THE EFFECT OF COBALT ON THE STRUCTURE AND PROPERTIES OF No.5 DIE STEEL

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SYNOPSIS

The tempering characteristics of No. 5 die steel, with varying amounts of cobalt, have been investigated. Microstructural changes were determined by preparing extraction replicas and examining these with the electron microscope. The carbides were extracted electrolytically, identified by X-ray diffraction and analysed by classical chemical techniques. The transformation temperatures (Ms, Mf, Ac_1 and Ac_3) were determined for No. 5 die steel with graduated cobalt additions by modified dilatometric methods. Hardenability and T.T.T. diagrams were also determined in order to compare the effect of cobalt on these properties. An attempt was made, by using electron probe microanalyser, to find evidence of partitioning of cobalt at the ferrite-austenite and ferrite-carbide interfaces during transformation. Impact tests were performed on three steels and, lastly, a die wear test was carried out under hot forging conditions.

The results indicate that the tempering resistance increases with increasing amount of cobalt. Cobalt refines the carbide particle size and reduces agglomeration. Cementite (Fe3C type structure) is the only carbide in tempered 3%Co

steel. No partitioning of cobalt is observed in any stage of transformation and cobalt has very little effect on impact strength and impact transition temperature of No. 5 die steel. All the transformation temperatures rise with cobalt content. A drastic fall in hardenability occurs with the addition of cobalt. The die wear test shows a significant improvement in the die wear properties with increasing cobalt content.

All these observations can be explained on the assumption that in the absence of large quantities of strong carbide formers, cobalt has the effect of reducing the carbon equivalent of the steel.

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1. INTRODUCTION

Although the element Cobalt was then unknown, the use of Cobalt compounds for colouring glass and glazes goes back as far as 4,500 years. It was only in the late nineteenth and early twentieth century when the use of metallic cobalt gained metallurgical attraction. Experiments on cobalt-chromium alloys were carried out in 1897, and in 1913 cobalt-chromium-tungsten alloys were prepared. The above alloys were named as Stellites and first applied commercially in 1917. In 1905 it was discovered that cobalt improved hot-hardness in high-speed steel and a few years later use of cobalt became general in the industry. Cobalt containing magnetic steel was developed in 1917, and in 1935 the Aluico series of magnetic alloys (iron, nickel, cobalt, aluminium) were developed simultaneously in America and Japan. Cobalt was used as a binding material for tungsten-carbide in Germany in 1923. There are other uses of cobalt, e.g. in electroplating, Co^{60} as gamma ray emitter, but the most important use of cobalt to-day is in high temperature alloys, most of which are cobalt base materials.

The effect of cobalt on plain-carbon steel and low alloy steel have recently received some interest simply for its beneficial effect on the high temperature properties of the material. The increased tempering resistance imparted by cobalt additions has been known for many years, but other very important thermal and mechanical properties such as transformation temperature, hardenability, impact properties, etc. have to be considered critically, for the suitability of a steel, when low alloy tool steels are concerned. The most puzzling thing is, that the effect of cobalt varies with the different alloying element in such a way, that it is almost impossible to make any prediction whatsoever. At present there is no scientific approach to a systematic solution of the problem of interactions of different alloying elements in steel and consequently, the experimental approach to study the effect of cobalt seems to be the only avenue left.

The reason why cobalt is an interesting alloying addition to be investigated, is like the carbide formers, e.g. tungsten, molybdenum etc., cobalt significantly increases the retention of hardness and improves the mechanical properties at elevated temperatures; but it is very unlikely that cobalt forms any stable carbides as the above mentioned elements do, so the actual mechanism involved in the process seems to be different from the other alloying elements. Many explanations as to the mechanism involved have been proposed but none of them has yet been able to explain all the associated facts.

In the United Kingdom alone the annual consumption of 'hot work die steel' is about 10,000 tons. The severity of working conditions necessitates stringent control of the properties, and consequently, a glossary of composition has already been listed in the standard books. The only standard British die steels are found in B.S.S. 224, 1938, 1949, which specifies four steels:

a) Plain carbon steels containing 0.6% carbon

b) 1% Ni.

c) 1.5% Ni., 0.75%Cr. steel

d) No. 5 die steel containing 0.50-0.60%C., 1.25-1.75% Ni., 0.5-0.8%Cr., 0.25-0.30%Mo., 0.5-0.8% Mn., 0.30%(max.) Si., Sulphur and Phosphorus 0.04%(max.).

The property requirements of hot work die steel in general terms are the stability of its structure and its resistance to deformation and wear under the service conditions, the ease with which the material can be heat treated etc. The above criteria are by no means exclusive. Reviews of property requirements have been given by Hopkins and Williams(27), Settle(28) and Bayliss(29).

No. 5 die steel used as hot work die steel finds its application as tools for general forging purposes, for plastic moulds and hot stampings. In selecting a steel for a given application, the metallurgist must give full consideration firstly to all the properties required to ensure satisfactory performance, and secondly, to fabrication problem and treatment of the steel. A low-carbon version of No. 5 die steel $1\frac{1}{2}$% Ni-Cr-Mo Steel (En 24) fully hardens to martensite in $1\frac{1}{2}$'' diameter sections during oil quenching, and the steel is ductile at about -20^0C. The use of nickel in the steel, therefore, not only increases the hardenability, but also reduces the susceptibility of a steel to brittle fracture. Only two of the alloying elements, nickel and molybdenum, depress the impact transition temperature, and in the case of the latter, marked benefit is obtained from additions up to 0.3%, but further additions have no appreciable effect. This is the reason why molybdenum is generally added between 0.2 to 0.3 in many low alloy steels. Chromium and manganese have an adverse effect on impact transition temperature, but a very cheap alloying addition for improving hardenability. Carbon has the most pronounced effect on hardenability. No. 5 die steel similar in composition to En24 except for the higher carbon content to give an eutectoid composition. This accounts for the higher hardenability and strength of No. 5 die steel at the expense of impact value. Higher carbon content also responsible for better wear resistance, which is an essential quality for the die steel.

The metallurgical chemistry of iron and cobalt will be briefly considered. Both elements belong to VIII transitional group of the 4th period in the periodic table with an atomic number and electron architecture respectively :

$26\mathrm{Fe}\ 1s^2\ 2s^2\ 2P^6\ 3s^2\ 3P^6\ 3d^6\ 4s^2$

$27\mathrm{Co}\ 1s^2\ 2s^2\ 2P^6\ 3s^2\ 3P^6\ 3d^7 4s^2$

Cobalt has the close-packed hexagonal (ε) structure at room temperatures and transforms to a face centered cubic (α) structure at approximately 417°C. Atomic diameter of face centered γ iron and β cobalt are 2.52 and 2.51 respectively. Both the elements have a normal valency two. A complete series of solid solubility between iron and cobalt exists in the austenite range. The solubility of cobalt in Ferrite (α iron) is quite extended up to 76% Co. at room temperature.

Recently, several investigations have been made relating to iron cobalt equilibria but they add nothing new except evidence for a superlattice at 50% cobalt and somewhat broader alpha plus gamma field in the region of 80% cobalt. A large amount of cobalt stabilises the gamma iron structure, moderate amounts affect the A3 temperature only very slightly.(36) All other alloying elements raise or lower A3 markedly. Cobalt increases the tendency of high carbon alloys to graphitise. This behaviour is not surprising in view of the fact that cobalt is not known to form any stable carbide. It forms a simple binary eutectic system with graphite. Consequently, very little improvement can be expected in the mechanical properties of iron-base alloys with the addition of cobalt. The solid solution strengthening effect of cobalt in iron is from about (3.16tons/in^2) 5kg/mm^2 yield strength to approximately (6.208tons/in^2) 9.8kg/mm^2 at 3% Co. However, the hardening effect of cobalt in iron, in the presence of carbon is accelerated by an unknown mechanism especially when carbide formers like chromium, molybdenum is present. An increase in 9 HV per 1% Co. has been found in 0.1C, 12Cr% steels when Co. is present up to 15%. It was found that in low carbon Fe-Mo. alloys the cobalt addition led to an increase in hardness due to the fact that the intermetallic precipitates were both smaller and more numerous. It may well be that this mechanism operates in higher carbon low alloy steels (0.5-0.6% carbon) when the intermetallic precipitates are replaced by the carbides. Cobalt increases the resistance to fourth stage tempering in alloy steels and in general it has been found from the existing evidence available, that the retention of hardness at a comparatively higher temperature and increase in impact values are a few of the contributions of a small amount of cobalt in alloy steels. They are a few of the main properties stringently needed for hot forging die steel.

No. 5 die steel is perhaps the cheapest die steel used for hot forging purposes. The present investigation is an experimental search for the improvement economically possible in No 5. die steel, with the addition of cobalt. Steels containing 0, 1, 2, 3, 5, 7, 8 and 10% cobalt have been investigated for tempering properties, transformation temperatures, impact properties, hardenability, carbide morphology, retained austenite, partioning of cobalt and die wear properties.

It is worth while to make a cost analysis for the No. 5 die steel, and calculate the amount of improvement in the mechanical properties (and consequently longer die life) is necessary to compensate the extra cost involved by cobalt additions and to make profit through its use.

The cost of No. 5 die steel in Great Britain remained constant from 1964/67 at £170. per ton, in oil quenched and tempered condition ready for machining. After devaluation the price went up, and the present value is £177. per ton. The price of cobalt varied enormously over the years. In 1950 commercially pure cobalt (99.9% Co.) cost 13/- per lb., and in 1954 the value went up to 18/6 per lb. In 1960 - 10/9 per lb., 1962 - 12/- per lb., and in 1967 - 13/3 per lb. After devaluation the price went up again, and the present price is 16/9 per lb. At present the cost of No. 5 die steel increases by approximately £18.8 per ton per percent of cobalt. This estimate is only from the material cost and considering the yield of cobalt is 100% in this steel. So, if for example a 5% cobalt is required in the steel, it must be remembered that the cost is going up by £94. per ton. Die sinking cost is ten times as much as the material cost which partially outweighs the extra cost involved.

An 'appendix' has been provided at the end of the thesis to separate some detailed experimental results and diagrams for clarity. Any table or figure number with a suffix capital 'A' has been placed in the appendix.

2. LITERATURE SURVEY

The influence of cobalt on the tempering characteristics of plain carbon steels have been investigated by Biswas and Seal(20), Irvine(26), Seal and Roy(1) and Loria(4). They all have concluded that cobalt increases the resistance to tempering. Similarly, in high alloy steel it is a well-accepted fact that the increase in red-hardness is enhanced by the addition of cobalt. Why cobalt contributes to the retention of hot hardness and tempering resistance is still an unresolved issue. Several attempts have already been made to explain the mechanism involved. Houdremont and Schrader(8), Geller and Novikova(11) and Kuo(7) have demonstrated that cobalt retards the precipitation of alloy carbides in tool steels. In Houdremont's opinion, cobalt reduces alloying element diffusion. Kuo postulated that the effect of cobalt was to reduce the rate of precipitation and agglomeration of alloy carbides. There are several other studies on the effect of cobalt which postulate several different mechanisms which are an equalisation of tungsten partitioning between carbide and matrix(12), migration of cobalt to the M_6C during tempering formation of $(Co, W)_6C$,(69) to the interaction of cobalt and vanadium(70), and to the formation of carbide containing cobalt.(9,10) Seal and Biswas(20) demonstrated that the increasing tempering resistance was due to the formation of Co_3C. Mulders and Wessling(67) suggest that cobalt does not affect the resistance to tempering, it only increases the solubility of ferrite forming elements in the austenite so that the carbide forming elements could be raised. This solvent effect of cobalt will prevent segregation which directly influence toughness. Kuo(7) interpreted the increase in hot hardness with cobalt in high speed steel as the fact that cobalt and chromium greatly retarded the precipitation and/or coagulation of W_2C.

Chandhok, Hirth and Dulis(6), recently investigated the effect of cobalt on increasing tempering resistance and related to the increased rate of nucleation and decreased rate of growth and agglomeration of alloy carbides. The increased rate of nucleation, according to the above authors, are due to the increase in carbon activity and the decreased rate of growth is related to an interface control mechanism. In high-alloy steel cobalt has been found to stabilise retained austenite (8)(46) whereas, the opposite is true in low alloy carbon steel(5). Cobalt increases the hardenability in high chromium steel(5), but in low alloy steels the hardenability is very sharply reduced. There are various other controversial opinions on the effect of cobalt, which will be discussed later but at present the examples given above show clearly that cobalt does not exert a continuous or systematic effect on the properties of alloy steels and its interaction with other alloying elements makes the situation more complex.

Chandhok(30) in his previous work showed that the carbon activity increases in austenite and ferrite. Later this investigation was confirmed by Smith.(37) During tempering of a 0.2% Carbon 2.2 molybdenum steel containing up to 10% cobalt, they found that the cobalt containing steels had smaller and more numerous carbide particles than that of cobalt-free steels. The effect of cobalt on the activity of carbon was also related to 'growth rate' by Chandhok. They preoposed an 'interface control' model as previously described by Heckel and Paxton,(47) and Darken(48) to account for the action of Si. in Fe. Si. C. alloys. Cobalt has been found to partition itself preferentially in the ferrite; and since cobalt increases the carbon activity coefficient in ferrite these authors postulate that the activity gradient for carbon diffusion into the carbide is reduced. This interface control mechanism should reduce the growth rate of carbides in cobalt-containing steels. They also found that cobalt had very little effect on carbon diffusivity in various Fe-Co and Fe-Co-W-Mo austenites, but was found to decrease carbon diffusivity in Fe-Co ferrite. The above authors postulate that the effect of cobalt on accelerating the austenite to pearlite transformation is due to the increase in carbon activity in austenite. Cobalt is known(31) to increase both the rate of nucleation and the rate of growth of pearlite from austenite. Zener(32) postulated that cobalt increases the free energy change in the austenite pearlite transformation. Hagel(33) et al. and Kramer and Pound(34) showed calorimetrically that the free energy change of the austenite-pearlite transformation was increased by cobalt additions. Kramer et al.(35) also measured the specific heats of plain carbon and 2% Co. entectoid steels and found that cobalt lowered the specific heat of pearlite, and an effect expected from the increase in Curie temperature with increasing cobalt. This effect would be expected to decrease ΔG so the experimental finding that ΔG increases must be due to a change in ΔHo, the enthalpy at $O^{o}K$. Considering the rate-controlling mechanism to be carbon diffusion in austenite, if there were little partitioning of cobalt to austenite at the pearlite austenite interface, cobalt would increase the activity coefficient and decrease the equilibrium carbon concentration in the austenite at the interface. The effective increase in carbon concentration gradient would increase the local carbon diffusion flux and hence the growth rate. From the carburisation and decarburisation tests Houdremont and Schrader(8) deduced that cobalt increases the diffusion rate of carbon in iron. Blanter(55) concluded that at temperatures of approximately 1200°C. the diffusion coefficient of carbon increases with increasing cobalt content up to 6%, for higher contents it remains constant. At lower temperatures, it increases with cobalt content up to 11% and remains constant for higher amounts. Smoluchowski(54) determined the diffusion coefficient of carbon in austenite containing up to 4% cobalt, his results showed that cobalt increases the diffusion coefficient especially at elevated temperatures. Hawkes and Mehl(36) in 1947 challenged the above statements and proved in several direct diffusion tests that cobalt can only have an adverse effect, if any at all, on the diffusion rate of carbon. In 1953, Yurkov and Kristal(2) studied the decarburisation of iron containing 4% carbon and up to 5% cobalt at 1000°C. They showed that the diffusion coefficient has a maximum at 3% cobalt and minima at 1 and 4% cobalt. The authors offered a possible explanation of their results based on interatomic bonds. The influence of cobalt on other physico-chemical properties has also been found to depend on cobalt concentration. The authors suggested that for cobalt contents of 1 and 4%, stable cobalt groups are formed which slow down the diffusion rate of carbon.

Appleton(63) investigated the diffusion of carbon in Fe-Co-C austenites as a function of cobalt concentration up to 12 at %, using an autoradiographic technique. The diffusion coefficient was found to decrease initially and then increase with increasing cobalt concentration, the effect was more marked at higher temperature of diffusion. These effects were paralleled by variations in the activation energy.

According to Aaronson and Domian(23) cobalt did not partition during the early stages of transformation at any temperature studied, however, partition did take place in the manganese and nickel. In 1927, Allison(49) made a comparative study of the effects of nickel and cobalt in steel. His conclusions were that cobalt promotes graphitisation, raises the A3 and A1 temperatures, has little or no effect on the eutectoid carbon concentrations. In the same year Scherer(50) observed that cobalt additions to carbon steels prevented them from hardening throughout. Houdremont and Schrader(51) made a careful study of the effect of cobalt on the hardenability of steel. They found a ten-fold increase in the critical cooling velocity of a series of 0.90% carbon steels in which the cobalt content increased from 0 to 7%. Esser, Eilender and Majer(52) later confirmed the results of Houdremont and Schrader and merely stated that cobalt austenite has a greater velocity of reaction to pearlite than does unalloyed austenite. Davenport determined S-curves for 0.95% carbon steels containing 0, 1 and 2% cobalt respectively. His results confirmed the results obtained by the German investigators. Hawkes and Mehl(36) concluded that the addition of cobalt increases the rate of decomposition of austenite at all temperatures between Ac_1 and Ms, and no change in the shape of the T.T.T. diagrams or in the nature of the austenite decomposition products formed. Cobalt decreases the hardenability and increases the rate of reaction of austenite to pearlite by increasing both rate of nucleation and rate of growth. Cobalt decreases the interlamellar spacing of pearlite. In repeated experiments, no effect by cobalt on the coefficient of diffusion of carbon in austenite could be demonstrated. Although there is evidence that cobalt increases this coefficient, the magnitude of the effect however, appears to be too small to explain the influence of cobalt on hardenability. Cobalt is the only element which has been shown to raise the temperature range over which martensite forms in homogeneous austenite. However, in a low alloy steel containing 0.05C., 2.25 Cr., 1 Mo%, and less than 5%Co(5) cobalt increases the incubation time for ferrite nucleation. This effect has been confirmed by continuous cooling treatment and Jominy tests. The hardenability is increased with the addition of cobalt. On the contrary, cobalt increases the rate of austenite transformation in similar steels of higher carbon contents. In chromium(5) steels, 0.1%C., 13%Cr., it has been found that the hardenability is increased with the increasing amount of cobalt. This investigation has revealed that cobalt has a definite γ field broadening effect when chromium is present in amount exceeding 10%, and when the chromium content is not very high the delta-ferrite is almost completely eliminated.

