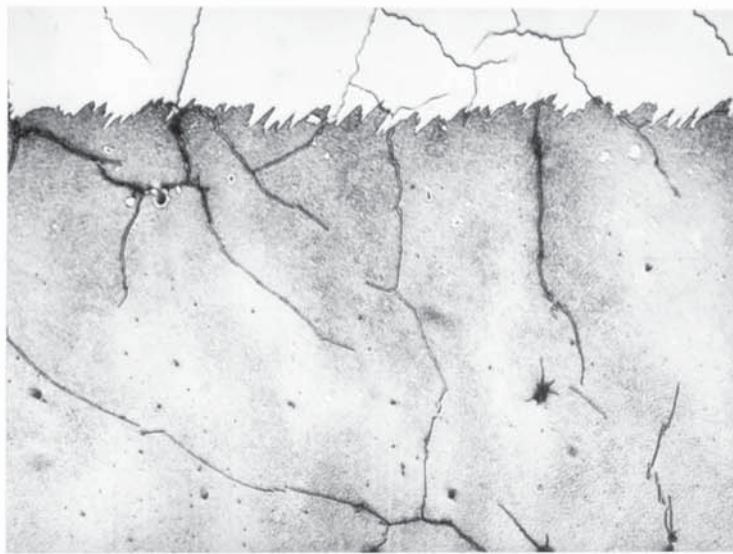
a) Cobalt-molybdenum alloy M19.
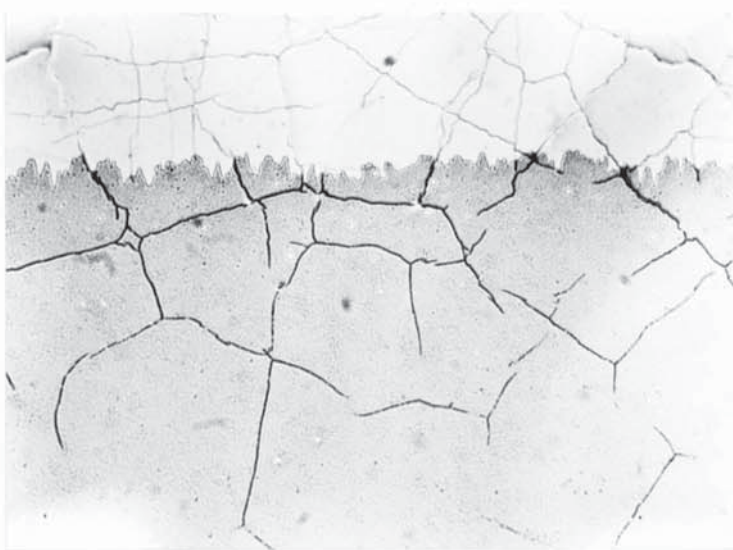
b) Cobalt-tungsten alloy W12.

Fig.67.   Taper sections showing cracks in the central
          plateau regions of dies plated with cobalt-alloys.
          1000 billets forged.   x 1000
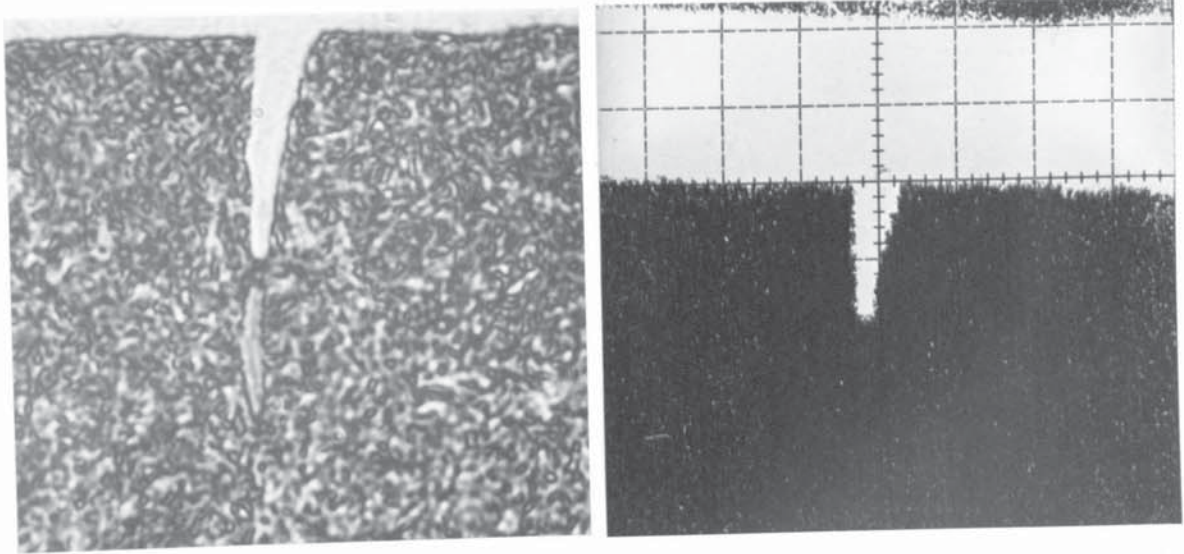
a) Optical cross-section x 1000 b) Cobalt X-rays   x 1000
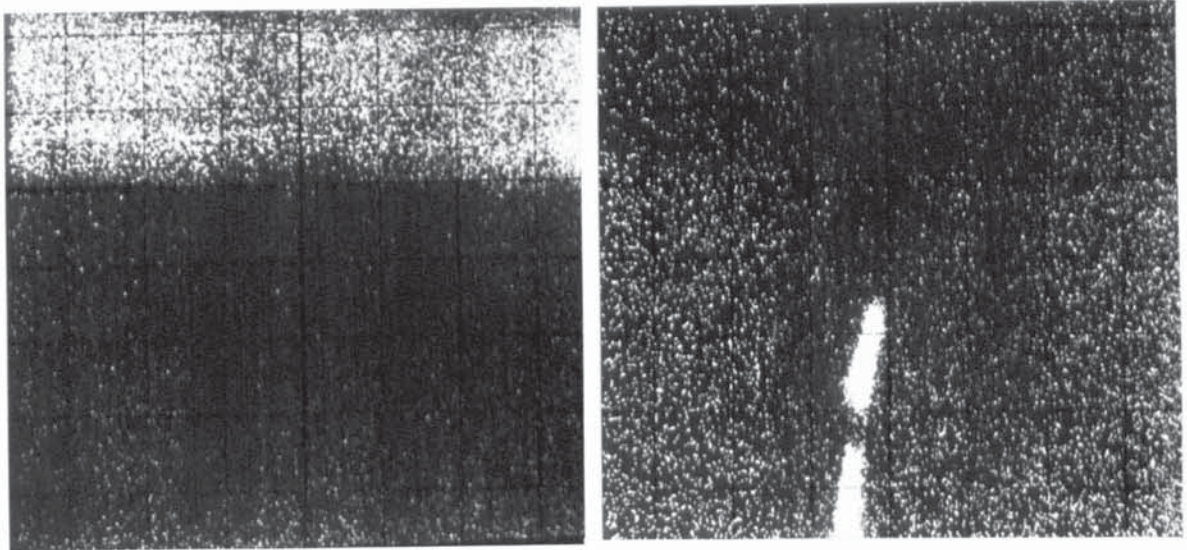
c) Molybdenum X-rays   x 1000 d) Manganese X-rays   x 1000

Fig.68.   X-ray photographs showing etched out manganese
           sulphide inclusion in steel substrate.
           Cobalt-molybdenum alloy M19.

too slow to give a molybdenum content as high as that in the bulk
deposit.

The general impression gained from examination of all of
the taper sections is that the presence of inclusions in the steel
was one of the primary causes of crack propagation in the dies.
It is considered that a significant increase in die life would be
obtained if such inclusions were reduced to a minimum by the use
of improved steel making technique.

11.4.

S.E.M. Examination of Flat Die Wear

11.4.1.

Unplated No.5 die steel.

Cracking of the die surface was revealed in the central
plateau region by the use of the S.E.M. as well as by taper sections.
The large "star" shaped surface crack shown in the scanning electron-
micrograph of the central plateau region, Fig.69 is very similar
to the defect marked 'A' in Fig.62a., which is a taper section of
the same part of the die. This was the most severe type of defect
and could readily lead to the keying of material being forged. The
wear ring region showed no cracking, but exhibited a certain amount
of flowing and erosion of the die surface, Fig.70.

11.4.2.