Cobalt seems to be the only element known which raises the Ms temperature. Chiswik and Greringer(57) concluded that cobalt, from 3.4 to 7.6 percent, raises the Ms point of a 1.12% carbon steel uniformly at a rate of about 19°C. per one percent cobalt; this rate may not hold at lower cobalt content.

In the opinion of some authors copper and aluminium elevate Ms, but there are quantitative discrepancies in the values presented. However, none of the alloying elements are found to alter in any way the kinetics of the austenite to martensite transformation as described by Greninger and Troiano for plain carbon steels. Krivosheev et al.(61) studied the starting temperature and rate of transformation of martensite in a roll cast iron. They found that the temperature of the onset of martensite transformation was raised by cobalt. The rate of martensite transformation was reduced about 30% by cobalt.

Connor and Dabkowski(62) studied the effect of cobalt in 5%Ni-Cr-Mo steel to determine whether the addition of cobalt to raise the Ms temperature would increase self tempering, without deleteriously reducing hardenability and whether cobalt additions would reduce the susceptibility to heat-affected-zone cracking. The results of high speed dilatometric measurements on specimens, heat treated to simulate water quenching conditions, indicated that the cobalt addition raised the Ms temperature by about 9.5°C. per % cobalt in the range 0 to 5% Co., and also increased self tempering of martensite. The addition of 8%Co. drastically reduced the hardenability so that an undesirable amount of coarse bainite was formed. Coutsouradis and Habraken(64) investigated the effect of cobalt on the transformation points with varying amounts of chromium in 0.7% carbon steel. It was found that both AC_3 and AC_1 were lowered with the increasing amount of cobalt with 12-27% chromium. At 12% chromium content Ms temperature did not change appreciably with the increase in cobalt content, but at about 17% chromium there was a slight lowering ofMs temperature. This small variation in Ms temperature may well be due to small variation in chromium content of the different casts investigated. On the other hand Andrews (65) suggested that there is a possibility that chromium may raise the Ms temperature, although, the practical experiments never supported this view. Retained austenite in steel is generally known to be lowered by the addition of cobalt. Trusculescu(40, 41) showed that the addition of 4% cobalt to a 9% nickel steel leads to a decrease in retained austenite and the austenite grain size. Cobalt has been found to stabilise retained austenite in high alloy steels(8), but the opposite is true in low alloy carbon steel.(5)

The summary of the general survey is as follows :

a) Cobalt generally increases the hot hardness and resistance to tempering in both plain carbon and alloy steels.

b) Ms temper is always raised by the addition of cobalt.

c) AC_1 and AC_3 is generally raised by cobalt.

d) Hardenability is lowered in most cases, but there are two instances where cobalt increases the hardenability.

e) Activity coefficient of carbon is increased but whether cobalt has any effect on diffusivity is still controversial.

f) Cobalt increases the nucleation rate of carbides and retards the growth.

g) No evidence of partitioning of cobalt between austenite-ferrite interface is available.

3. EXPERIMENTAL PROCEDURE & RESULTS

3.1 Preparation of the alloy

The basis of the melt was scrap No. 5 die steel provided by Walter Somers Limited, Halesowen.

Ingots 3 in. square in section weighing approximately 25lbs. were made in a 40kw. Birlefco HF induction furnace. Instead of using usual monolithic furnace lining, sillimanite crucibles of 25-30lb. capacity were used backed by Zircon sand and outlined with thin asbestos sheet round the furnace. A new sillimanite crucible was used for each cast to avoid contamination from the previous cast. No controlled atmosphere was used. A grey cast-iron mould with solid bottom and split on the diagonal was used. A small amount of soft glass was used as a flux to form a viscous slag which was removed with an iron rod just before the deoxidation started. Powdered "Feedex", supplied by Foseco, was used for an exothermic hot top. The surface of the first ingot, which was cast in the mould coated with commercial graphite mould-dressing and pre-heated to a temperature of 500°C., was very unsatisfactory. The primary pipe was about 3 inches deep with small and scattered secondary pipe. The preheat temperature of the mould was lowered so that, at a medium pouring speed a directional solidification could be obtained. The surface of the ingot although much improved, was not very satisfactory. The primary pipe was confined only in the feederhead and a very small amount of secondary pipe confined at the top end of the ingot. The best result was obtained by coating the mould with a thin layer of soot from oxyacetylene torch and the preheat temperature of the mould at 200°C. The surface was excellent and by controlling the pouring speed the pipe was controlled as a small depression on the feeder head. The pouring temperature was 1600°C.

Loss of elements during melting:-

A complete analysis was done by wet classical method, before and after melting without any alloying addition or deoxidants. The results of the analysis are given below in Table I.

Table 1

CHEMICAL ANALYSIS OF A TRIAL CAST WITHOUT ANY ADDITION TO COMPENSATE THE LOSS DURING MELTING

Elements	Percent composition	
	before melting	after melting
Carbon	0.52	0.30
Silicon	0.18	0.028
Sulphur	0.031	0.031
Phosphorus	0.029	0.032
Manganese	0.61	0.14
Chromium	0.55	0.57
Molybdenum	0.28	0.29
Nickel	1.51	1.52

The elements carbon, silicon and manganese have been oxidised to a considerable extent but the other elements were unchanged. On the basis of the chemical analysis in Table I, the compensating additions were estimated. Carbon, in the form of electrode graphite was added with the scrap steel charge, whereas, manganese in the form of 80/20 low carbon Ferro-manganese and silicon in the form of 80/20 low carbon Ferro-silicon were added as a de-oxidiser to serve both the purposes. Ferro-manganese was added approximately 3 minutes before casting followed by Ferro-silicon almost immediately before the metal was teemed. The amount of the additions per 25lb. of scrap steel were as follows: 42 gms. of graphite, 85 gms. of Ferro-manganese and 42 gms. of Ferro-silicon. The result of the analysis is given in Table 2, and at the same time the homogeneity of the elements had been checked.

Table 2

CHEMICAL ANALYSIS OF THE TOP AND BOTTOM OF THE INGOT, TO ESTIMATE THE AMOUNT OF SEGREGATION

Elements	Top of the Ingot %	Bottom of the Ingot %
Carbon	0.69	0.69
Manganese	0.69	0.73
Silicon	0.50	0.50

It is clear from the results in Table 2, that the elements were quite uniformly distributed throughout the ingot, without any appreciable segregation, but the amounts came out far too high from the specification of No. 5 die steel. Consequently, the additions, revised and corrected for the next cast were as follows: Carbon 25gms., Ferro-manganese 71 gms., Ferro-silicon 12 gms., based on 25lbs. of melt. The analysis of the cast is given in Table 3.

Table 3

Elements	Specifications for No. 5 die steel %	Analysis of the cast %
Carbon	0.50 - 0.60	0.56
Silicon	0.30 max.	0.19
Manganese	0.50 - 0.80	0.65
Sulphur	0.04 max.	0.031
Phosphorus	0.04 max.	0.030
Nickel	1.25 - 1.75	1.51
Chromium	0.50 - 0.80	0.55
Molybdenum	0.25 - 0.30	0.28

Table 3 shows that the analyses were exactly within the specification.

Cobalt addition: Seven casts were made with the necessary cobalt additions ranging from nominal 0 - 8% cobalt. Commercially pure cobalt (99.9%Co, 0.1%Ni) was charged along with the scrap steel in the crucible and the ingot was cast exactly in the same way described before. The feeder head containing the pipe was sawn off. The chemical composition of the casts is given in Table 4.

Table 4 CAST ANALYSIS

Cast No.	Nominal Co. content	C %	Si %	Mn %	Ni %	Cr %	Mo %	Co %
0	0	0.56	0.18	0.76	1.75	0.58	0.27	0.069
1	1	0.58	0.11	0.70	1.57	0.55	0.28	1.01
2	2	0.58	0.19	0.65	1.70	0.62	0.28	2.00
3	3	0.58	0.23	0.72	1.64	0.69	0.21	3.03
5	5	0.56	0.20	0.80	1.56	0.57	0.29	5.16
7	7	0.52	0.17	0.60	1.52	0.57	0.29	6.98
8	8	0.60	0.20	0.72	1.60	0.55	0.28	8.00

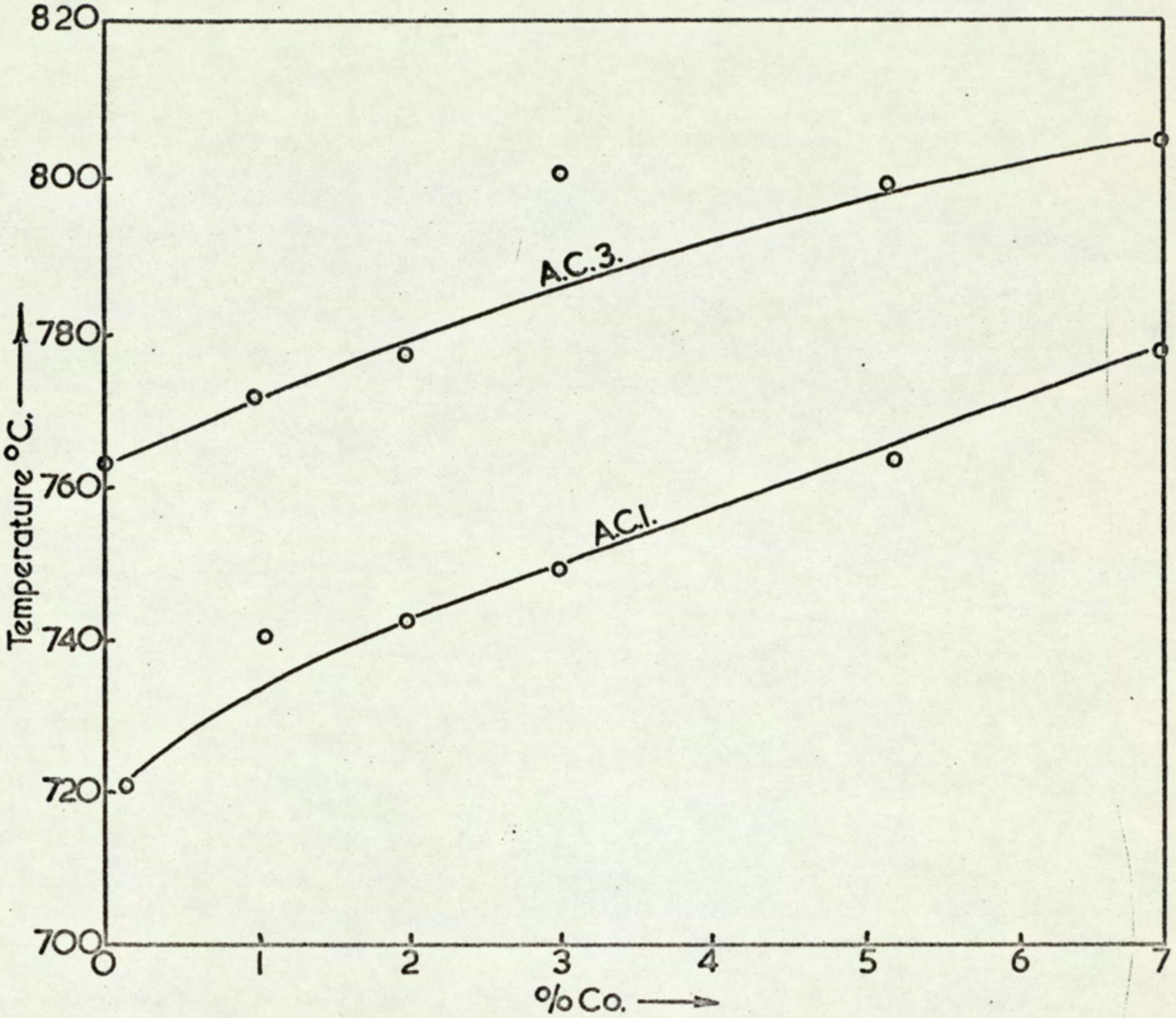
Sulphur 0.032%., Phosphorus 0.032% max. in all casts

3.2 Ingot Processing

The surface of the ingots were generally satisfactory and no dressing was required before hot working. Three ingots, cast (0, 1, 7) were first hot pressed to the form of a slab 1" thick, the rest of the ingots were hot rolled directly from the cast ingots. Specimens about $\frac{3}{4}$" square sections were cut with an abrasive cutting wheel and then were hot rolled at 1100-1150°C. to the necessary reductions for the preparations of specimens.

3.3 Determination of Critical Temperatures

One inch long and 0.125" diameter specimens were machined from the hot rolled material. The classical dilatometric method was used. The dilatometer was fitted with a "Baty" dial gauge, having a sensitivity of 0.0001" per division. A vertical electric furnace was used for heating the specimen at a rate of 15°C. per minute. A Chromel-Alumel thermocouple was used to measure the temperature, the hot junction of which was attached to the specimen through a hole drilled into the silica tube, the cold junction was placed in a test tube with a thermometer to record the cold junction temperature. The potentiometer and dial gauge reading was taken at intervals of 0.2 millivolt. The millivoltage was plotted against expansion (Fig. I a-f A) from the graph the beginning and end of transformation, during heating cycle AC_1 and AC_3 were determined. Correction was made for the cold junction temperature, and repeated experiments agreed within ±1°C. The relation between transformation temperature and cobalt content is shown in Fig. 2. The transformation temperatures are certainly not the equilibrium temperatures of transformation, because the heating rate (15°C/min) is too fast for equilibrium to be achieved. Nevertheless, by keeping all other



Transformation temperature v. % Co. at the heating rate of 15°C/min.

Fig. 2.

variables constant, this experiment showed the general effect of cobalt on the transformation temperature. Fig. 2 shows that both AC_1 and AC_3 are raised almost linearly with the increasing amount of cobalt.

3.4 Determination of M_s and M_f Temperatures

The Greniger and Troiano technique was attempted and the results were unsatisfactory due to the formation of lower bainite which was indistinguishable from tempered martensite. Dilatometric tests gave erratic and spurious results. Consequently, a dilatometer was specially designed where the dial gauge was replaced by a Taylor-Hobson Magnagauge. This electronic device has as its sensing head an inductive displacement transducer, and this is mounted on a dilatometer head (Fig. 3). The magnagauge is normally used by reading a calibrated scale on the instrument, but for these experiments a voltage output from the magnagauge was applied to the Y axis terminals of an X-Y plotter. Linear movement of the transducer (initiated by the expansion or contraction of the specimen) resulted in proportional voltage inputs on the Y axis. The sensitivity of the magnagauge transducer is from +0.0005"to - 0.0005" over the full scale. For the above experiment however, a separate scale reading from +0.005" to -0.005" was

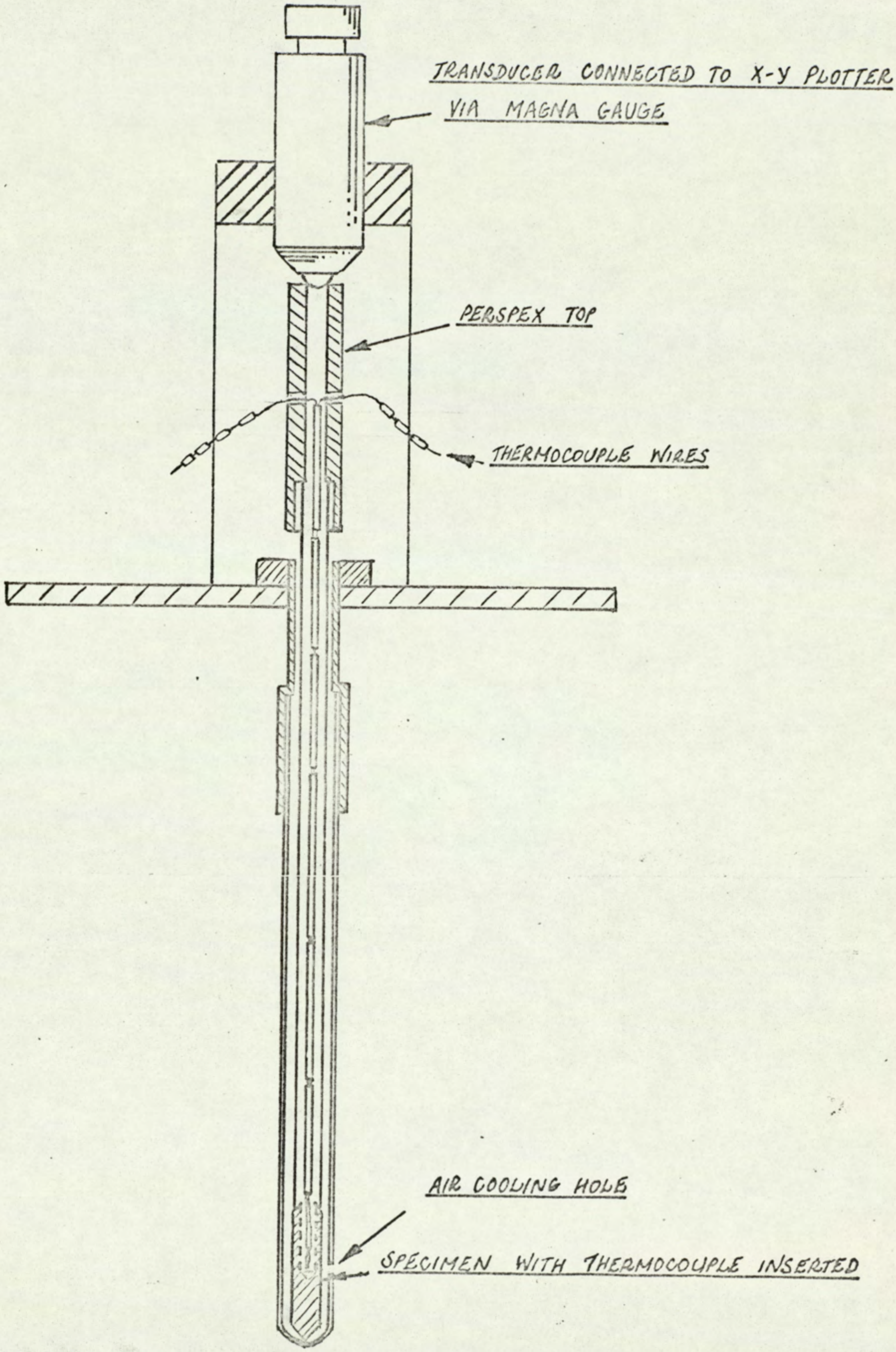


Fig.1.

FIG.3. DILATOMETER ASSEMBLY FOR MEASURING M.S.&M.F. TEMPERATURE

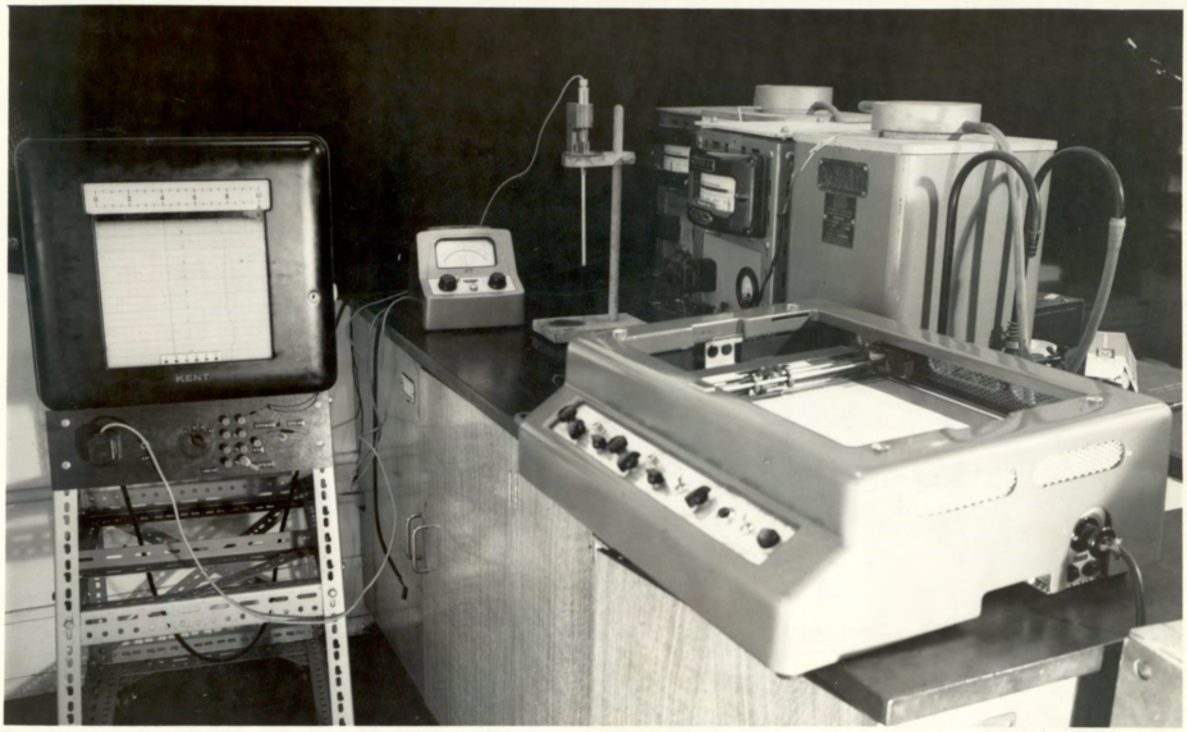


Fig. 4. Photograph of the set up for the determination of the martensitic transformation temperatures.

adequate.

A hole was drilled on top of the specimen ($\frac{3}{4}$" long 0.1" diameter) longitudinally, half way into the specimen into which a Pt - Pt, 13%Rh thermocouple was inserted to record the exact temperature of the specimen during transformation. The specimen was supported at the closed end of the outer silica tube. To facilitate rapid cooling of the specimen by an air-blast, a hole was drilled through the silica tube near the specimen. The inner silica tube, open at both ends, with one end resting on the specimen, through which the insulated thermocouple was threaded and taken out of the apparatus at the other end fitted with a perspex top which provided both the outlets for the thermocouple wires at the sides and contact surface with the transducer ball on top. In this way it was possible to note the temperature without disturbing the specimen during transformation (Fig. 3).

The volume change during transformation was recorded as a change in electric current through a transducer which was connected to the Y axis and the thermocouple indicating the temperature of the specimen was connected to the X axis of the X-Y recorder. The complete set-up is shown in Fig 4. The silica tube containing the specimen was heated to 850°C in

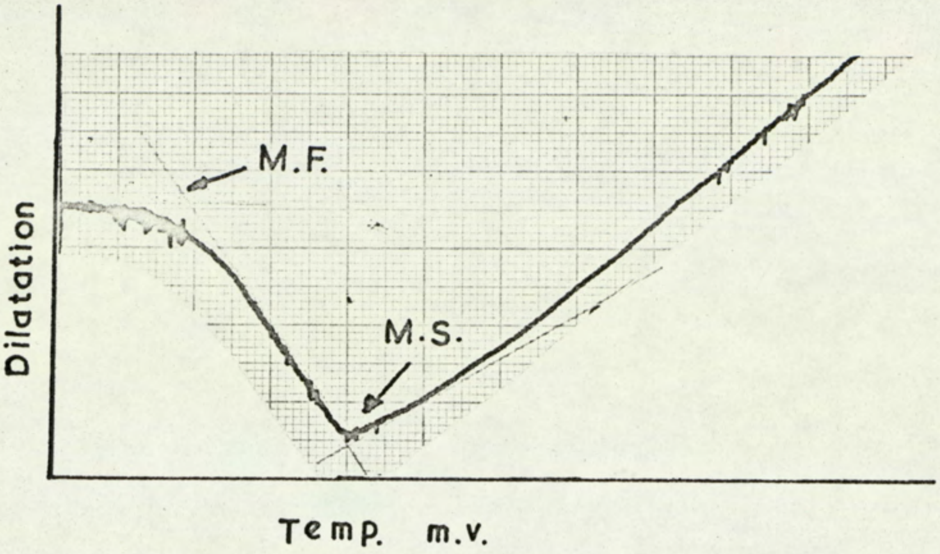


FIG.5a. Typical curve showing a volume change at the martensitic transformation temperatures
1%Co, Room Temp. 22°C, 1" = 1 m.v.

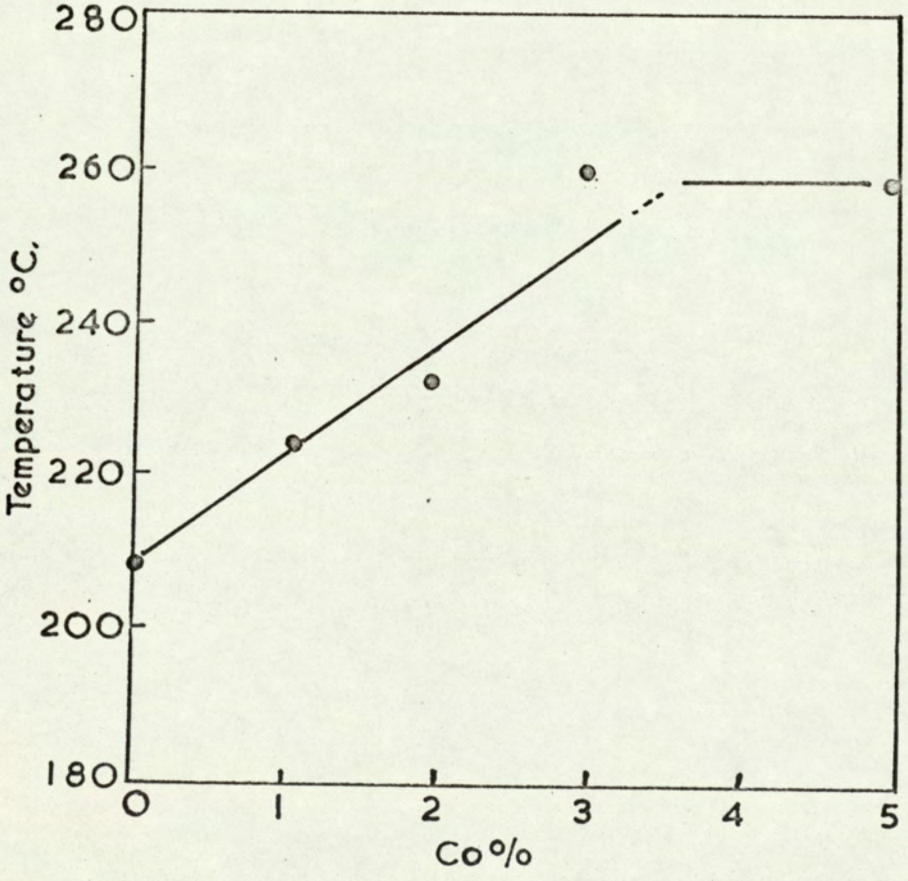


FIG. 5b. Relation between the martensitic transformation temperatures and the cobalt contents in No. 5 die-steel

a vertical electric furnace (this austenitising temperature was found out from the determination of AC_3 temperature) soaked for 30 minutes and was quickly cooled in a blast of cold air which was sufficient to arrest all the intermediate transformations for specimens containing up to 5% Co. The hardenability of the steels containing more than 5% cobalt was too low to stop any intermediate transformation by the above procedure and the temperature at which martensitic transformation occurred was completely obscured by the continuous transformation of austenite during the whole cooling period. Quenching in water was not successful, because the inertia of the machine could not keep pace with rapid contraction rate of the equipment and consequently traced a spurious graph.

The X-Y recorder automatically recorded a graph and the martensitic transformation temperature was read directly from the graph with necessary corrections. The graph paper was previously standardised and marked for the temperature with a standard potentiometer. Fig. 3 shows the arrangement of the dilatometer for the determination of M_s temperature with a photograph of the experiment in Fig. 4. Fig 5a. shows a typical example of the experimental curves obtained from the

Table 5. Effect of cobalt on the martensitic transformation temperatures.

Steel No.	Nominal cobalt %	Ms°C	M50°C	Mf90°C
0	0	209	I62	89
I	I	224	I65	I02
2	2	230	I67	II3
3	3	260	I99	I48
5	5	259	I93	I48

above experiment, which have been used successfully to determine M_s, M_{50} and M_{90}. The total volume expansion due to the martensitic transformation was considered as 90% transformation and on that basis 50% transformation was calculated. The results are given in Table 5. Fig. 5b shows the relation between M_s temperature and cobalt content. The M_s temperature is raised linearly up to 3%Co., and above 3% cobalt the M_s temperature becomes independent of cobalt. The experimental data is no way sufficient to prove this fact exclusively. Only one experiment was done at 5% Co. Fig. 5c. A. is another typical experimental curve at a higher cobalt content showing the failure to determine accurately the exact temperature where austenite starts to transform to martensite. This is because the rate of decomposition of austenite is accelerated severely by cobalt to arrest the intermediate transformation product. Other methods give spurious results because of the banded structure and autotempering of martensite. The M_s temperature vary from 209°C. at 0%Co. to 260°C. at 3% Co., ie. about 17°C. rise in M_s temperature per 1% of cobalt. Similarly, the M_{f90} temperatures vary from 89°C. at 0%Co. to 148°C. at 3%Co., ie. a rise of 19.6°C per 1% cobalt. It must be realised that the accuracy of determination of the M_s temperatures is greater than that of the Mf_{90} temperatures because of the proximity of M_f to room temperatures, where the inflexion of the curve becomes less distinct.

3.5 Retained Austenite Determination

If a considerable amount of retained austenite were present in the steel after quenching, it would present difficulties in the investigation of tempering characteristics, because the retained austenite would transform during tempering giving a comparatively soft high temperature transformation product. Therefore, an investigation was made to determine the magnitude of this problem in the as-quenched materials. $\frac{3}{4}$" square specimens were cut from 0.1" thick rolled plate reduced 50% from the cast ingots. The flat faces were ground and polished before heat treatment, austenitised 30 minutes at 850°C. in a salt bath and quenched in oil to room temperature. The surfaces were repolished cautiously to avoid any transformations during the polishing process. The polished surfaces were then etched in 40% aqueous HNO_3.

X-ray technique: "Direct comparison" method was used where the integrated intensity of a diffraction line from the α phase is compared with the integrated intensity of a diffraction line from the γ phase. The concentration of γ in the sample is then obtained from

$$\frac{I\gamma}{I\alpha} = \frac{R\gamma}{R\alpha} = \frac{C\gamma}{C\alpha} \quad \text{where,}$$

$I\gamma$ = integrated intensity of the austenite line chosen

$I\alpha$ = integrated intensity of the ferrite line chosen

$R\gamma$ $R\alpha$ = constant depending on the particular line chosen

C = concentration of phase present

The samples were irradiated by Cu K α radiation and the conditions were as follows :

(a) Fully stabilised Siemens Crystalloflex 4 X-ray diffraction generator.

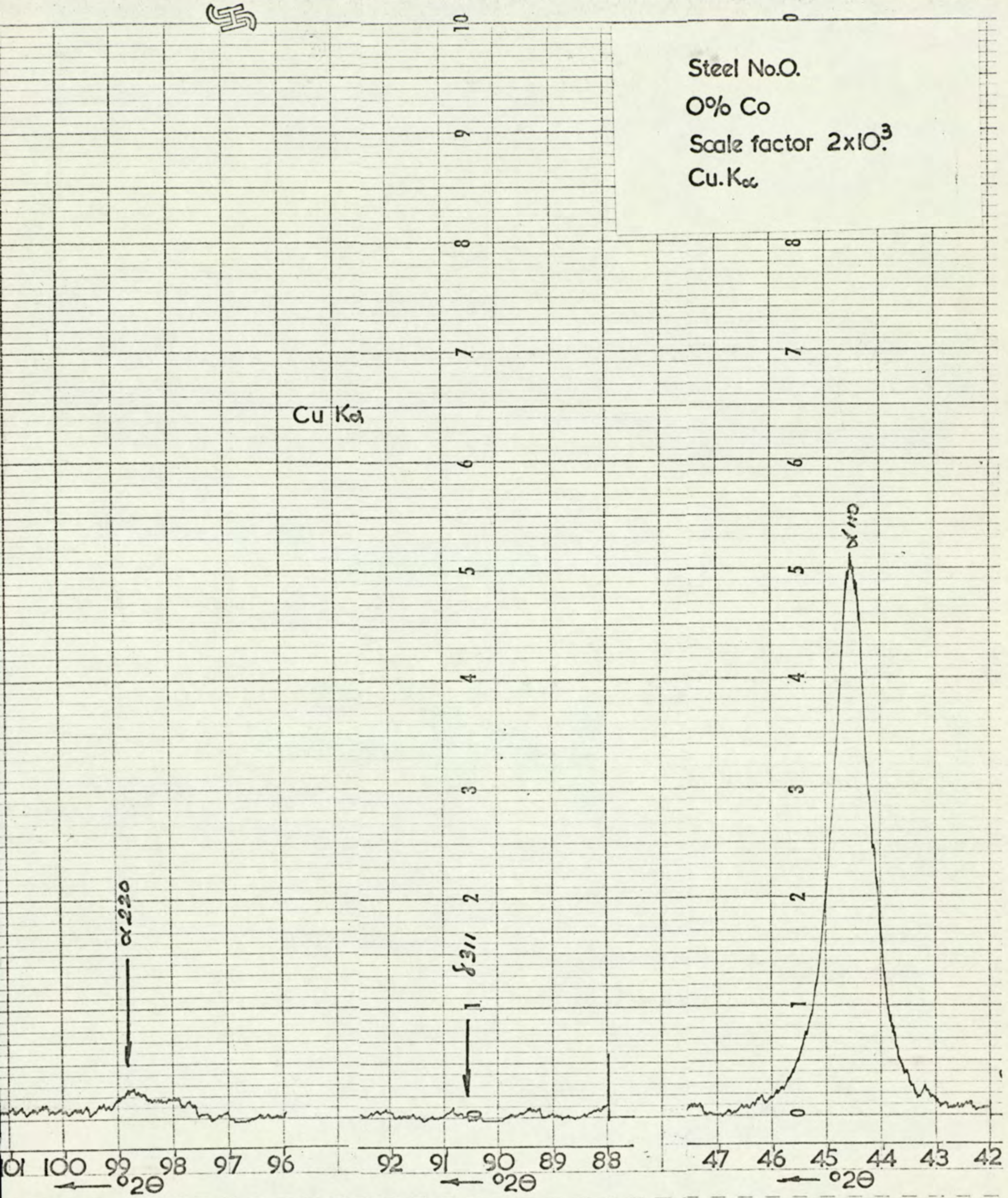
(b) Siemens wide angle goniometer, 2.4mm aperture slit, 0.1mm counter slit.