Cobalt-nickel alloys

It was very difficult to obtain surface topography pictures
of the worn regions of the dies plated with the cobalt-nickel alloys
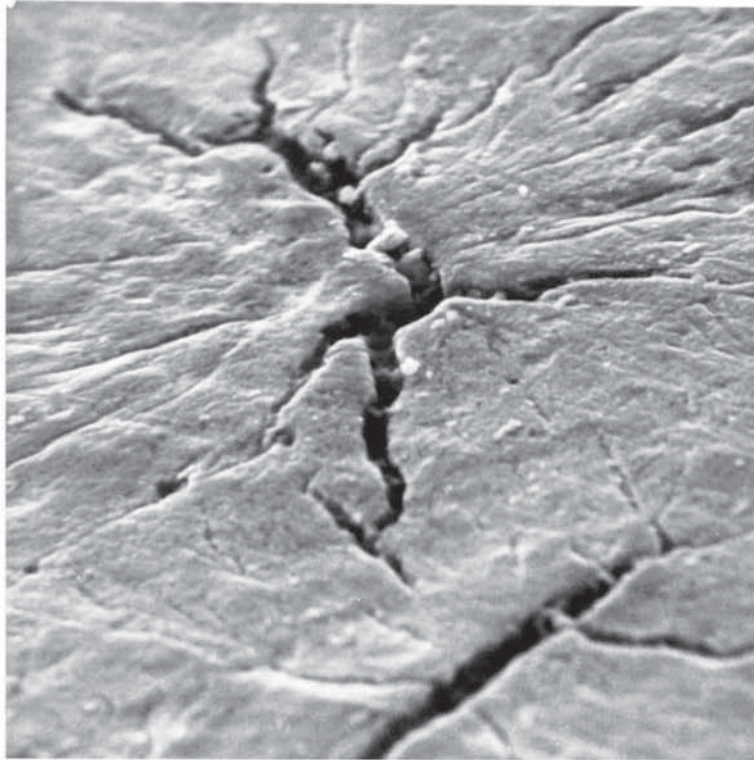
Fig.69. Scanning electronmicrograph showing large 'star' shaped crack in the central plateau region of an unplated Electem 5 die.
1000 billets forged. x 1500
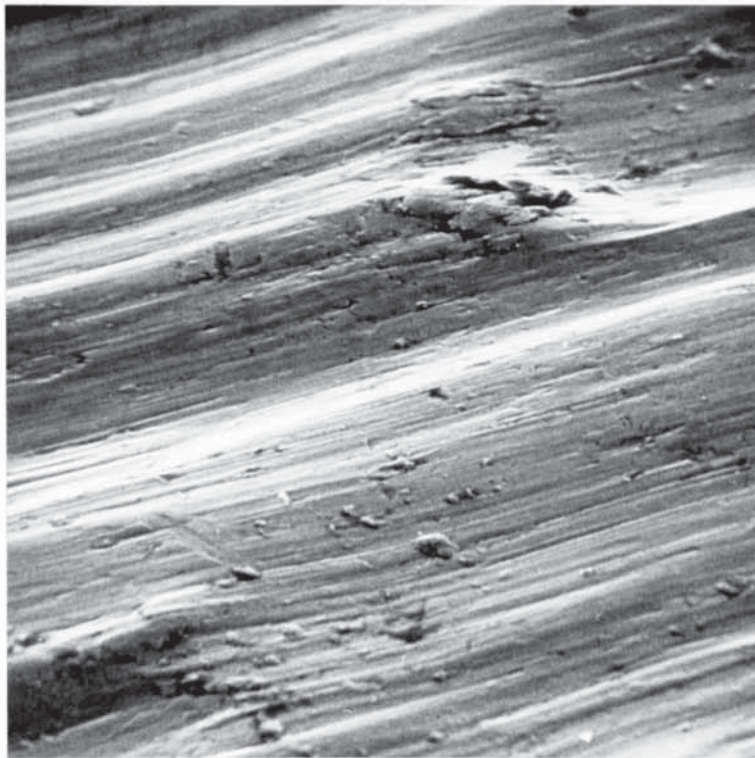
Fig.70 Scanning electronmicrograph of wear ring region of an unplated Electem 5 die.
1000 billets forged. x 300

due to adherant scale which masked the surface.   In many cases
the central plateau region and wear ring appeared almost identical.
It was only when pieces of oxide were seen to have flaked from the
surface that the difference in the surface topography of these two
regions could be discerned.   When this occurred it could be seen
that the information gained from the taper sections was reinforced.
It was possible to analyse the oxide qualitatively using the S.E.M.
dispersive x-ray technique although the surface was relatively rough.
It contained a fairly high iron concentration even after the descaling
operation as shown by the analysis traces, Fig.71.   Since the
alloy coating had not been penetrated this confirmed that iron oxide
from the billets had been incorporated into the die surface.

The entire wear areas of dies plated with a 45% nickel -
55% cobalt coating from a sulphamate bath (N8) and a 48% nickel -
52% cobalt coating obtained from a sulphate bath (N3) are illustrated
in Fig.72.   These show the type of partial (Fig.72a) and complete
(Fig.72b) erosion of the coating in the wear ring region which was
experienced with almost all of the cobalt-nickel alloys tested.
Fig.73 shows typical debris which piled up at the outer edge of
the wear ring on most of the dies.   The die illustrated was plated
in the sulphamate bath N8.   The cracking of the coating in the
central plateau region is illustrated in Fig.72c on a die plated
with a 48% nickel - 52% cobalt coating obtained from the sulphate
bath N3.
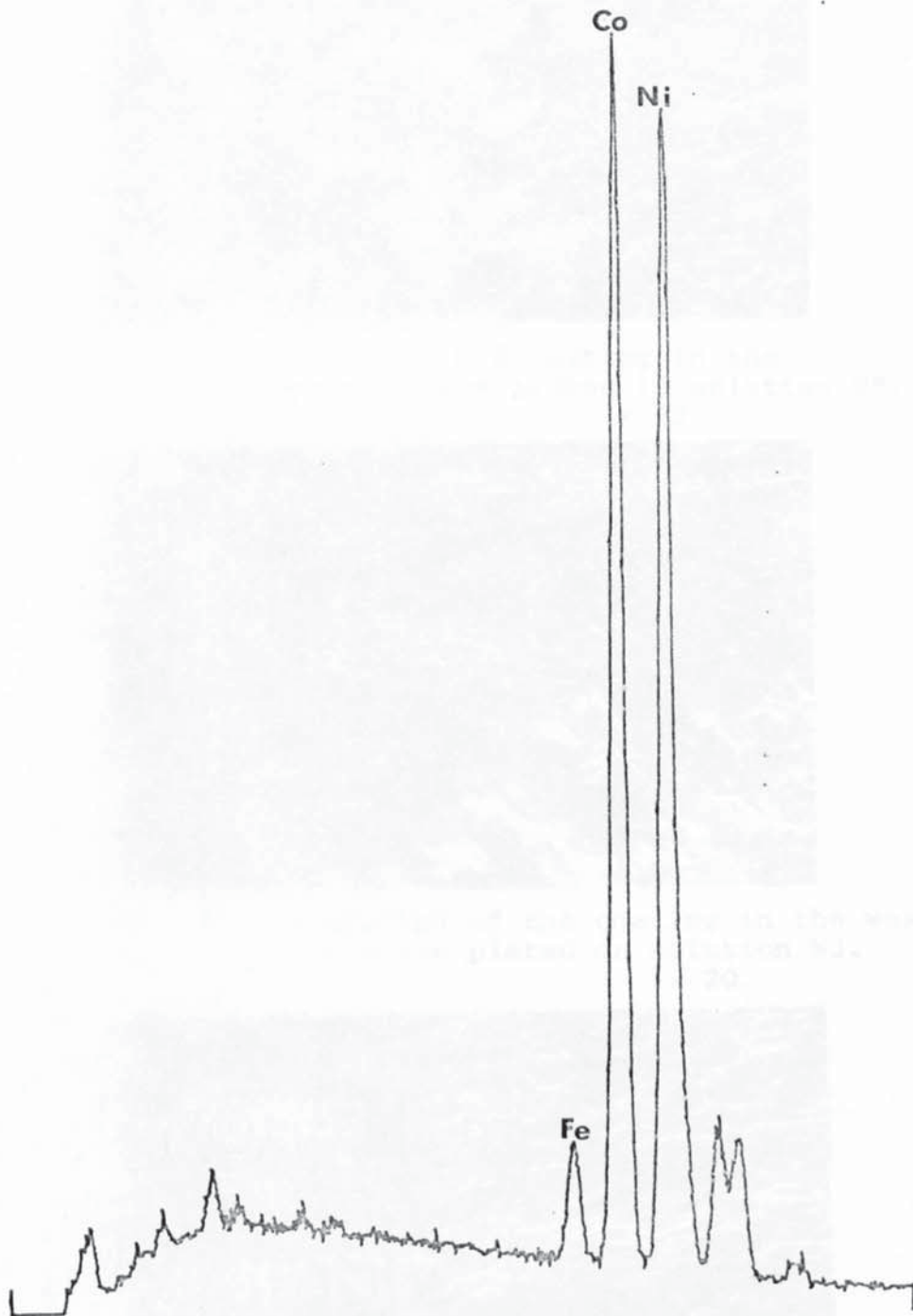
Fig.71.   S.E.M. analysis trace showing the presence
of iron in the central plateau region of a
die plated with a cobalt-nickel alloy coating
containing 32% cobalt-sulphate bath N4.
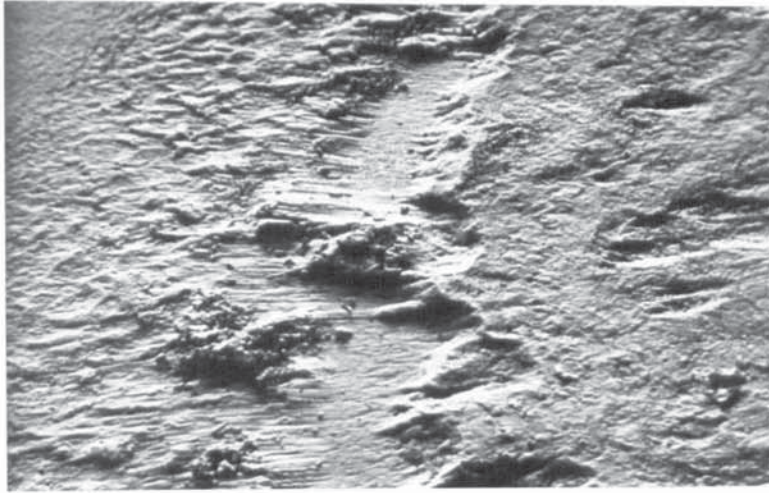
a) Partial penetration of die coating in the
   wear ring region of a die plated in solution N8.