(c) Siemens single crystal monochromator with curved LiF cyrstal.

(d) Siemens proportional counter type B.

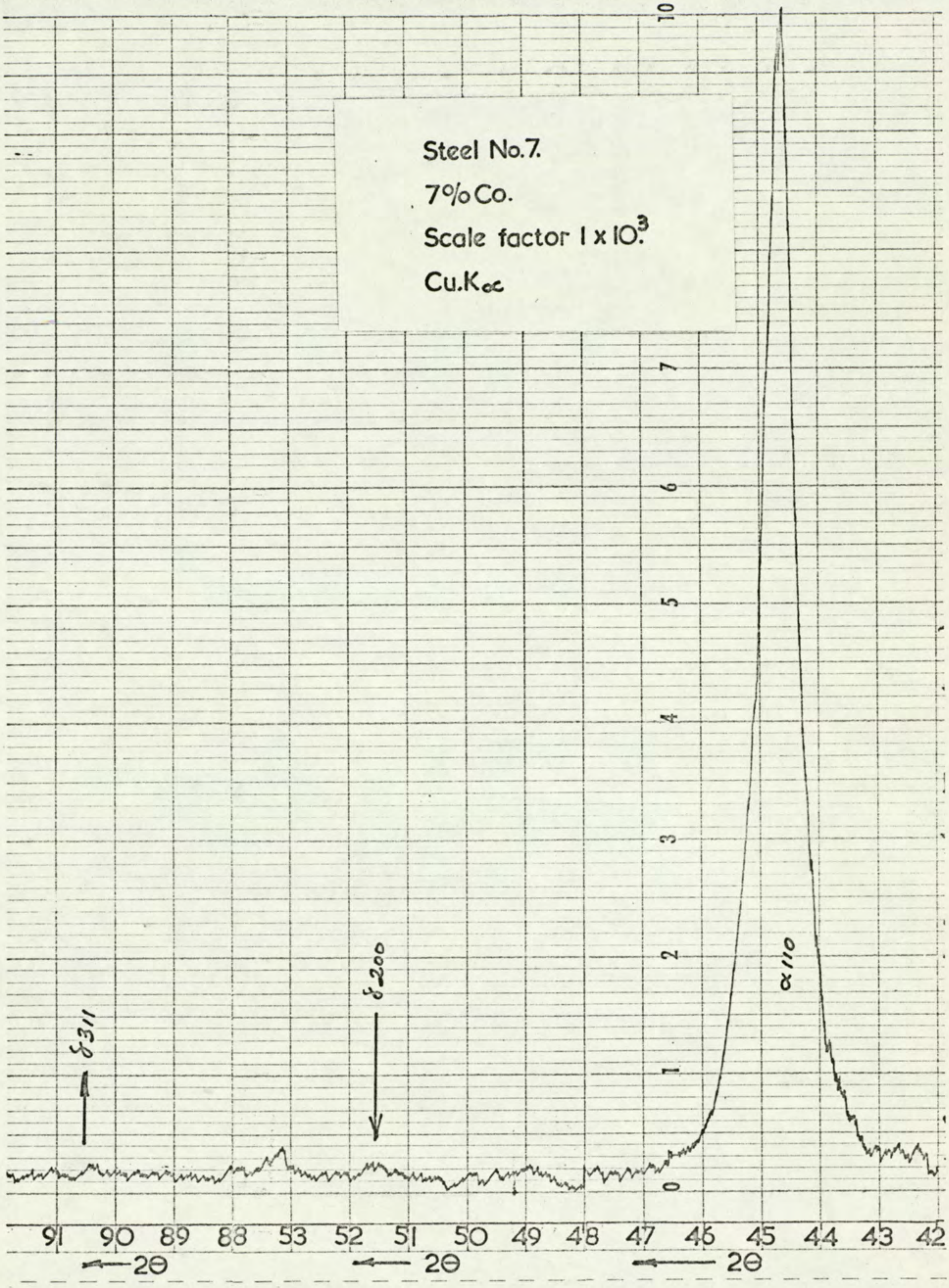
(e) Pulse height discriminator - 6volt channel.

The goniometer was aligned according to Siemens instructions Eg404/2c. Each sample was mounted in a specimen holder and wide angle scans were taken of selected α Alpha and γ Gamma lines. The lines normally chosen were 311 γ line and 110 α line. No definite indication of γ line was obtained as shown in Figs. 6a and 6b. Step scanning with the



X-Ray diffractometer record showing scan through austenite (311) line

FIG. 6a.



X-Ray diffractometer trace showing scan through austenite lines (311) & (20

FIG. 6b.

monochromator using 0.02^{o} increments per minute through 311 γ line, showed no appreciable improvements in resolution. Specimens containing O and 7% cobalt were examined. The glancing angle method also showed no presence of retained austenite.

Pepperhoff technique : In this technique Zinc Selenide is vacuum deposited on polished unetched specimen. The high refractive index of the deposited alloy increases the contrast between different phases. This technique is known to be quite effective to detect very small amount retained austenite in martensitic matrix. No austenite was detected using this technique.

Therefore, with the techniques employed, it can be concluded that the retained austenite content in both samples is certainly less than 0.5% and most probably less than 0.2% by volume, and that the cobalt additions do not promote retention of austenite. This agrees with the raising of Ms temperature.

3.6 Determination of the Time Temperature Transformation Diagram

T.T.T. diagrams were determined dilatometrically for steels containing 0, 1 and 3% cobalt respectively, using a conventional dilatometer. The dial gauge was replaced by a transducer and any change in volume after a certain period of time at a constant temperature was recorded on a continuous chart recorder. The chart record was fitted with extra resistances to lower the voltage input, because the voltage output of the transducer was considerably high.

Constant temperature lead bath was designed, but the attack of lead on hot silica tube was discouraging. So, ordinary vertical electric furnace was used as a constant temperature furnace. The fluctuation of temperature during experiment was reduced to a minimum with the help of high resistor fitted to the automatic controller.

The dilatometer tube containing the specimen, (1" long and 0.1" diameter machined from the rolled bar) was heated at 850°C. for 30 minutes to austenitise completely, cooled to the required transformation temperature by a blast of air and then quickly placed in the constant temperature furnace. The whole cooling operation took 6/7 seconds which was negligible considering that the actual time for the start of transformation in most cases for these steelswas at least 1 minute, and usually much longer. A typical recording on the chart indicating the start of transformation is shown in Fig. 7A

For steels with moderate hardenability the above method

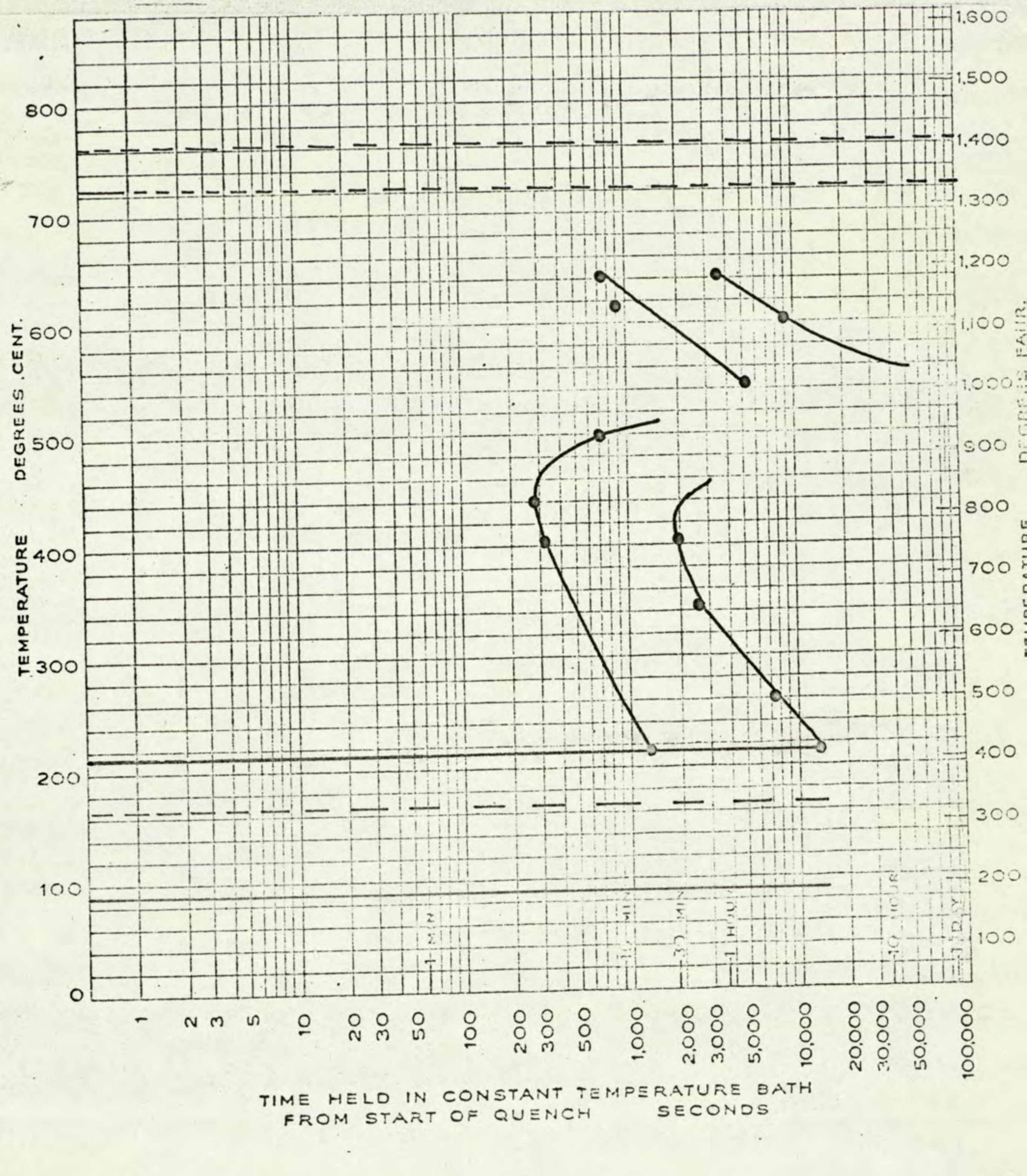


FIG.8a. Partial T.T.T. diagram of No.5 die steel with 0 %Co.
A.S.T.M. grain size: 7 - 9.

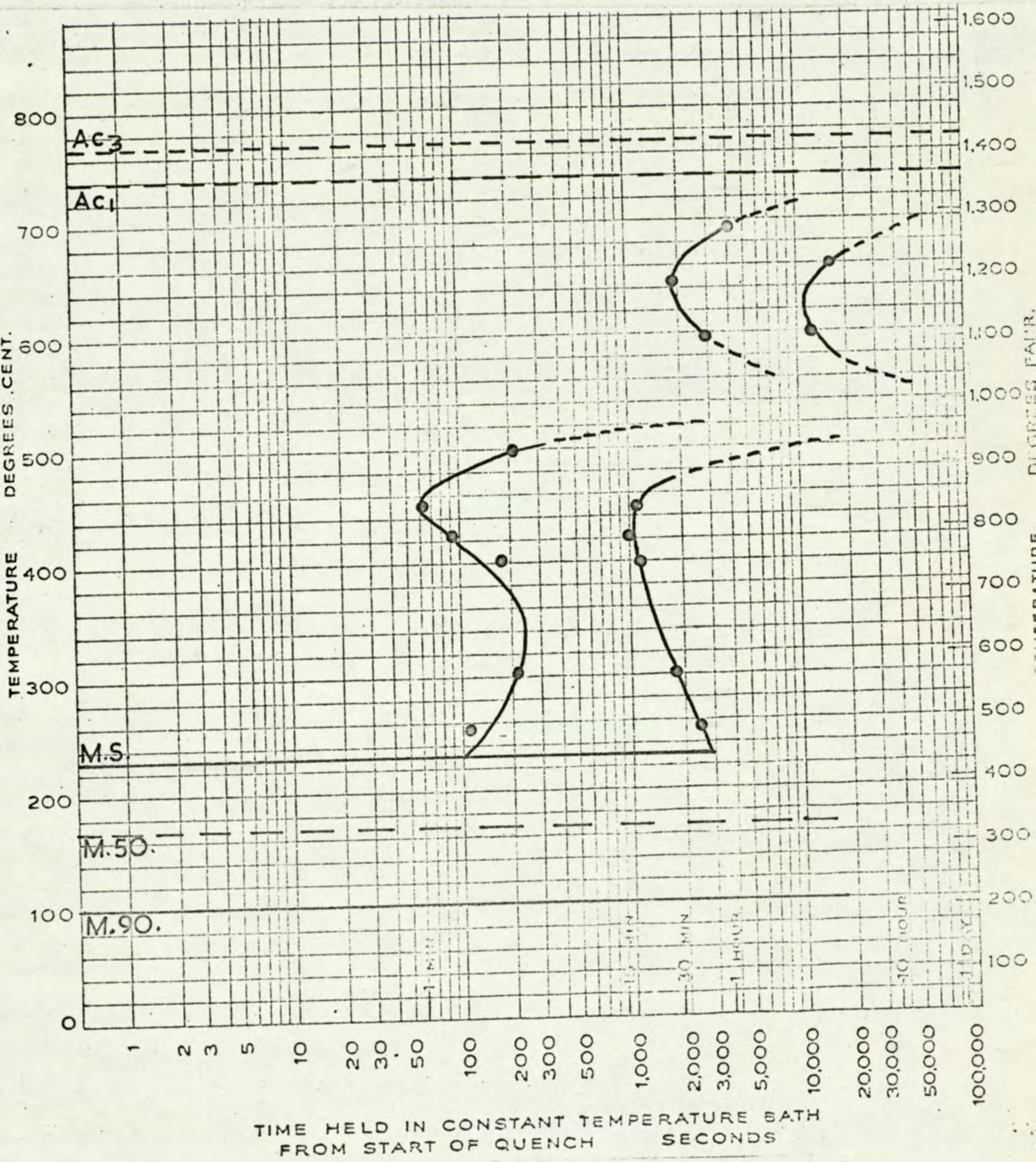


FIG. 8b. Partial T.T.T. diagram of No. 5 die steel with 1 %Co. A.S.T.M. grain size 7-9.

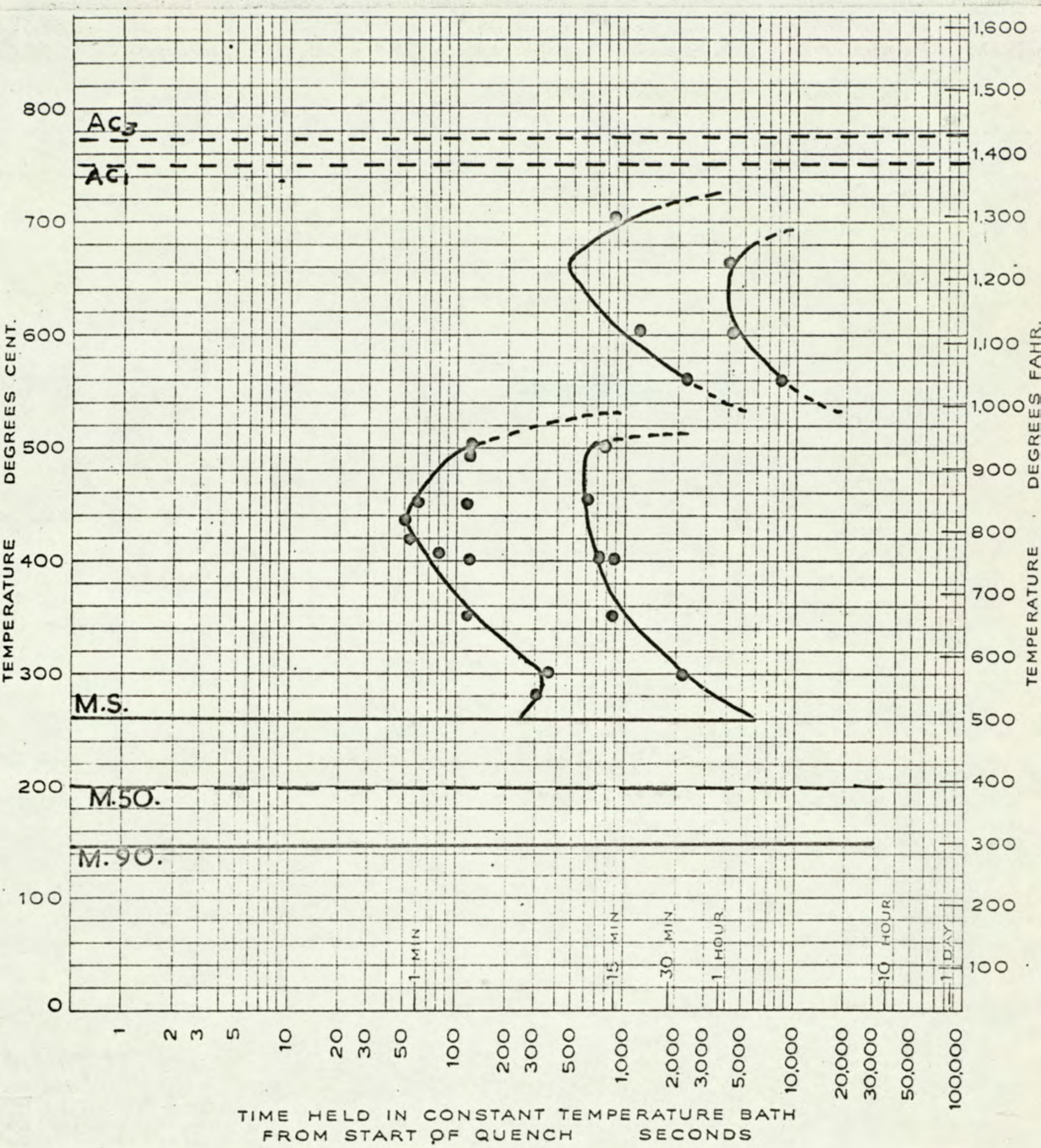


FIG. 8c. Partial T.T.T. diagram of No.5 die steel with 3 %Co. A.S.T.M. grain size 7-9.

proved to be quicker and more efficient than the classical bracketting technique, but with high cobalt steels the hardenability was too low for this method to be satisfactory. Partial diagrams for steels containing 0%, 1% and 3% cobalt were determined and are shown in Figs. 8a, 8b, 8c respectively.

Both pearlitic and bainitic hardenability are reduced with the increasing amount of cobalt and the effect on pearlitic hardenability is very pronounced. Cobalt does not seem to depress or raise the temperature of the noses of the pearlite or bainite curves, nor does it seem to affect the total reaction time.

3.7 Investigation of Tempering Characteristics

Ingots reduced to 50% by hot rolling were annealed at 700°C. and held at that temperature for 6 hours, after which the charge was furnace cooled to room temperature.

The specimens for the tempering experiments were in the form of ½in. cubes machined from the annealed bars. The samples were austenitised in a chloride salt bath at 830°C. ± 10°C. for 20 minutes, oil quenched and then tempered in electric muffle furnaces at different temperatures controlled to ± 1°C. After the tempering treatment the surfaces of the

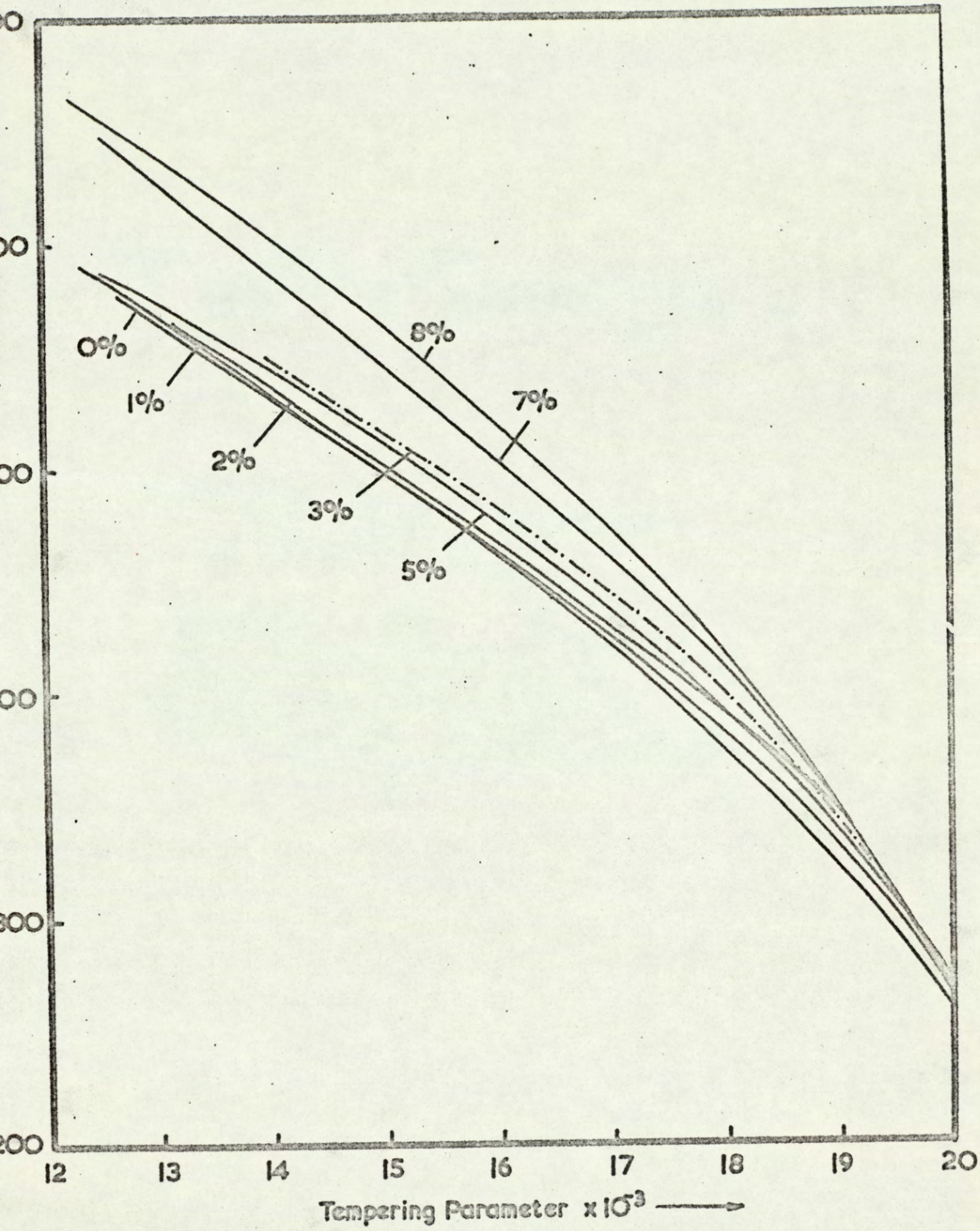


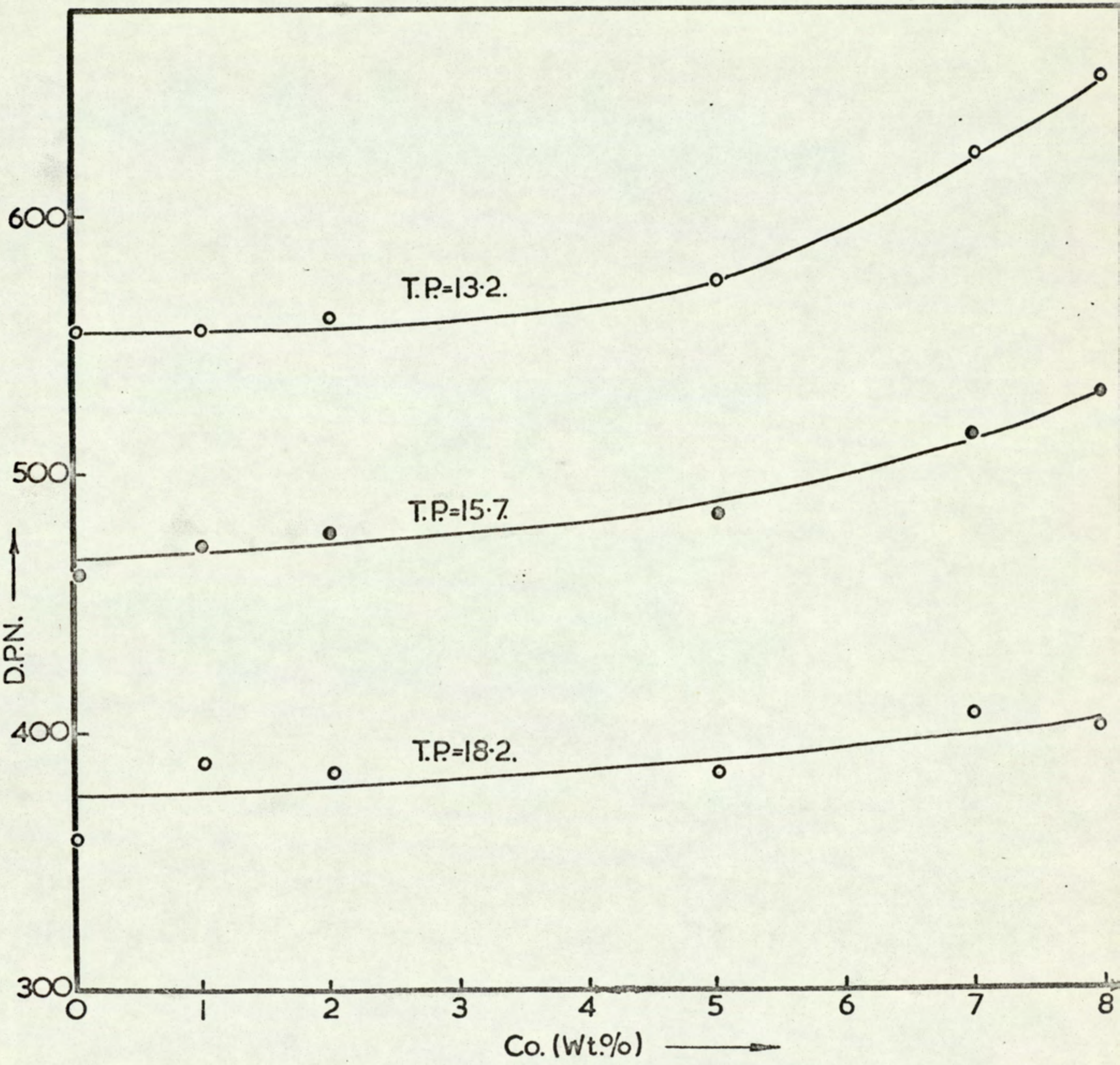
Fig. 10. Hardness v Tempering Parameter for varying %Co. in steel

Table 6 Hardness of Tempered Samples.

Steel No.		0	1	2	5	7	8	Tempering Parameter x 10^{-3}
Nominal cobalt content %		0	1	2	5	7	8	
				HARDNESS DPN 30				
As quenched		775	780	769	780	769	767	
Tempering Temp. °C	Time H.							
350	2	575	579	583		644	668	12.65
	20	554	555	561		623		13.27
	22	561	570	571		622	652	13.30
	73½	516	503	521	564	580	580	13.62
400	21	499	505	481		568	571	14.34
	72				543			14.71
450	74	481	484	490		514	520	15.81
500	2	465	470	476		514	530	15.69
	20	474	445			436		16.46
	70	425	425			454		16.88
550	2	420	410			454		16.70
	5				420			16.0
	50	398	396	385		439	429	17.85
	100	387	400	403		430		18.10
	144	358	387	383		406	402	18.23
600	2	380	385			420		17.72
	4	371	375			400		17.98
	4½				399			18.00
650	2	334	328			350		18.73
	46½	257	270	274	277	270	268	20.0

specimens were ground scale. For each treatment a separate specimen was used. Hardness was measured on each sample in Vickers diamond Pyramid Hardness Testing machine with 30kg. load throughout.

Hollomon and Jaffe(13) discovered that the combined effects of time and temperature can be accounted for in a parameter T(C+logt), where T is the temperature in degrees absolute and t is the time in hours. The value of C is constant and generally taken as equal to 20 for all steels. When hardness is plotted against corresponding values of tempering parameter, master tempering curves are obtained which permit tempering characteristics to be compared. The tempering treatments, hardness and the values of tempering parameter are recorded in Table 6. The results are plotted for each of the alloys in Fig. 9(a-f)A, except for the cast No. 3, which is shown in Fig. 10 along with the others for easy comparison. The dotted line represents 3% cobalt steels. From Fig. 10 it appears that the 3% Co. steel is slightly more resistant to tempering than the 5%Co. steel. But, because the 3%Co. steel was tempered in a different furnace on separate occasions from the other test pieces, it is probable that a small amount of variation in furnace condition was responsible



Effect of Co. on hardness at three values of Tempering Parameter T.P.x10^{-3}

FIG.11.

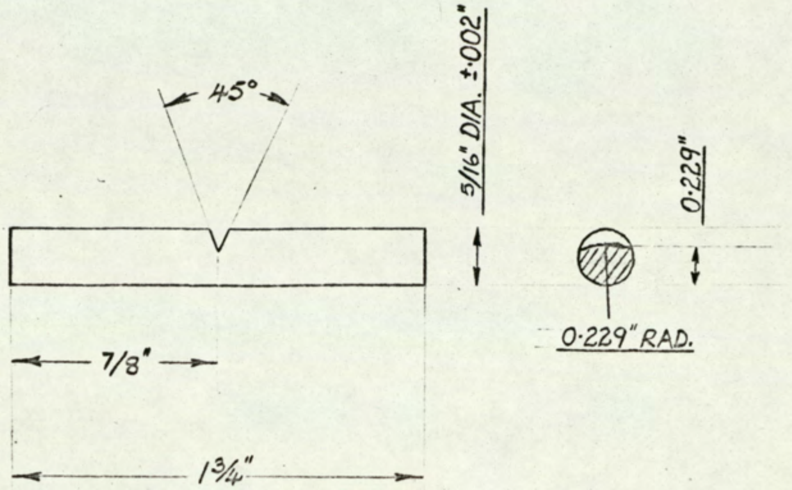
for the slight variation between the two lists. The results show that at a low value of tempering parameter (ie. low tempering temperatures) an appreciable amount of resistance to tempering can be obtained from No. 5 die steel by the addition of more than 5% cobalt . The steels fall into two distinct groups - those containing up to 5% cobalt which show only slight but general improvement in tempering resistance, and those containing more than 5% cobalt which are remarkably better, particularly at low temperatures. Therefore, any significant retardation of the tempering processes, particularly in the lower temperature ranges, would require the addition of relatively large amount of cobalt. At higher temperature of tempering, ie. the third stage, the improvements are slight, even with greater than 5% cobalt. It is clear from Fig. 11 that the rate of increase in hardness with respect to cobalt content is higher at a low parameter value and at cobalt contents of more than 5%. As the value of the parameter increases this rate falls and the curve tends to be horizontal. At a parameter value of 13.2×10^3 the hardness of a specimen with 8% cobalt is about 90 HV harder than one with 5% cobalt. The difference is about 50 HV at a parameter value of 15.7×10^3 and virtually nil at a parameter value of 18.2×10^3.

3.8 Impact Tests

Previous experimental work(5) led to the conclusion that the addition of cobalt improves the toughness of low alloy steels but the effect was not consistent and reproducible. Accordingly, the effect of the addition of cobalt on the toughness of the No. 5 was studied.

Three alloys were chosen to investigate the effect of cobalt on the impact property of No.5die steel, are 0%, 1% and 5% cobalt respectively. They were hot rolled from the ingot to 50% reduction at 1100°-1150°C., the rolled bars were then austenitised in a chloride salt bath at 850°C. for 30 minutes and oil quenched. The quenched bars were then tempered at 650°C. for 48 hours. This time-temperature combination gives approximately an equal hardness for the steels, which is 260±5V.P.N. This is obvious from the tempering results, that at a very high parameter value the hardnesses become approximately equal.

The impact test specimens were machined from the heat treated bars for the Hounsfield balanced impact testing machine. A sketch of the specimen with dimensions is given in Fig. 12. Tests were carried out at various temperatures ranging from -60°C. to 200°C. The test results are given in Table 7.



HOUNSFIELD BALANCED IMPACT SPECIMEN

Fig.12.

Table 7. Impact Test Results

Hardness V.P.N.	265	257	250
Temperature °C	0%Co	1%Co	5%Co
200°C	19 (D)	19 (D)	16 (90°/D)
27°C	17½ (90%D)	16 (90%D)	10 (90%D)
5°C	12½ (60%D)	12½(50%D)	7½(30%D)
0°C	13½ (30%D)	13½(30%D)	5½(10%D)
-5°C	11½ (30%D)	12½(30%D)	5 (10%D)
-20°C	10½(20%D)	9(10%D)	------
-40°C	12½(5%D)	6½(2%D)	4½(2%D)
-60°C	5 (B)	3½(B)	1½(B)

D = Ductile fracture,

B = Brittle fracture.