x 25
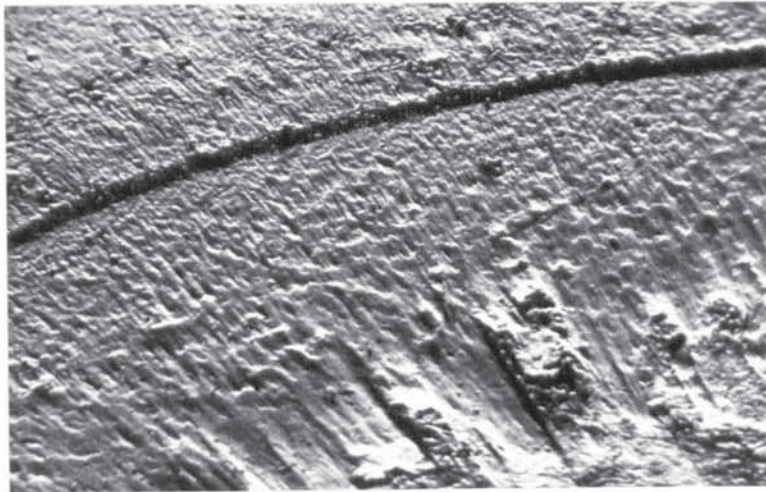
b) Complete penetration of the coating in the wear
   ring region of a die plated on solution N3.

x 20
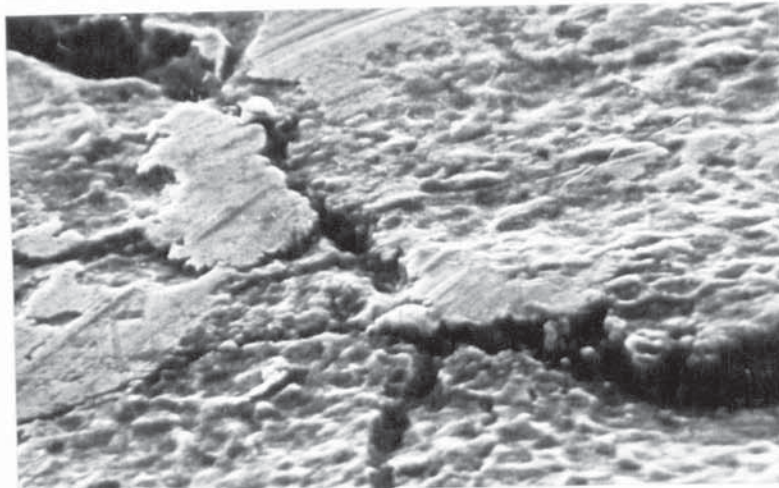
c) Cracks in the central plateau region of a die
   plated in solution N3.

x 1500

Fig.72.　Scanning electronmicrographs of dies plated with
         cobalt-nickel alloys.
         1000 billets
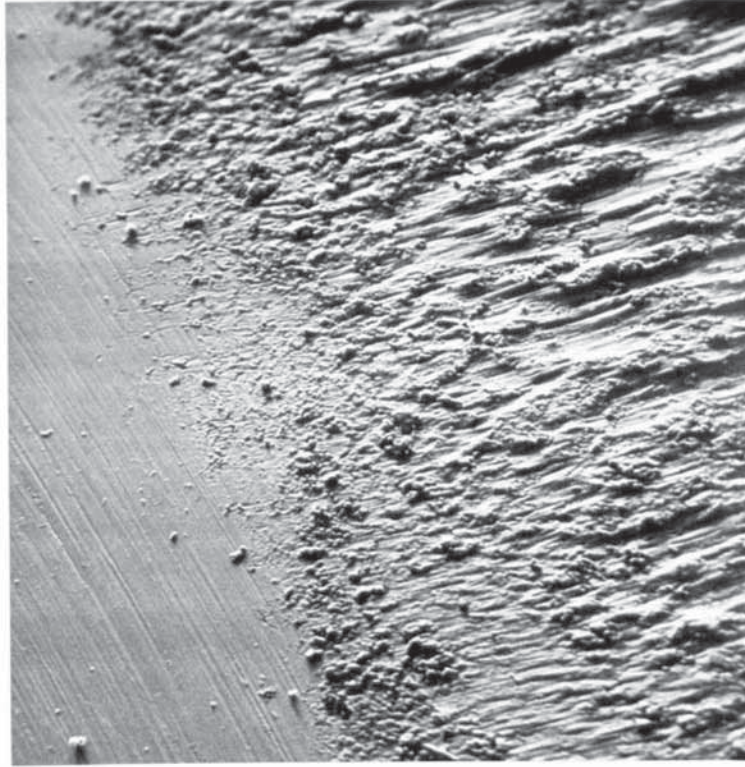
Fig.73.   Scanning electronmicrograph of a die plated with
cobalt-nickel alloy N8 showing debris which
accumulated at the outer edge of the wear ring
during the forging test.
1000 billets forged.   x 75

11.4.3.

Cobalt-molybdenum and cobalt-tungsten alloys.

The surface examination of the cobalt-molybdenum and cobalt-tungsten coated dies was much easier than was the case with the cobalt-nickel alloys due to the absence of scale on the surface. The two alloy coatings plated from the baths containing 150g/1 cobaltous sulphate and 200g/1 sodium heptonate exhibited almost identical surface topography in both the central plateau and wear-ring region therefore the following description of typical cobalt-molybdenum coatings also applies to the cobalt-tungsten alloys tested.

Fig.74 shows high and low magnification scanning electro-micrographs of the central plateau and wear ring regions of the die plated in solution M17 and containing 14% molybdenum. The grinding marks which are clearly visible in the central plateau region (Fig.74a and b) can be seen to have almost disappeared in the wear ring region (Fig.74c and d). The polishing away of the grinding marks in the wear ring region gives an indication of the very shallow wear which took place on all of the alloy coatings with wear volumes of less than $1.0 \times 10^{-3} cm^3$. It can be seen that the abrasion of the surface in the wear ring region has left ho deep channels or trenches as was the case with the unplated Electem die. (Compare Fig.70 with Fig.74a and b). Several dies did experience gouging of the surface in this area but it was slight and isolated.