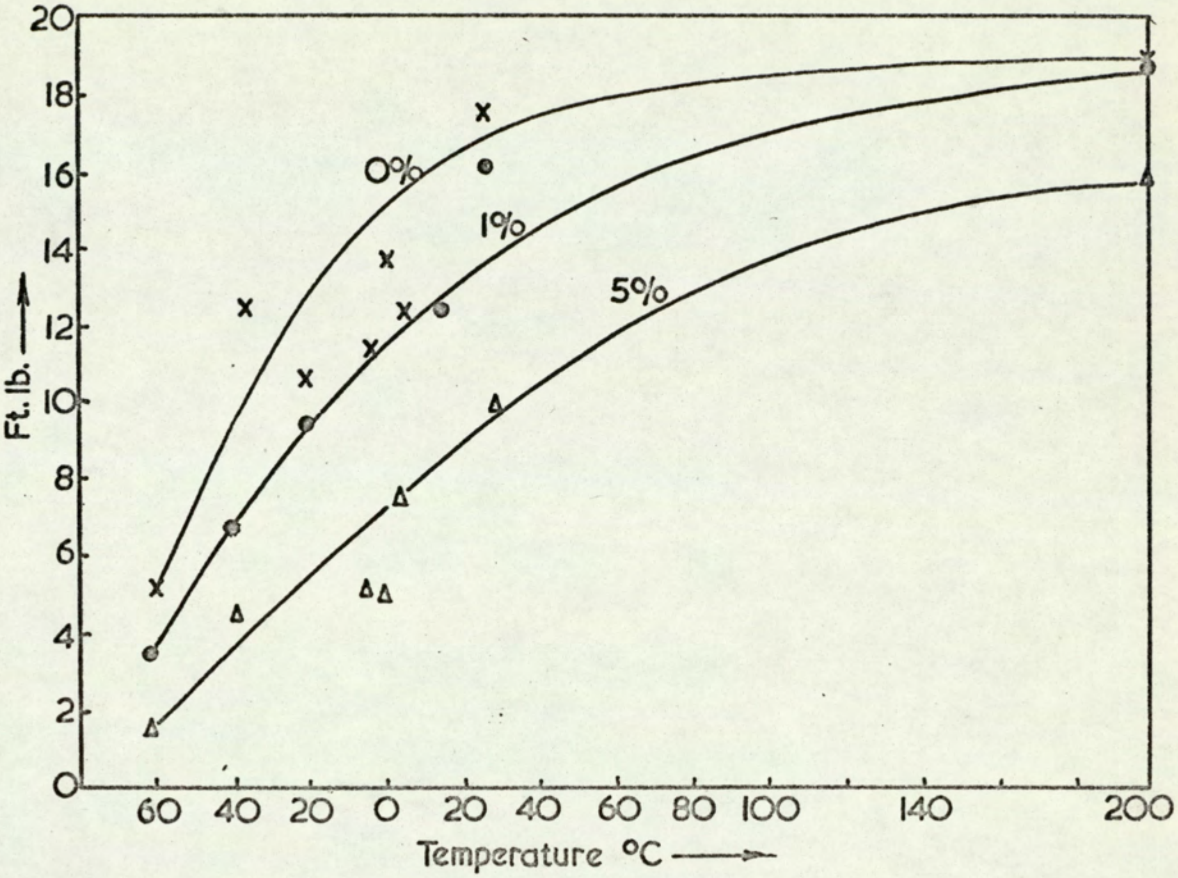


Fig. 13. Effect of Co. on impact property

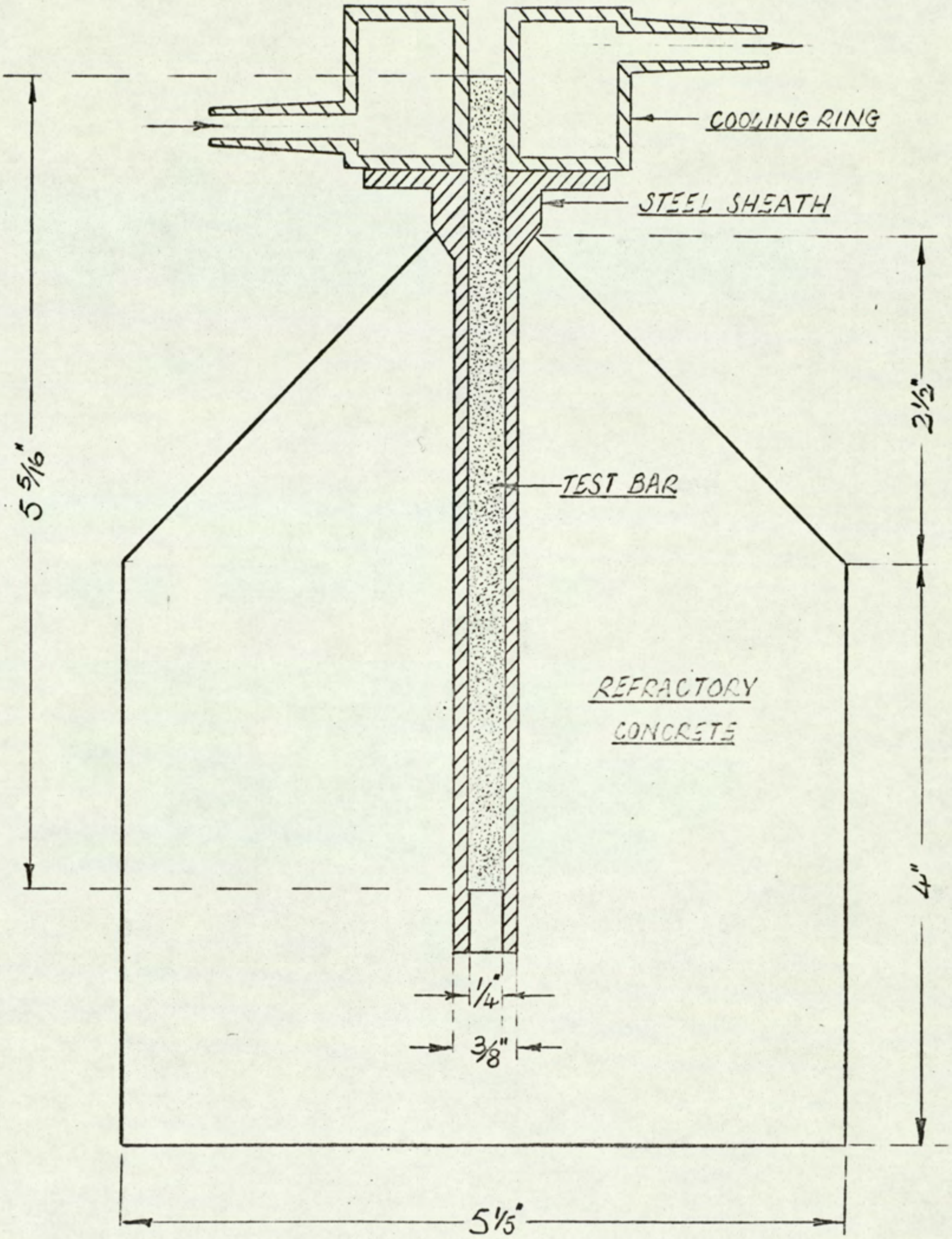
Fig. 13 shows the effect of cobalt on impact properties.

It is evident from Fig. 13 that at an identical heat treatment condition and approximately similar hardness conditions, the impact strength is slightly reduced by the cobalt and virtually no effect of cobalt on the transition temperature of No. 5 die steel, at least up to 3%Co. level.

3.9 Hardenability

It is not possible to use the simple Jominy Test for steels of high hardenability, because the cooling rate is too fast to reveal any hardenability differences. As a practical alternative, the hardenability test used in this work was based on a newly developed method of Dutch origin(14).

The hardenability of highly hardenably alloy can be determined by use of this arrangement as shown in Fig. 14. The specimens were machined, from rolled bar reduced 50% by hot rolling from the ingot. The specimen, 5.5/16" long and $\frac{1}{4}$" diameter was heated in the stainless steel lined hole in the cone of refractory concrete. The projecting end of the specimen was quenched by the water cooled ring which produced a wide range of cooling rates along the bar as it cooled. After the cooling process was complete, hardness variation along the bar was measured.



HARDENABILITY TESTING ASSEMBLY

Fig.14.

In the equipment used, the refractory concrete cone was made by casting a slurry of chrome-magnesite refractory with sodium silicate bonding. The maximum particle size of the refractory was 1/8" diameter. The central hole was formed by a wax core which melted when the core was fired. The hole was dressed with a carbide tipped drill. The stainless steel sheath was made from tube, closing the bottom by welding: the collar was also welded to the other end. The water cooled quenching cap was made of 70/30 brass fitted with two long copper tubes at the inlet and outlet.

To carry out a test, the concrete cone was pre-heated in an electric furnace for three hours to a constant temperature of 840°C. Then, the specimen with the stainless steel sheath was inserted in the refractory cone and heated for a further 30 minutes to austenitise it completely. The cone, containing the tube and the specimen was quickly taken out of the furnace and the water cooled cap was placed securely on the projecting end of the specimen. The test piece took three hours to cool to room temperature. Oxidation of the specimen was negligible. Two diametrically opposite flats were ground to a depth of 0.01" and the Vickers hardness was measured along the length. A jig was made to hold the specimen during hardness measure-

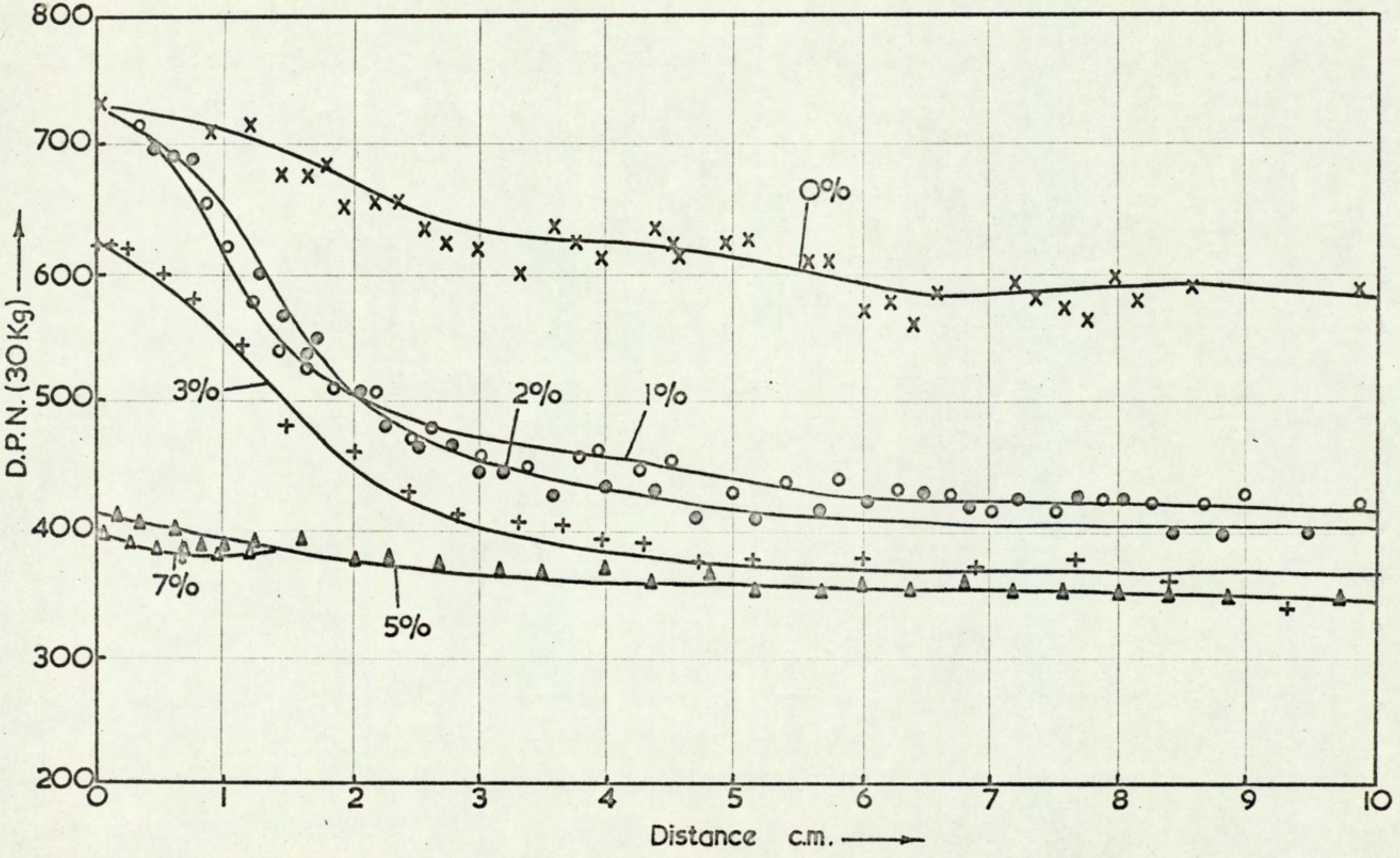


Fig.15. Hardenability curves of steels with varying Co. content

ment. The mean of the readings of each side, was taken. The results are plotted and shown in Fig. 15. The results give a comparison of the hardenabilities of different cobalt containing steels. Fig. 15 shows that the cobalt-free steel is almost entirely martensitic, where as there is a great fall in hardenability with one percent cobalt. The addition of 2% Co. steel is similar. Three percent cobalt steel did not reach the maximum possible hardness even at the quenched end, and takes an intermediate position between two percent and five percent cobalt-steel. The specimen with 5% Co. does not harden fully at the quenched end. The microstructure in the specimen with zero percent cobalt is mainly martensitic at the quenched end and a mixture of lower bainite and martensite at the opposite end. The specimens containing 1-3% cobalt show fine pearlite at the soft end, and mainly martensite with a few patches of lower bainite at the quenched end.

At intermediate position there is a mixture of martensite, upper and lower bainite. The five percent cobalt alloy shows only pearlite of increasing coarseness along the length of the specimen.

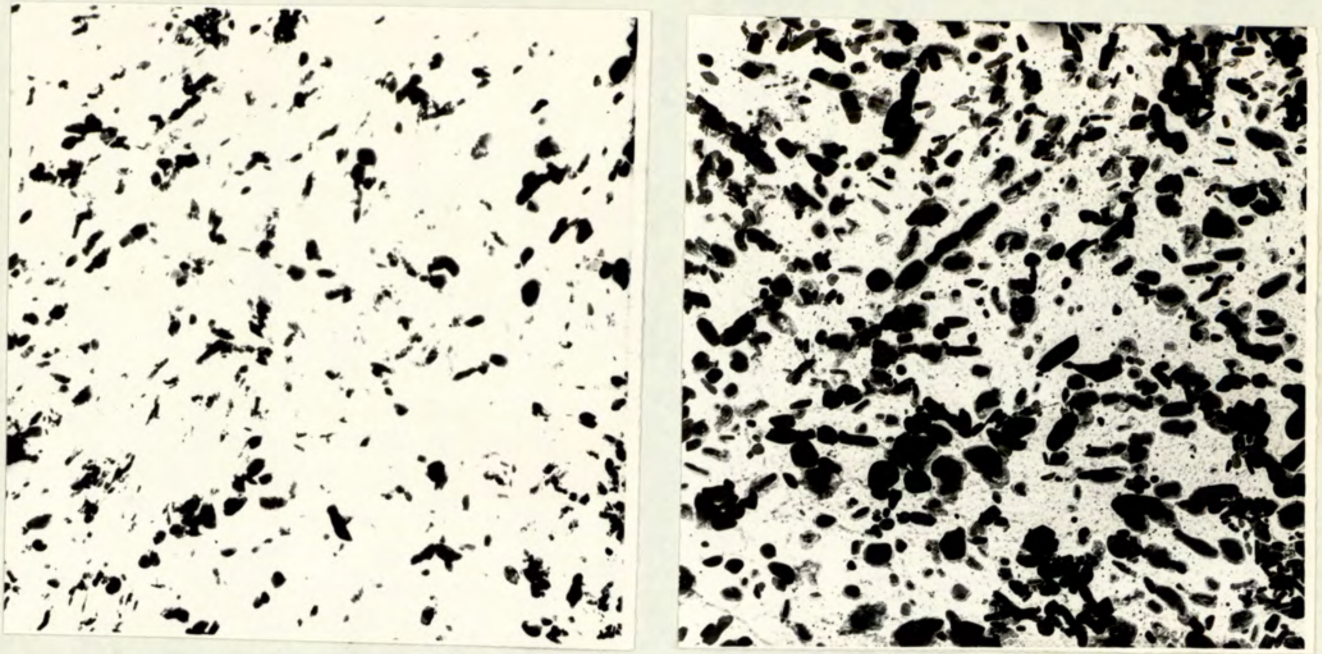
To investigate the influence of cobalt on the microstructure of No. 5 die steel in the air cooled condition, three specimens containing respectively 0, 3 and 7% cobalt were chosen. All the specimens were cut from the hot rolled bar and machined to ½" cube. They were all austenitised together in a salt bath at 840°C. for 30 minutes and cooled in the open air. The photomicrographs are shown in Fig. 28A in the Appendix. The micrographs show that the structure from approximately 90% martensite at 0% cobalt changes gradually to a fully bainitic and pearlitic structure at 7% cobalt.

3.10 Distribution of carbides

The carbides formed during tempering of a quenched specimen were too small to study under optical microscope. Consequently, the carbides were extracted and studied under the electron microscope.(15)

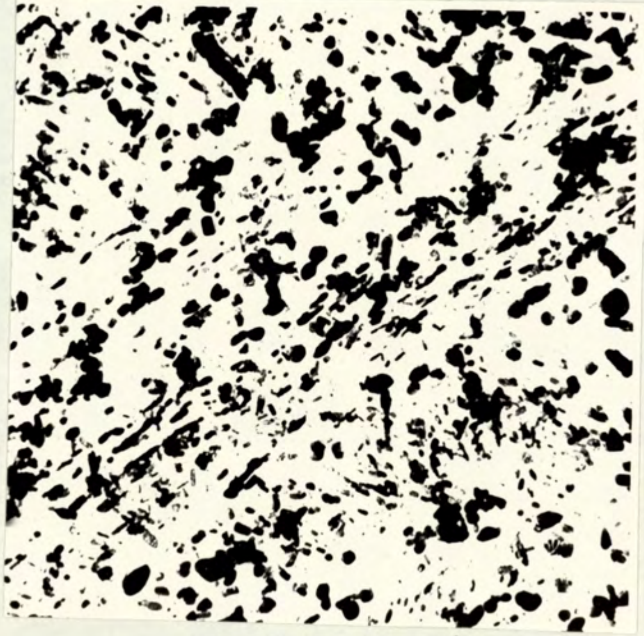
The ½" cube specimens (taken from the hardness test) containing 0%, 1% and 7% cobalt in one set and 0% and 3% cobalt in another set were austenised at 850°C. for half an hour in a chloride salt bath and oil quenched. The first set were tempered at 650°C. for 2 hours and the second set were tempered at 600°C. for 4 hours. The specimens were finally polished to ¼mu diamond paste and etched very lightly in 2% nital just to remove the polished surface layer.

Extraction replicas were produced by vacuum deposition of thin



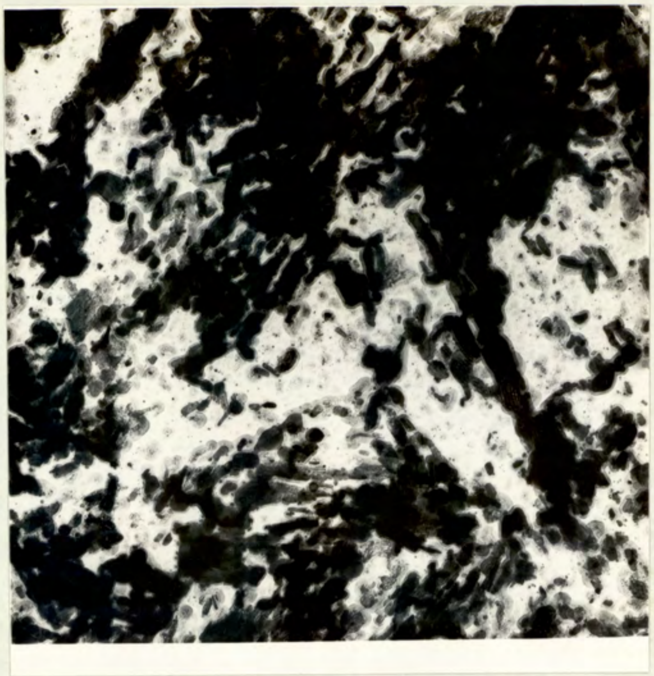
Steel No.0. 0%Co.

Steel No.I. 1%Co.

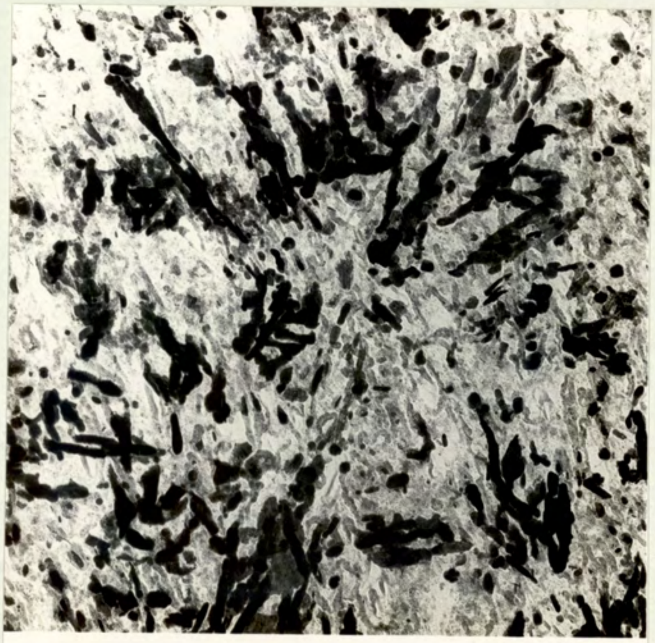


Steel No.7. 7%Co.

Fig.16. Extraction replica electron micrographs of quenched and tempered specimens. Tempered at 650°C for 2 hrs. X10,000.



Steel No.0. 0%Co.



Steel No.3. 3%Co.

FIG.17. Extraction replica electron micrographs of quenched and tempered specimens. Tempered at 600°C for 4 hrs. X 20000.

layer of carbon on the lightly etched specimen and extracting the layers in 2% nital solution. The extracted replicas were examined under the electron microscope. The electron micrographs are shown in Fig. 16 and Fig. 17 respectively.

The carbides in No. 5 die steels containing different amounts of cobalt show a distinct difference in shape and distribution. Carbides tend to form in more sites as the amount of cobalt is increased. The structure of the carbide becomes finer and the carbide particles are more numerous as the amount of cobalt is increased. Electron micrograph of the cobalt-free specimen shows an incomplete or partial extraction of carbides. However, it is evident from the electron micrographs of O, 1 and 7% cobalt specimens in Fig. 16 that the addition of cobalt increases the nucleation centres for carbide particles. Two types of particle shape are observed in all steels, angular and spheroidal, but electron diffraction patterns made on the extracted carbides show that they are basically the same and have identical crystal structures. They both show an Fe3C type structure and there are relatively more angular particles in the higher cobalt steels.

Fig. 17 shows the electron micrographs of 0 and 3% cobalt steels respectively at a magnification of X20,000. These steel specimens were tempered at a lower temperature and for a longer time, and reveal very clearly the tendency for the carbides to agglomerate during long time tempering. The carbides in 0% cobalt steel are tending to cluster together during the growth process, whereas in the steel with 3% cobalt the carbides are isolated and growing in a needle shape without thickening.

3.11 Chemical Extraction of Carbides

To study their structure and composition it was necessary to extract the carbides chemically. Carbides were extracted by an electrolytic process(16) from a quenched and tempered specimen. The specimen containing 3% cobalt (a representative composition), in the form of a 0.2" thick strip, had been quenched from 850°C., and tempered for four hours at 650°C. to coarser carbide. The specimen was ground and polished to remove the oxide film, washed in acetone to remove any grease. The cathode was a stainless steel plate separated from the specimen anode by a porous pot. The porous porcelain pot was placed at the centre of the open(16) electrolytic cell. The electrolyte solution was renewed intermittently by a fresh supply of new solution.

The electrolyte was 15% sodium-citrate and 1% potassium thiocyanate solution. A current density of 0.05 amp/sq.in. was used. The extracted carbide was filtered and washed thoroughly with distilled water to remove all the soluble salts, and analysed chemically and by X-ray diffraction.

3.12 Chemical Analysis of Carbide

The extracted carbide was analysed spectrographically in a qualitatine way and virtually no cobalt was found to dissolve in the carbide lattice, Fig. 18A. The major elements found were manganese and chromium, traces of molybdenum and considerable amount of Nickel were also found.

Quantitative chemical analysis was done by classical methods and the results are given in Table 8.

3.13 X-ray diffraction Analysis of extracted carbides

The instrument was a Siemens Wide angle Goniometer, and Crystalloflex 4 with a stabilised X-ray generator. The apparatus had a chromium target, a vanadium filter and Xenon-filled proportional counter. A 2.4mm tube slit, 0.1mm counter (receiving slit) and a pulse height discriminator (10volt channel) were used.

The washed and dried carbide was ground in a pestle and mortar and was pressed on to a rectangular aluminium

Table 8. The extracted carbide from a 3%Co steel was analysed spectrographically in a qualitative way and no cobalt was found to be dissolved in to the carbide lattice. The major elements found were manganese, chromium, molybdenum and nickel. The spectrogram is given in fig.I8.A, in the appendix.

Chemical analysis of the extracted carbide.

Carbon	6.9 %
Manganese	0.25 %
Nickel	0.6 %
Chromium	0.I %
Molybdenum	trace

The carbon content corresponds to Fe3C composition, the stoichiometric composition gives 6.67 %C. Cobalt absent and the remainder iron.

Table 9. X-ray analysis of the extracted carbide.

Relative intensity I/I_1	hkl	2θ (A S T M) Fe_3C	2θ for steel examined
65	II2,02I	57.54	57.35
60	I2I	66.I0	65.90
70	2I0	67.56	67.25
60	022	69.I0	68.70
I00	103	69.48	69.20
55	2II	7I.I0	70.80

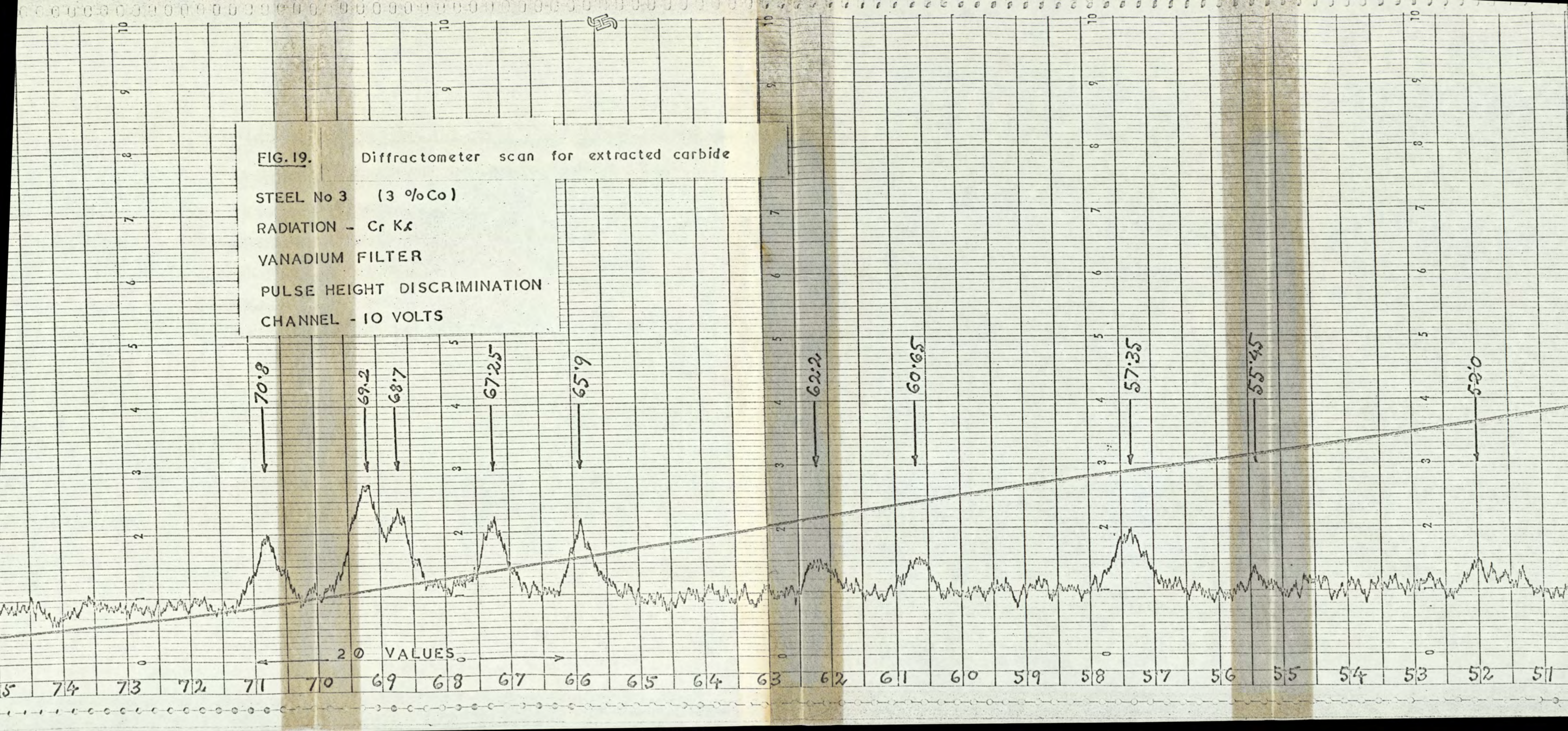


FIG. 19. Diffractometer scan for extracted carbide

STEEL No 3 (3 %Co)

RADIATION - Cr Kα

VANADIUM FILTER

PULSE HEIGHT DISCRIMINATION

CHANNEL - 10 VOLTS

block to make a compact and flat specimen suitable for the X-ray diffractometer. Chromium Kα radiation was used. A trace from the diffractometer chart recorder is shown partially in Fig. 19. These lines coincide with the Fe_3C cementite structure (17) with only a small line shift towards smaller 'alpha' values. Table 9 gives the value of relative intensity, corresponding lattice plane (h k l), and '2θ' values for pure Fe_3C, along with the actual 2θ values obtained experimentally.

From the 2θ values obtained experimentally, and from the relative intensities of the reflections as obtained by quantitative X-ray diffractometry, the carbides were identified as cementite (Fe_3C). Other possible carbide structures were not observed in the X-ray powder diffraction patterns.

A small line shift to lower values of θ was observed for each carbide line, as compared with the A.S.T.M. index classification for Fe_3C structure, indicating a slightly higher 'd' spacing for the planes of the carbide. This shift is probably caused by the presence of alloying elements in solution in the carbides.

No cobalt was found to be dissolved in the carbide lattice and it can be concluded that cobalt plays no part in changing the 'd' spacings of the cementite.

3.14 Partitioning of Cobalt during Transformation

In order to pursue the problem of the decreased hardenability of the cobalt-containing steels, an attempt was made to obtain evidence of partitioning of cobalt during transformation using electron probe microanalyser. The initial tests carried out on steels containing 5% cobalt revealed that the amount of pro-entectoid ferrite was so small that it was not possible to find a path long enough for a trace to be made.

To increase the amount of pro-entectoid ferrite, another cast of steel was produced having a lower carbon content. It contained 0.2% carbon, 5% cobalt and the nickel, chromium, molybdenum and manganese contents typical of No. 5 die steel. This material after hot forging and annealing, was austenitised at 900°C., transferred to a furnace maintained at 750°C. for 5 minutes and then water quenched. This heat treatment allowed partial transformation and the quenched structure consisted of ferrite and martensite. An electron probe microscan was made of this structure but no evidence was obtained of a significant amount of partitioning of cobalt.

A further attempt was made to detect partitioning during the tempering of martensite. Samples 0.1 inch in diameter by 0.2 inch in length containing 0, 2 and 5% cobalt respectively, were water quenched from a salt bath at 840°C. and tempered at 650°C. for 30 minutes. Electron probe analysis failed to show any discontinuity in cobalt distribution.

These observations along with the other evidence (23) show that cobalt does not partition at the interface during any stage of transformation.

3.15 Die wear test

An attempt to estimate the behaviour of the cobalt containing material was made by testing specimens in an experimental press used to assess the wear characteristics of hot forging die steels. The press itself is an electrically driven flywheel and crank type press, having a stroke of 3 inches. Pneumatic servo cylinders operate an automatic mechanism which feeds $\frac{3}{4}$" x $\frac{1}{2}$" dia. steel slugs in an upright position on to the flat die, insert mounted on the moving ram compresses the slug to approximately $\frac{1}{4}$" thickness. This reduction of the slug can be varied by adjusting the movement of the ram.

A high frequency induction heater heats the slugs before compression to a temperature which is determined by variation of the power output from the set.

The feed mechanism is controlled by a cam timer which repeats the sequence of feeding at regular intervals. The forging stroke is initiated electrically at the end of the feed cycle, and a pneumatic cylinder engaged the flywheel to the crank, and completes the forging stroke. Ejection of the forged slug is automatic.

Thus the press can be used for the automatic forging of slugs over a range of temperatures. In practice one slug is forged every 10 seconds, and once the equipment is running this is completely automatic. The provisions of the die inserts of different materials enables comparative tests to be made of the wear characteristics of die steels under identical conditions. Also forging conditions may be varied. Tests may be prolonged or short. In general the press is a useful tool in establishing basic criteria of a die wear and life under simulated forging conditions. A diagram of the press is shown in Fig. 20.
The testing conditions used to evaluate the wear characteristics of the cobalt-bearing No. 5 die steel wear as follows:
Slugs $\frac{3}{4}$" long x $\frac{1}{2}$" diameter of En 3A steel containing 0.25% carbon heated to approximately 1100°C. $\pm$ 50°C. were used as the forging stock. For each trial 750 slugs were forged to approximately $\frac{1}{4}$" thickness. The die material under test was