The extent of cracking experienced by the alloy coatings
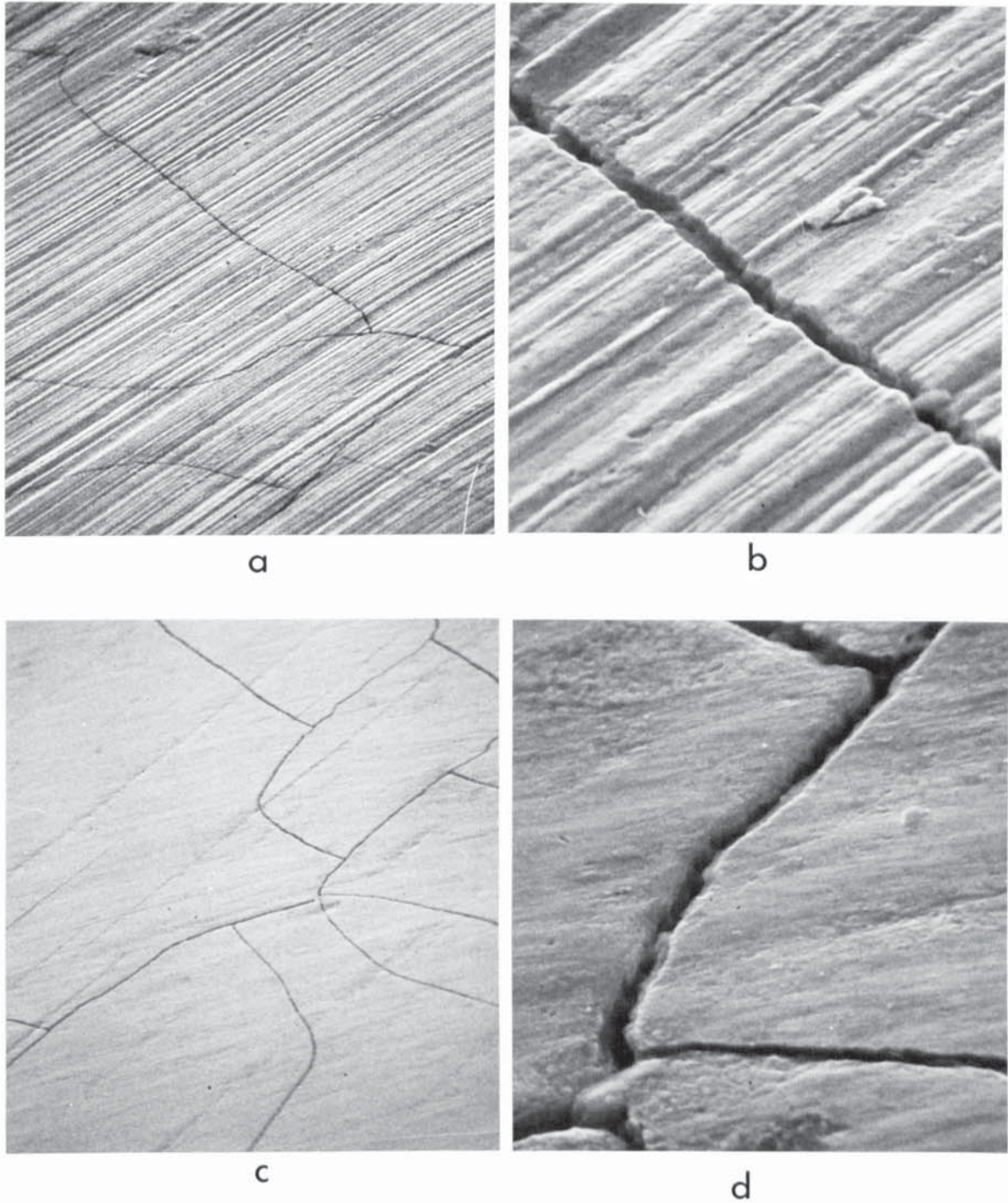
Fig.74.   Scanning electronmicrographs of various regions
          of the die plated using bath M17.
          1000 billets forged.

a) and b)   Central plateau showing cracking but
            no scale formation.
            Note grinding marks.

c) and d)   Wear ring showing cracking but little
            erosion except polishing away of
            grinding marks.
            Magnification: a) and c) x 150; b) and
                            d) x 1500

is clearly illustrated in all four of the scanning electromicrographs
shown in Fig.74.   The cracks may be seen to be present in the
central plateau and wear ring region of the die and appear to
be the same width in both regions.   Those in the wear ring differ
slightly from those in the central plateau region in that they have
slightly rounded edges due to the flow of metal across them.
Although cracks are present in the coating they are not as severe
as those experienced with the unplated Electem and their configuration
is such that keying of material is less likely.

The surface topography of the worn regions of dies having
wear volumes of $1.0 \times 10^{-3} cm^3$ and above was very similar to that
just described.   The main difference was that due to the higher
erosion of the coating in the wear ring region the grinding marks
were completely worn away and in some cases gouging of the surface
was apparent, Fig.75.   In contrast to the cobalt-nickel alloys the
outer edge of the wear ring of all alloys whether of low or high
wear volume was completely free of debris and no 'step' in the
surface was apparent.
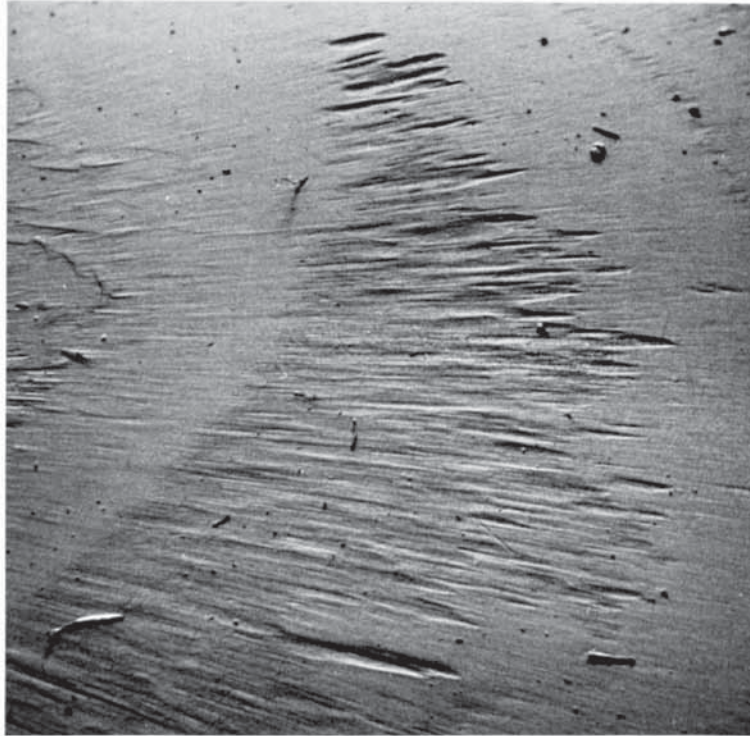
Fig.75,　Scanning electronmicrograph showing gouging of
the surface of a die plated with cobalt-molybdenum
alloy M6.
1000 billets forged.　x 20

12. DISCUSSION

Most plating variables usually influence the composition of electrodeposited alloys and so analysis of deposits constituted an essential part of this work. When feasible, foils were prepared specifically for analysis and subsequently analysed by conventional wet methods. However, when it was necessary to analyse a coating deposited on a die, electron proble microanalysis was employed. The alloy contents obtained in these ways gave inconsistent results as foils were usually found to contain a lower concentration of alloying element than deposits obtained on dies (compare Figs. 33 and 36 with Table X). This also applies, but to a lesser extent, to the deposits obtained on brass panels. The fact that the alloys were electrodeposited onto aluminium, brass and steel could be responsible for these differences as could the agitation effects mentioned in section 10.7. However it is thought more likely that the different alloy contents were caused by variations in current density and by the methods of analysis. The current density variations were due to the different shapes of the specimens concerned and it is known that variation of current density is one of the main factors which determine the composition of an alloy electrodeposit. It is unfortunate there-fore that time did not permit an investigation into the effects of current density on the alloy content of the deposits. The samples for analysis taken from dies and brass plates were cut from as near the centre of the specimen as was possible. Therefore they would be expected to be of high alloy content as this is a low current density region. The analysis carried out on them using the E.P.M.A. was essentially a line analysis at a particular point in the coating

whereas the alloy contents obtained from the wet analysis of
foils was an average value for deposits obtained over a range
of current densities. This average analysis value for the wet
analysis of foils was due to the fact that a reasonable sample
weight was required for accurate wet analysis and therefore at
least two-thirds of the foil were used. The low alloy deposits
from the high current density regions near the edges of the foil
would be likely to result in a lower average alloy content.
Consequently for deposits from a particular solution, it is not
surprising that foils had a lower alloy content than coatings
on dies.

Although wear resistant coatings of both cobalt-
molybdenum and cobalt-tungsten have been produced it is possible
that the performance of the alloys could be further enhanced by
additional purification of the alloy plating baths. The reason
for this is that alloy additions were made to the bath in the
form of general purpose reagent sodium molybdate and sodium
tungstate salts. This introduced the impurities associated with
these salts into the bath. The effects of these impurities were
particularly apparent in the case of the cobalt-tungsten baths
due to the relatively high concentration of sodium tungstate used.
It was therefore necessary to plate at low current density for a
short time after the addition of alloying element had been made
to the bath in an attempt to remove these impurities. The
duration of 'plating out' was restricted however in order that
depletion of the concentration of alloying element in solution
was not severe. This problem can obviously be overcome by adding
an excess of the alloying element to the bath and then 'plating out'

until analysis of the solution indicates the correct concentration of alloying element present. However such a time consuming practice could not be employed in this investigation. The importance of purification of the solution cannot be over-emphasised as illustrated by the following wear test reults.

Several flat die wear tests were carried out on cobalt-molybdenum an d cobalt-tungsten alloy coatings obtained from unpurified solutions. The base solutions were not plated at low current density to remove metallic contaminants but the sodium heptonate used had been purified. The reason for this was that the only anode material obtainable at that time was rolled cobalt sheet which was very expensive (approximately £60/Kg.) compared to electrolytic cobalt chip (approximately £3.50/Kg.) which was used for subsequent work.

The wear results obtained from these die sets are given in Table XVI. Comparing these results with those obtained for dies plated from purified solutions (Table XII) shows that the mean wear volumes are up to seven times greater. The most wear resistant coatings are therefore only obtained if metallic contaminants are removed by extensive 'plating out' of the baths.

The straight line relationships which were found to exist between deposit hardness and alloy content for the cobalt-molybdenum and cobalt-tungsten alloys mean that graphs of hardness against wear volume, Figs. 76a and b, are almost identical in shape to the graphs obtained for percentage alloying element against wear volume, Fig.55. Thus, as would be expected, an increase

TABLE XVI. Wear Volume of Flat Dies Plated from Unpurified Solutions.
1000 Billets Forged

Solution Code	Wear Volume x10^{-3} cm^3		
	Top Die	Bottom Die	Mean
M6	6.40	8.22	7.31
M9	12.52	8.40	10.46
M16	4.91	2.80	3.86
M17	4.35	3.30	3.83
M19	1.75	1.73	1.74
W11	6.27	1.85	4.06
W12	2.93	1.98	2.46
W13	3.42	0.41	1.92
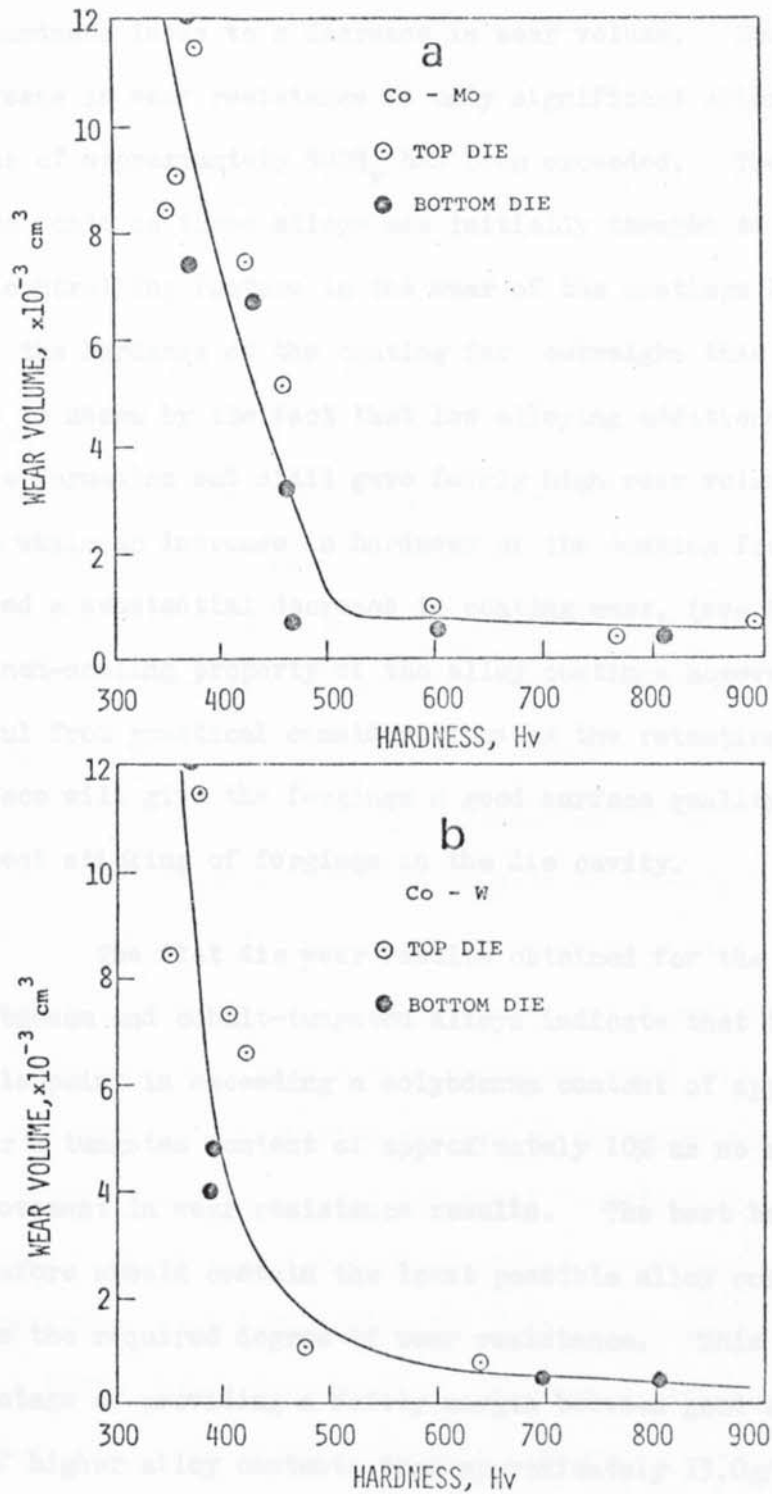
Fig.76.   Relationship between the hardness of cobalt
          alloy coatings and their degree of wear after
          forging 1000 billets.
          a)   Cobalt-molybdenum
          b)   Cobalt-tungsten

in hardness leads to a decrease in wear volume. However this increase in wear resistance is only significant after a hardness value of approximately $500H_v$ has been exceeded. The lack of oxide scale on these alloys was initially thought to be one of the controlling factors in the wear of the coatings but it appears that the hardness of the coating far outweighs this in importance. This is shown by the fact that low alloying additions inhibited scale formation but still gave fairly high wear volumes (see Table XII) while an increase in hardness of the coating from $400-500H_v$ caused a substantial decrease in coating wear, (see Fig. 76). The non-scaling property of the alloy coatings however is very useful from practical considerations as the retention of a smooth surface will give the forgings a good surface quality and help to prevent sticking of forgings in the die cavity.

The flat die wear results obtained for the cobalt-molybdenum and cobalt-tungsten alloys indicate that there is little point in exceeding a molybdenum content of approximately 6% or a tungsten content of approximately 10% as no significant improvement in wear resistance results. The best baths to employ therefore should contain the least possible alloy content which gives the required degree of wear resistance. This has the added advantage of providing a safety margin between good and bad deposits as if higher alloy contents than approximately 13.0g/l sodium molybdate and 50g/l sodium tungstate are used in the baths then the deposits become very cracked and brittle, particularly in the case of the cobalt-molybdenum alloys. This is of great importance when plating complex shapes as current density variations could

produce areas of poor deposit if too narrow a safety margin were employed. The most likely defect in this respect is that cracked and flaking regions would be formed on high current density areas, as shown by the Hull cell panels, if too high an alloy content were employed.

The graph of hardness against wear volume for the cobalt-nickel alloys, Fig.77, is opposite in slope to that obtained for the cobalt-molybdenum and cobalt-tungsten. This is due to the fact that the relationship between hardness of the deposit and percentage nickel has a negative slope. Therefore in contrast to the cobalt-molybdenum and cobalt-tungsten alloy systems an increase in hardness of the deposit causes an increase in wear volume. This effect has been observed by the author during a previous investigation into the effects of structure on the wear resistance of No.5 die steel. It was found that a martensitic structure of approximately $750H_v$ and a bainitic structure of approximately $400H_v$ gave almost twice the wear volume obtained with a tempered martensite structure of approximately $400H_v$. The wear characteristics of No.5 die steel therefore appear to be controlled largely by the type of structure present and not by its hardness. Similarly with the cobalt-nickel alloys it appears that a factor other than hardness determines the rate of wear of the coatings. It is possible that a change in structure is also responsible for the change in wear resistance of the coatings.

The wear of the alloy coatings is likely to be influenced by the rate of work hardening of the deposit. It has been shown[88] that cobalt work hardens very rapidly and under the high loading
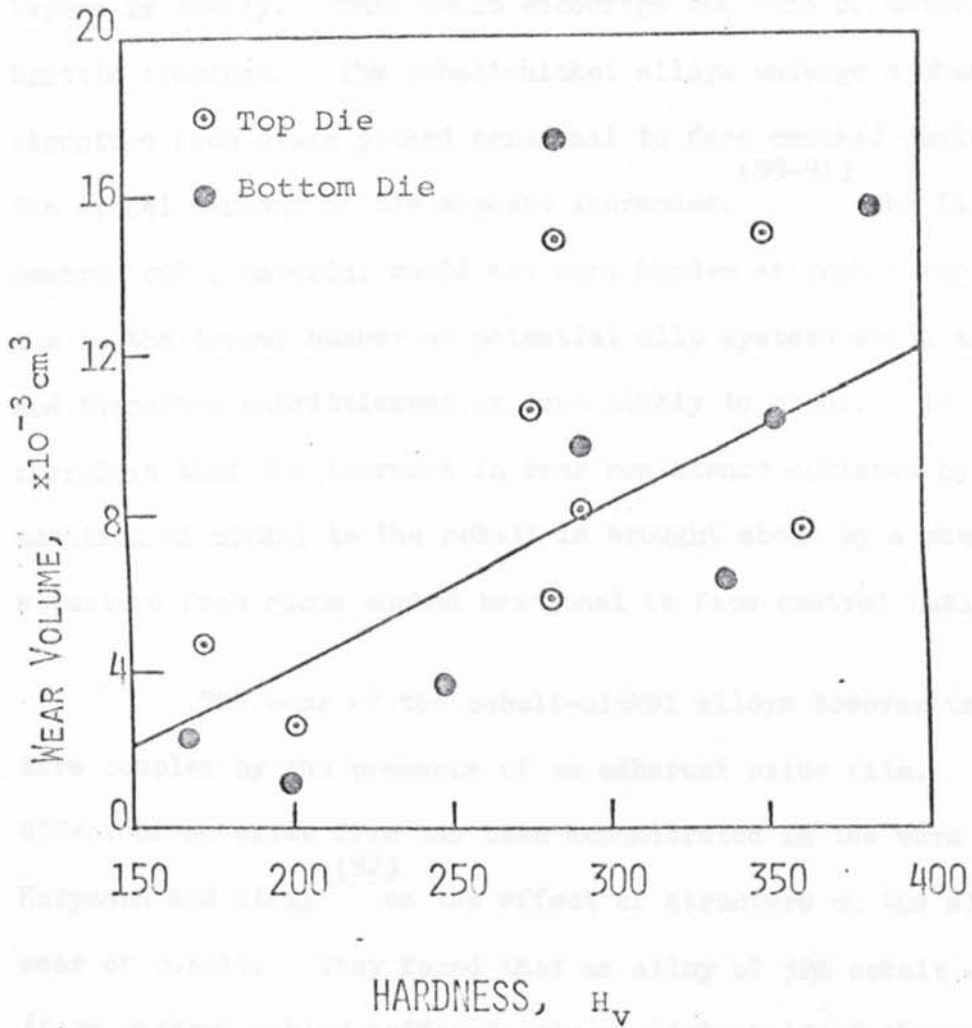
Fig. 77. Relationship between the hardness of
Co-Ni coatings and their degree of wear
after forging 1000 billets.

experienced in the forging operation embrittlement of the surface layers is likely. This would encourage the loss of material by brittle fracture. The cobalt-nickel alloys undergo a change in structure from close packed hexagonal to face centred cubic as the nickel content of the deposit increases. (89-91) The face centred cubic material would not work harden at such a rapid rate due to the larger number of potential slip systems which are present and therefore embrittlement is less likely to occur. It is possible therefore that the increase in wear resistance achieved by the addition of nickel to the cobalt is brought about by a change in structure from close packed hexagonal to face centred cubic.

The wear of the cobalt-nickel alloys however is made more complex by the presence of an adherent oxide film. The effect of an oxide film has been demonstrated in the work of Huppmann and Clegg (92) on the effect of structure on the sliding wear of cobalt. They found that an alloy of 92% cobalt - 8% iron (face centred cubic) suffered approximately half of the wear of pure cobalt (close packed hexagonal) at a sliding distance of 1×10^4 cm. This decrease in wear was thought to be due to the formation of an oxide layer on the surface of the alloy. In a similar manner the formation of an oxide film on the surface of the cobalt-nickel alloys may inhibit wear of the coating. The composition of this oxide will vary with the alloy content of the deposit and the type of oxide formed will determine both its abrasive action and the ease with which it will combine with scale from the hot billets. In consequence only certain alloy composit- ions may form oxide films of a protective nature. It therefore

seems likely that the wear of these coatings is controlled both by the structure present and by the type of oxide film formed on the surface.

Although the cobalt-nickel alloys gave poor wear resistance certain of them suffered little or no cracking during the forging test. The use of such coatings on forging dies to prevent cracking of the die steel need not be precluded if a strip and replate procedure is adopted. The strip and replate procedure could be repeated at the end of shifts until failure of the die steel occurred or tolerance limits were exceeded and not restored on plating. Machining costs would be considerably reduced and the stripping and replating costs should not be too great. This technique can be considered as a means of providing temporary protection of the die steel. Although the use of plated coatings on die steels of higher quality than No.5 has not been investigated, it is possible that these are the materials which could benefit most from temporary protection. The amount of die steel wear at regions where the coating was penetrated after a shift or so would be negligible. If this system were to function satisfactorily in producing an extended die life, the cost of a more expensive die steel would be justified since the major cost in die production is incurred in the die sinking operation.

In order to assess the performance of the alloy coatings produced in this work the wear volumes of other electrodeposited coatings, surface treatments and alloy steels subjected to the 1000 billet forging test are given in Table XVII. The coated and

TABLE XVII. Wear Volumes Obtained for Various Steels and Coatings after Forging 1000 Billets

Die Material	Mean Wear Volume $\times 10^{-3} cm^3$
5% Chromium Steel	0.90
3% Ni/3% Mo Steel	0.33
5% Cr/2% W Steel	2.04
Nitrided	1.77
Chromised +	0.28
10 μm Regular Chromium (C1)*	0.59
25 μm Microcracked Chromium (C2)*	0.31
90 μm 83% Co/17% Ni (N2)	
10 μm Regular+Chromium (C1)*	0.70
90 μm 83% Co/17% NI (N2)	
10 μm Microcracked Chromium (C2)*	0.45
125 μm 'Tribomet'	4.08
250 μm 'Tribomet'	3.00

+Billet reduction 1.9-0.5 cm
Bulk die temperature approximately 350° C.

*Chromium solutions used for die plating

Solution Code	COMPOSITION g/ℓ			Current Density A/dm²	Temp. °C
	Chromic Acid	Sulphuric Acid	Fluoresilicic Acid		
C1	500	5	-	10	38
C2	150	0.35	3.0	19	42

surface treated dies were all tested by the author whereas the
results for the alloy steels were from a previous investigation
carried out at the University of Aston in Birmingham.

The wear resistance of the cobalt alloy coatings
developed in this work can be seen to be better than all but the
most highly alloyed steels and is comparable to results obtained
for regular chromium coatings. The other electrodeposited
chromium coating employed was a micro-cracked deposit which
performed very well during the forging test. The wear volume
obtained was very small and subsequent examination of the die by
taper section revealed that little or no cracking of the steel
substrate had taken place. The lack of cracking experienced
by this die set was presumably due to the great number of cracks
present in the coating preventing the build up of high stresses.
A comparison between the cracking obtained in the central plateau
region of dies plated with regular and micro-cracked chromium is
shown in Fig.78. As can be seen the regular chromium produced
cracking which was similar in severity to that encountered on dies
plated with the wear resistant cobalt alloys (compare with Fig.67).
Although the chromium plated dies suffered very little wear, scale
formation did occur, particularly on the bottom die. Fig.79 shows
photographs comparing the extent of scaling on a chromium plated
die with the lack of scaling encountered on a cobalt-molybdenum
plated die. This scale must have been picked up from the billets,
but it did adhere quite firmly to the surface and could be removed
only by the electrolytic treatment.

The third chromium surface treatment listed in the table
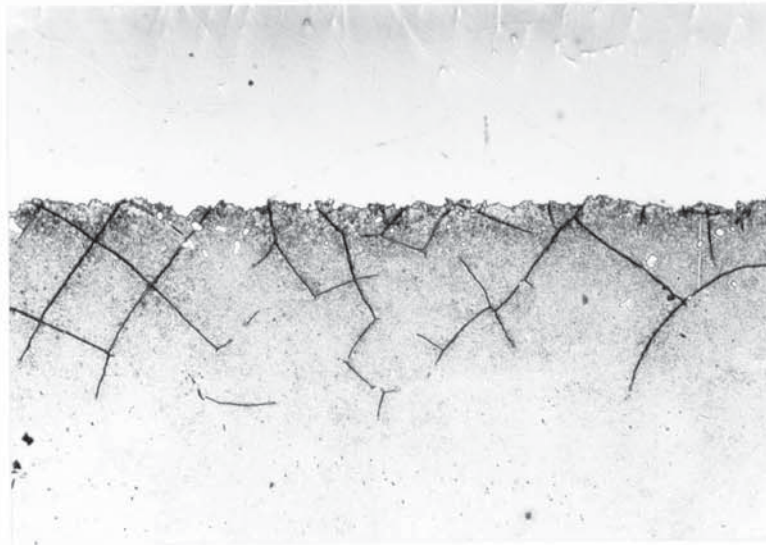
a) Conventional chromium, C1.
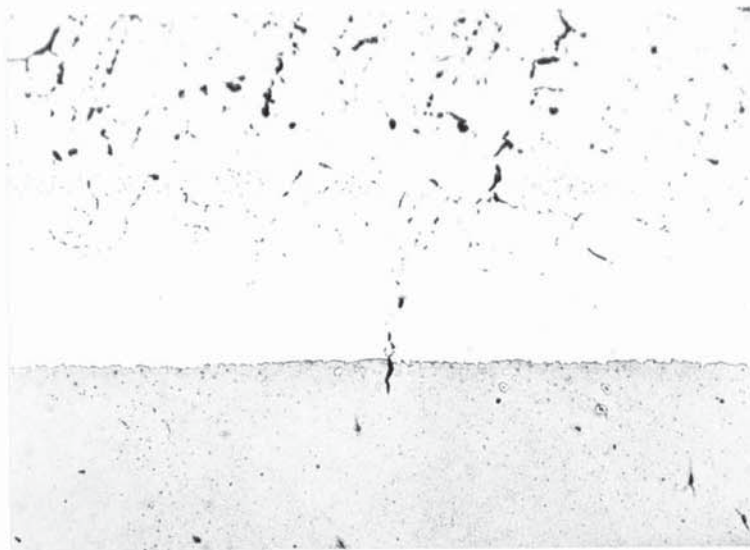
b) Micro-cracked chromium, C2.

Fig.78. Taper sections showing the cracking produced in the steel substrate using chromium coatings. 1000 billets forged. x 1000
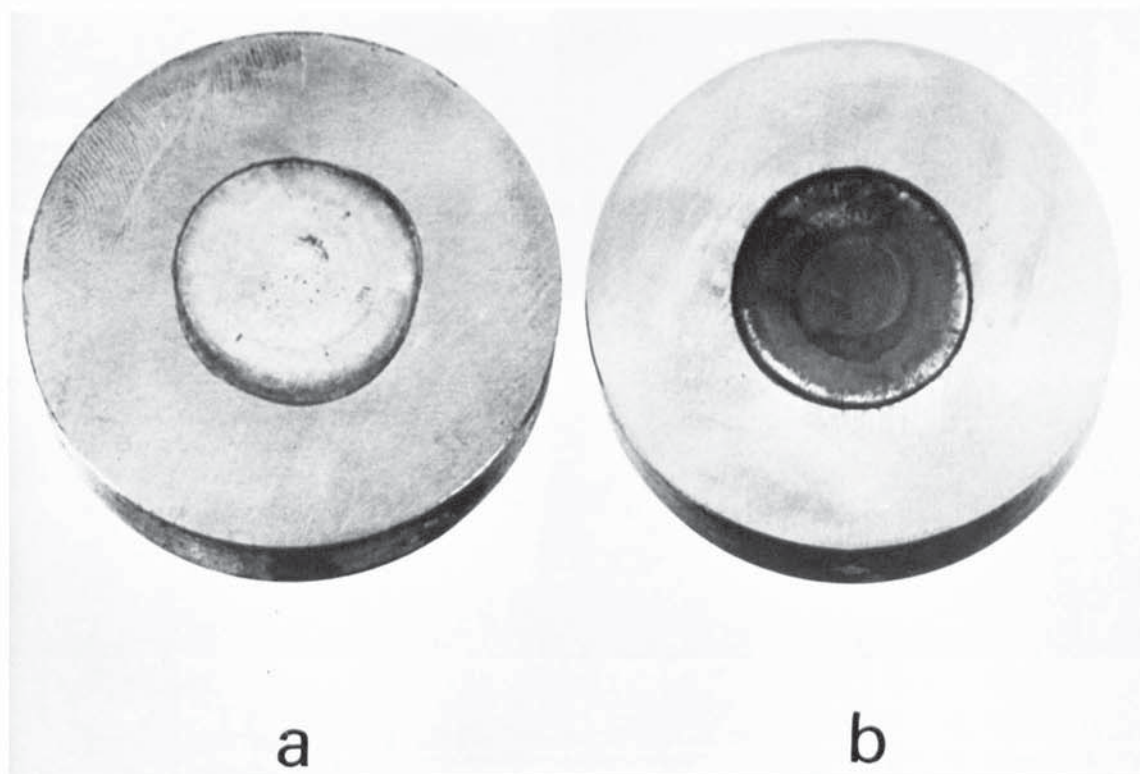
Fig.79.　Scale formation on:-

a)　Die plated with cobalt-molybdenum alloy
from solution M7.

b)　Die plated with conventional chromium.

1000 billets forged.

is one obtained by gas chromising the surface of an Electem 5 die. This treatment produced the most wear resistant surface of all the alloys and coatings which have been tested by the author. The standard forging test produced no detectable wear of the die surface and wear was only obtained by greatly increasing the severity of the test conditions. The bulk die temperatures for top and bottom dies were raised to 300°C and 400°C respectively and the billet reduction increased to 1.80 - 0.50cm. This very high wear resistance however was accompanied by some of the most severe cracking of the die surface encountered in this investigation as shown by Fig.80.

The coating which was of particular interest was the composite material containing chromium carbide particles in a cobalt matrix (known commercially as 'Tribomet'). Two coating thicknesses of 125um and 250um were employed on Electem 5 dies. The adhesion of the scale formed on the surface was similar to the unplated Electem 5 and could be removed by the electrolytic treatment. The wear volumes obtained for these coatings were mixed but the average wear was comparable to unplated Electem 5 and therefore inferior to the most wear resistant cobalt alloy coatings. The low wear resistance of these coatings is surprising in view of the fact that chromium carbide is the main constituant of the very wear resistant coating formed in the gas chromising process. (The carbide is formed by the reaction of chromium with the carbon present in the steel). Taper sections of the dies revealed that severe cracking of the coating and of the die steel had also taken place as shown in Fig.81.
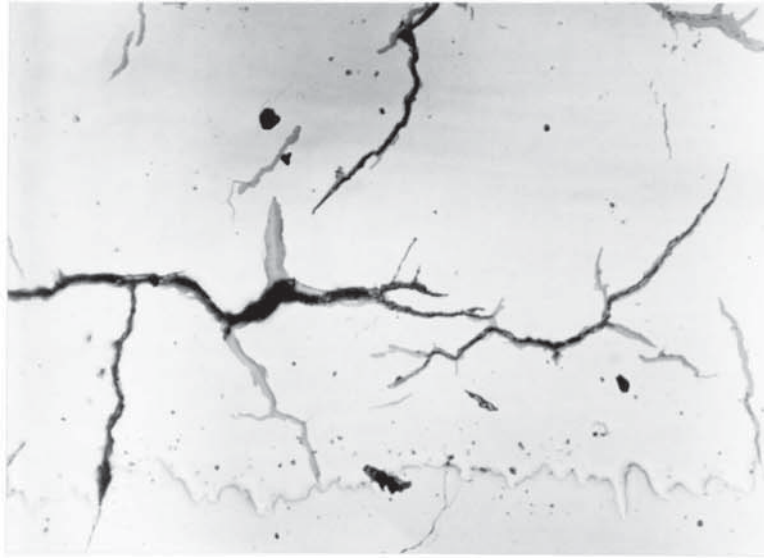
Fig.80. Taper section of chromised die showing severe
cracking in the central plateau region.
2000 billets forged.   x 1000
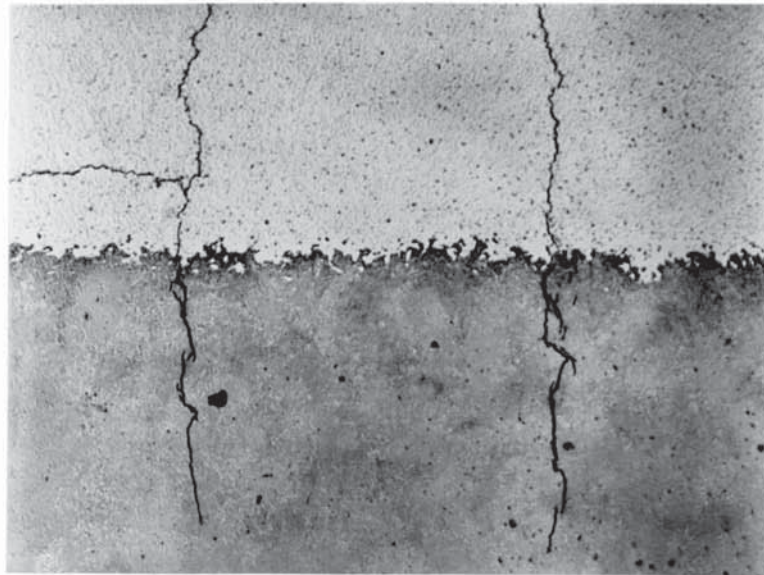
Fig.81. Taper section of die plated with 'Tribomet'
coating showing cracking of the die steel and
coating.
1000 billets forged.   x 1000

Two further 'composite' coatings were tried in the
form of double layer electrodeposites. This was an attempt
to benefit from a relatively soft lower layer, which it was
thought would prevent cracking of the die steel, covered with
a hard wear resistant overlay. The 17% nickel - 83% cobalt alloy
deposited from the sulphate bath was chosen as the soft, ductile
deposit since, as reported in section 11.3.2., this prevented
cracking of the underlying steel although it was worn away in
the wear ring region. The same two chromium deposits just
discussed, conventional regular and microcracked, were utilised
as the hard wear resistant overlays. Both sets of dies performed
extremely well during the forging tests, almost certainly due to
the top coats of chromium, and gave wear volumes comparable to
those obtained for chromium coatings plated directly onto the die
steel. As would be expected the scaling behaviour of these die
sets was identical to that observed previously for chromium.

The taper sections of the dies revealed rather surprising
results in that in the central plateau region cracks penetrated
from the chromium layer, through the relatively soft cobalt-nickel
layer into the steel substrate. This occured with both the
regular chromium and micro-cracked chromium systems as shown by
Fig.82. It seems that the cracks present in the chromium act
as such high stress raisers that even a soft underlay is unable to
prevent their propagation. The use of such a duplex system there-
fore appears to offer no advantages over the direct application of
the chromium to the die surface. In fact in the case of the micro-
cracked system the cracking suffered by the die was greater than
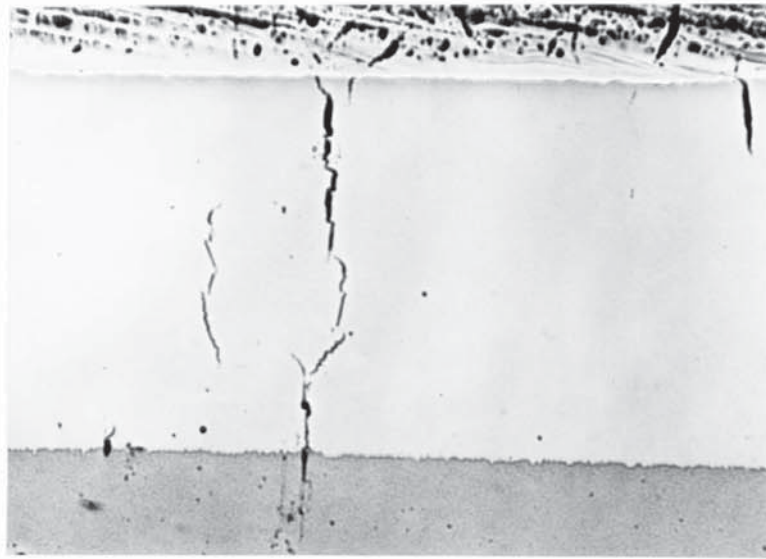
Fig.82. Taper sections of 'composite' chromium/cobalt-nickel
coatings showing cracks propagating through
cobalt-nickel layer into the die steel.

when the coating was applied direct. This may have been caused
by the fact that the initial crack density was not as great as
in the case of the one plated directly onto the die steel there-
by causing higher stress concentrations. It is possible that
the differences in surface condition of the underlying metals
could have influenced the crack pattern since this is known to
be feasible, [79] although it is less likely to be of importance in
the case of thick deposits of this type.

The results obtained from examination of the above
dies and those plated with the cobalt alloys developed in this
work indicate that, with the exception of micro-cracked chromium,
good wear resistance is always accompanied by cracking of the
central plateau region of the die. In the case of the chromium
coatings, and most probably the cobalt-molybdenum and cobalt-
tungsten alloys, the cracks were present in the as plated condition.
It would appear that although the flat die wear test is useful for
comparing the resistance to erosion of the coatings it does not
evaluate the effects of such cracking. It is obvious that in
the flat die situation the cracking of the dies is of little
importance as severe cracking, illustrated by the chromised coating,
has little effect on the performance of the die. In an industrial
die however high tensile stresses may be encountered as compared
to the mainly compressive stresses present in the flat die test.
The presence of cracks under such circumstances may cause rapid
failure of the die. Therefore although several of the chromium
and cobalt alloy coatings suffered little erosive wear when plated
onto flat dies this can only be regarded as a guide to their possible

performance on shaped dies and care must be taken in relating the results obtained to dies in industrial service.

The cracking of the die in the central plateau region was originally thought to be due to thermal fatigue of the die surface.   However results obtained from the thermal cycling test indicate that very little cracking is induced by the temperature fluctuations experienced by these dies and therefore most of the cracking observed must be stress induced.   The flat die test therefore again fails to simulate true industrial conditions as thermal fatigue cracking is known to be a problem and to cause industrial die failure.   The difference between the flat die test and industrial conditions appears to be that a lower surface temperature is achieved with the flat dies than is experianced with many industrial dies (93) particularly when producing closed die forgings.   Higher temperatures would therefore have to be employed for thermal cycling tests in order to evaluate the coatings under conditions closer to industrial experiance.

The above considerations lead to the conclusion that the small shaped die tests developed in this work, and certainly the large shaped dies used, give a better indication of coating performance under industrial conditions than does the flat die test.   However even the results of these tests must be treated with slight caution as they are accelerated tests.   The shaped dies nevertheless appear to provide a better comparative test as is emphasised by the fact that of the five most wear resistant

cobalt alloy coatings obtained on flat dies only one or two produced significant reductions in wear when used on shaped dies. The use of shaped dies also tests the ability of the coating to protect different shapes as it appears that the shape of the die influences the effectiveness of the coating in reducing wear. This is apparent from the results obtained with shape 4 and shape 6 which show that the two coatings which performed well on die shape 6 suffered severe adhesion failure when plated onto die shape 4. These two coatings also did not provide the greatest wear resistance when used on the flat dies. This confirms practical experience with chromium plated dies which indicates that not all die shapes have an improved life when plated.

13. CONCLUSIONS

Cobalt-molybdenum and cobalt-tungsten plating baths have been developed that operate at more favourable plating conditions and higher cathode current efficiencies (60-70%) than most of the ones reported previously in the literature. As far as the author is aware the cobalt-tungsten alloy deposits obtained in this work are the first such coatings to be obtained in a coherent and useable form from an acid type bath. The most successful baths had the basic formulation of 150g/l cobaltous sulphate $CoSO_4.7H_2O$, 28g/l sodium chloride, 40g/l boric acid and 100g/l sodium heptonate. Typical operating conditions employed were as follows:

Current density 4A/dm^2

Temperature 55°C

pH 1.5-2.0

The coatings had a fairly high internal stress and in consequence many were cracked in the as plated condition. The cracks however had little effect on the performance of the coatings when plated onto flat experimental dies or when they were subjected to thermal cycling tests.

Coatings deposited from several of the alloy baths (M16, M17, M19, W12 and W13) have proved to be successful in increasing the life of flat, upset forging dies. Two of the coatings, M16 and W12, have also been successful in reducing the wear of experimental shaped dies. The alloys were relatively hard and did not scale during the forging test,

both these factors assisted in reducing erosion of the die
surface.   Cobalt-nickel alloys did not have these properties
and were considered of little value as coatings on hot forging
dies unless a special strip and replate procedure were employed.

It has been shown that hardness is related directly
to the percentage of alloying element in the electrodeposits,
the hardness increasing with an increasing amount of the alloy-
ing element in the case of the cobalt-molybdenum and cobalt-
tungsten alloys but that the reverse is true for the cobalt-
nickel system.   The relationship between the extent of wear
and the alloy content of the coatings has been determined,
Figs 53 and 55.   A particular concentration of molybdate or
tungstate ions must be present in the plating baths if a
significant increase in the performance of coatings deposited
from them is to be achieved.   In the case of cobalt-molybdenum
a concentration of about 3g/l sodium molybdate was required and
at the plating conditions employed an alloy was deposited con-
taining approximately 4% molybdenum.   For cobalt-tungsten the
relevent concentrations were about 20g/l sodium tungstate to
give a coating containing approximately 8% tungsten.

Coatings deposited on shaped dies did not exhibit
excessive build up in high current density areas.   A moderate
amount of grinding and polishing was the only additional operation
necessary before forging.   Failure to remove slight edge build
up resulted in the first few billets sticking in the die.   It
is fortunate that recesses which are the regions most difficult
to plate are usually the parts of the surface profile of a die

subjected to the least wear. The more extensive machining operations carried out on the shaped dies as compared to the flat dies showed the alloy coatings were readily machinable using normal grinding methods and a high polish was obtainable on their surface. These points are of particular practical interest as machining costs can be very high for 'difficult' materials and a high quality surface finish is often required on dies.

The forging tests employed were of different duration since their degrees of severity also varied but they serve to give a comparison of performance in each test. It seems from the tests carried out that the performance of a particular coating may be influenced by the shape of die or the test procedure. Therefore although the alloy deposits show consider- able potential as wear resistant coatings on experimental hot forging dies their true usefulness may only be assessed under industrial hot forging conditions.

14. SUGGESTIONS FOR FUTURE WORK

Since some of the cobalt molybdenum and cobalt-tungsten alloy coatings have performed in such an encouraging manner on experimental dies the next stage in the work should involve the plating and evaluation of industrial dies. This will necessitate the operation of a much larger bath than that employed in the present work. The transfer from the 1-5 litre scale up to pilot scale operation of the solutions will involve a number of problems such as routine control of the electrolyte, maintenance of constant properties of the deposit and the availability of suitable anode material. The latter will itself require a subsidiary investigation on the production of either cast or electrolytic anode material. The operation of a large bath for an extended period of time may possibly lead to difficulties caused by break-down products accumulating in the bath or build up of sodium ions from the addition of sodium molybdate or sodium tungstate if alloy anodes are not employed. The properties of the deposits therefore would require further study to observe changes which may occur as the solutions age.

The variation of alloy content with current density is probably one of the most important properties of the deposits which requires investigation. This is of particular importance if complex shapes are to be coated effectively. Heat-treatment of alloys having a higher alloy content than those examined so far requires investigation. Structure of the electrodeposits could be evaluated in more detail by the use of x-ray studies to determine lattice parameters, prefered orientation and fibre texture.

It is thought that the use of these alloys may be extended into other types of wear situation particularly for applications such as high temperature bearings, coatings for use on other types of die (e.g. zinc/aluminium die-casting dies), coatings on piston rings, hard facings for value seats and coatings for components subjected to sliding wear.

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