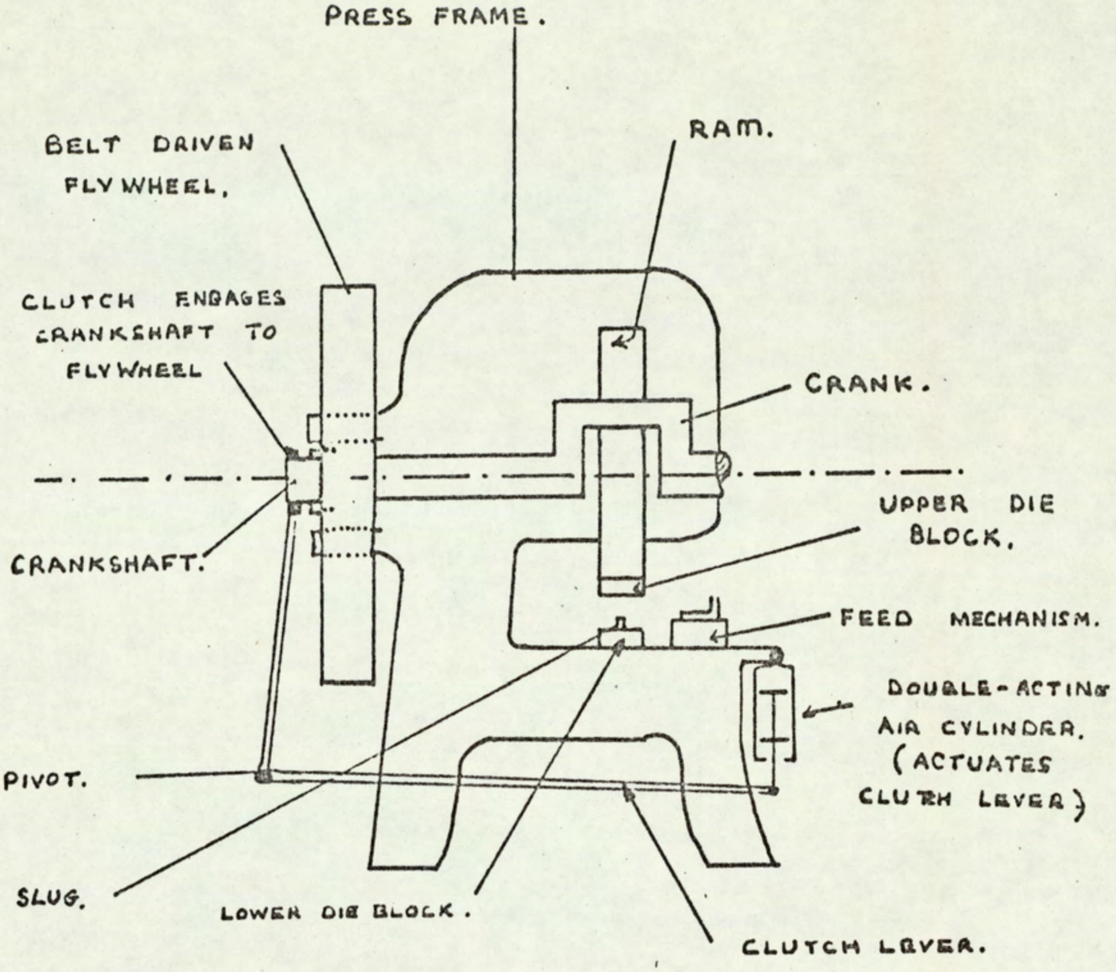


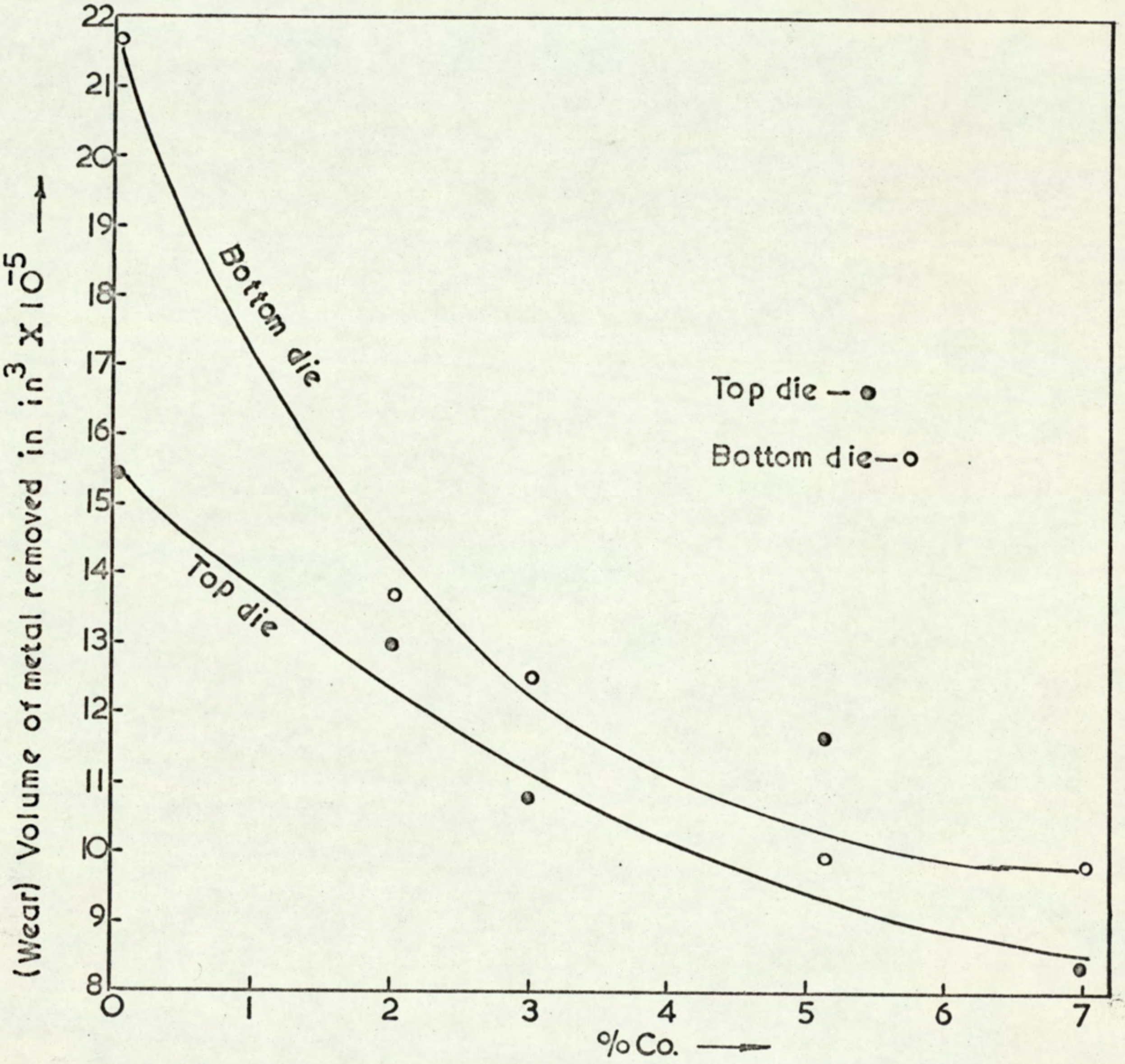
FIG.20 DRAWING OF PRESS

in the form of circular die inserts $2\frac{1}{4}$" diameter x 3/8 " in thickness. After hardening by quenching in oil from 850°C. (soaked for half an hour) and tempering at 600°C. for 45 minutes, the surfaces were ground. The hardnesses of the specimens varied from 400-450 H.V. The forging tests were carried out with the dies heated to 150°C. by means of heaters mounted in the die bolsters. The temperature was controlled by a thermocouple recessed into the centre of the die to 140°C - 185°C. When the forging had been completed, the cold dies were removed from the bolsters and descaled electrolytically in an inhibited 5% sulphuric solution at 74°C. The method for descaling was as follows :

> The back and edges of the die were electrically insulated by painting with a lacquer (Fortolac). The electrolytic solution of 5% sulphuric acid was heated in a beaker and a few drops of quinoline was added with stirring. When the solution was 74°C. the carbon rod, connected to the cathode of the electropolishing unit, was inserted into the solution. The die was connected to the anode and was immersed in to the solution with the help of a crocodile clip. The current was controlled to 4.2 amps for the whole die surface. Occasional burnishing was necessary

with a very soft plastic brush to remove any adhering scale. The whole operation took approximately one minute. When the surface was scale free and silvery, the die was quickly taken out of the solution and thoroughly washed with water and then with alcohol. The lacquer was removed from the back of the die by dissolving in acetone, and was ready for the measurement.(19)

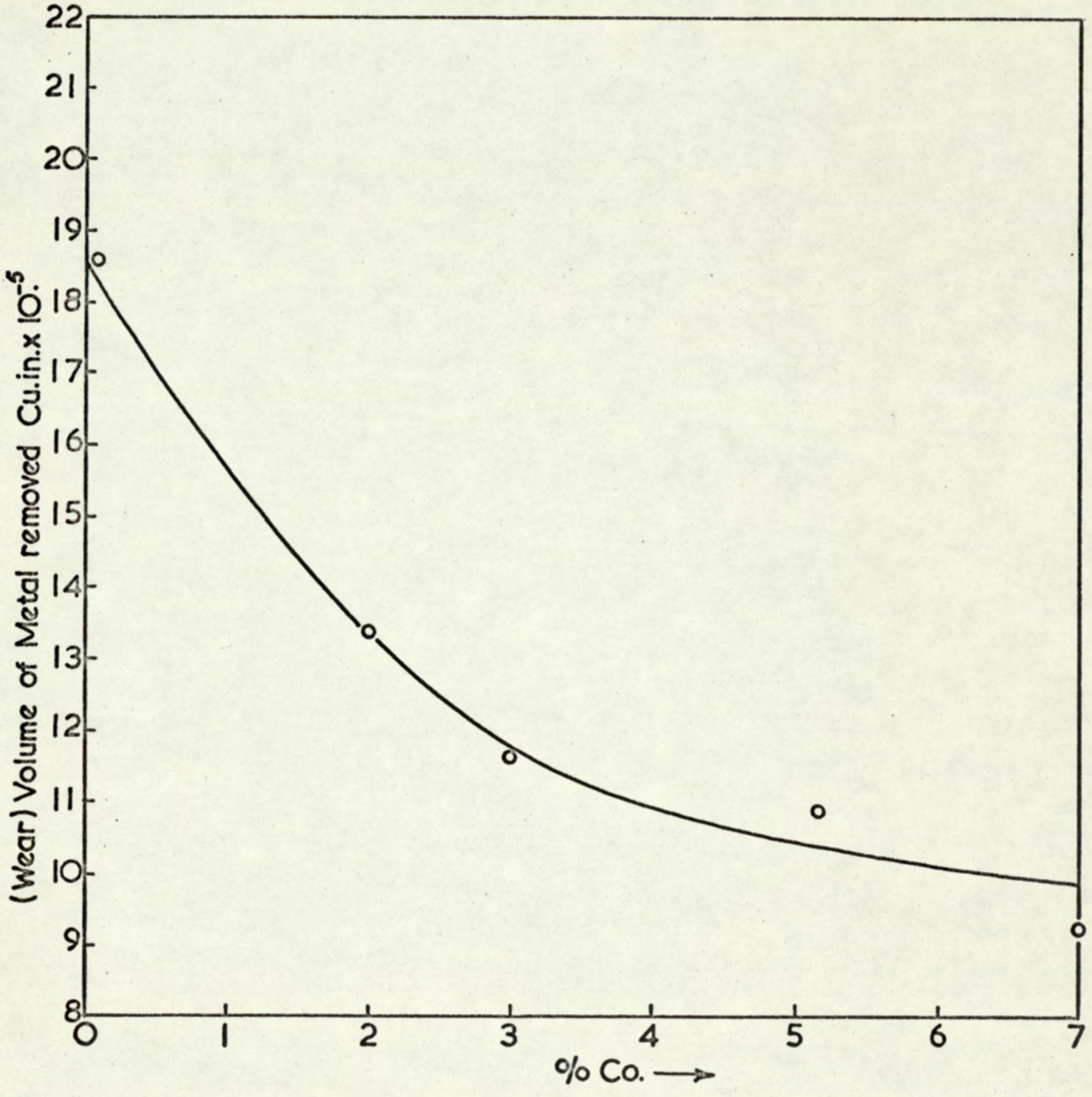
The amount of wear that the die surface had suffered was measured by measuring the surface profile using a Taylor Hobson Talylin 1 (112/816-7) instrument to traverse the die surface in conjunction with a rectilinear recorder at four different diameters. The dies were marked with pencil through the centre point of the wear pattern (Fig. 25), four lines at 45° to each other. The marking was in such a way so that each number corresponded to the similar position of the Top and Bottom die, just for comparison. (Fig. 27A) shows a typical trace of magnified profile on which the planimeter measurement was taken. The results are shown in Table 10. The 3% and 7% cobalt alloys tested, used 650 and 1100 slugs respectively. In the Table 10, the results have been recalculated to a norm of 750 by assuming a linear relationship. (This assumption has been justified by subsequent work in the University of Aston).



Relation between the wear of the die and Co content at a hardness of 400 V.P.N.

750 slugs reduced by forging, at approx. 1100°C., from 0'750" to 0'250".

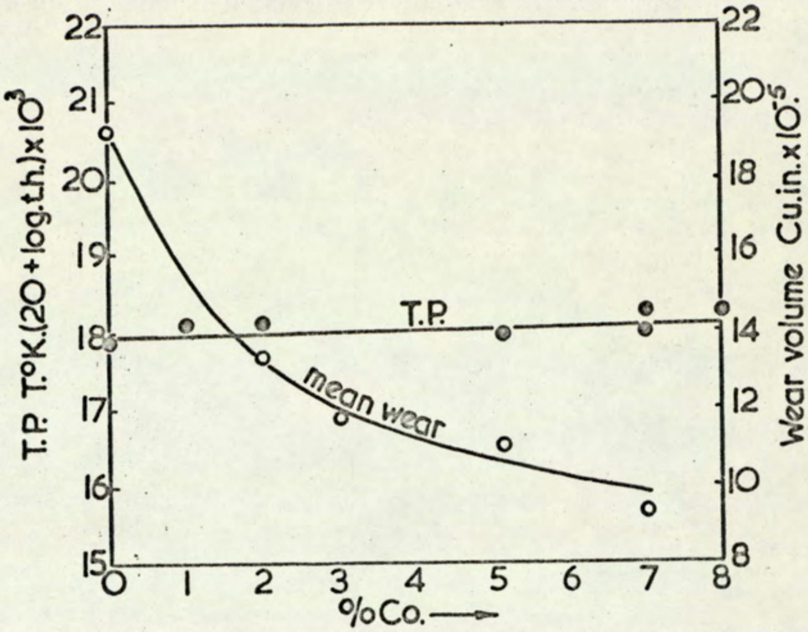
Fig. 21.



Relation between mean wear of the die and cobalt content at a hardness of 400 V.P.N.

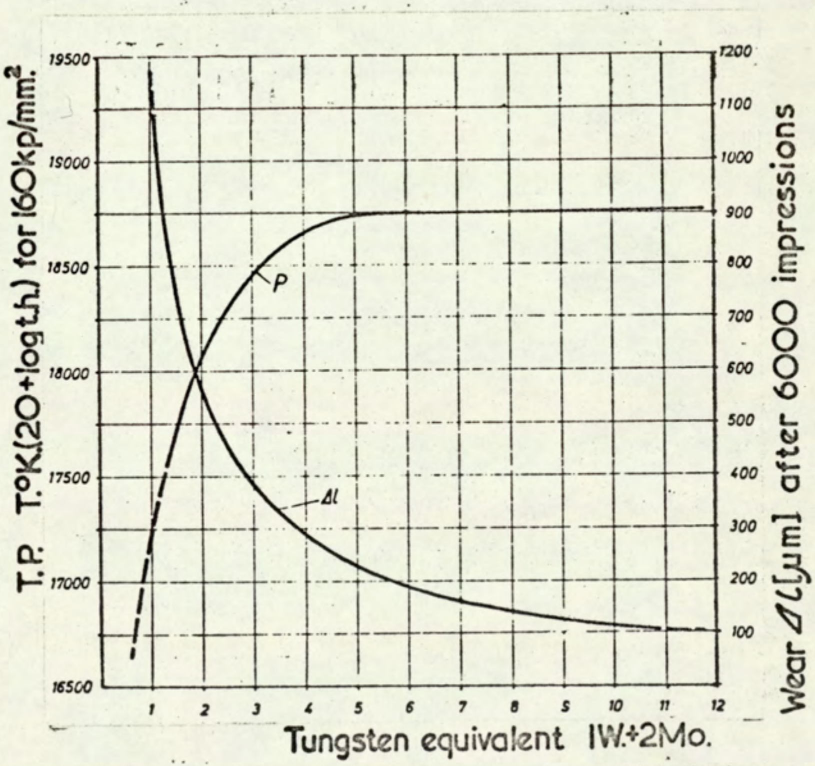
750 slugs were reduced by forging, at approx. 1100°C., from 0·750" to 0·250"

Fig. 22.



Variation of tempering parameter and mean wear with cobalt content at 400V.P.N.

Fig.23.



Showing dependency of T.P. and wear on IW.+2Mo. content with 0·4%C, 2·5%Cr, and 0·5%V.

Fig.24.

See Ref. 39. Fig(Bild)50.

Fig. 25. Photograph of a die showing the wear pattern at the centre. X 2.

Wear is expressed in arbitrary units which are obtained as the average area of the four Talylin traces. The value is therefore a comparative measure of the volume of metal removed from the dies. The complete table of the experimental results are given in the appendix in Table 11A.

The above 'die wear' experiment was repeated but the tempering treatment was altered to obtain samples of the same hardness. The dies were all oil quenched from 850°C., tempered for three quarters of an hour as previously, but subsequently tempered each at 300°C. until a hardness of 400H.V. ± 3 had been achieved. The dies were then re-ground and 750 slugs were forged under the identical condition as the previous test. This time the measurement was taken by connecting the Talylin tracer to the Solarton Analogue computer which was connected to the automatic punching machine. The punching machine punched out the data tape. Solarton Analogue computer scale was adjusted to give four punches per second and the Talylin scale was adjusted to "magnification 4" to give 0 - 999 in Solarton Analogue computer to represent 0.001 inch. This information, along with the appropriate programme in Algol language, was fed into the computer to obtain numerical value of the volume of metal removed from the die in cubic

TABLE 10

Die wear test results under identical heat treatment conditions. (Austenitised 30 minutes at 850°C, oil quenched and tempered at 600°C for 45 minutes.)

%Co	Die	Wear
0	Top. Bot.	293. 365.
2	Top. Bot.	276. 287.
2	Top. Bot.	252. 280.
3	Top. Bot.	210. 179
3	Top. Bot.	192. 234.
5	Top. Bot.	239. 266
5	Top. Bot.	220. 219.
7	Top. Bot.	106. 81.

TABLE 12

Die Wear Results by Computation

Specimens of identical hardness (400 V.P.N.)

Steel No.	Nominal % Co.	Mean Volume of Wear x 10^{-5} in^3 For Top Die	Mean Volume of Wear x 10^{-5} in^3 For Bottom Die	Mean Volume of Combined Wear 10^{-5} in^3 Top and Bottom Die
0	0	15.445	21.701	18.573
2 2	2 2	13.029	13.723	13.376
3 3	3 3	10.811	12.565	11.688
5 5	5 5	11.732	10.007	10.869
7	7	8.467	9.984	9.225

inches. Table 12, shows the mean value of the results, whereas Table (13a-13bA) in the appendix gives the complete set of values obtained from the computer.

"Diameter" indicates the diameter of the wear pattern computer has calculated, and the "Points" means the number of numerical data the computer has been supplied with for each trace.

Fig. 21, is a plot of the die wear against cobalt content for the top and bottom die. Fig. 22 is a plot of mean die wear, between top and bottom die against cobalt content.

Fig. 23 shows the relation between tempering parameter and die wear at 400 H.V. for the increasing amount of cobalt whereas Fig. 24(39) shows the relation between tempering parameter at 160 kp/mm^2 for the increasing amount of tungsten equivalent ie. (1W+2Mo).

The die wear results show that there is a clear improvement in the wear properties of the die as the amount of cobalt is increased. The improvement is significant as the amount of cobalt is increased up to 3-4%, but beyond this value the rate of improvement falls off. This is true for specimens that have received identical heat treatment and have same hardness.

The relation between tempering parameter and die wear properties are shown in Fig. 23.

The rise in the tempering parameter of No. 5 die steel is not as marked with the increasing amount of cobalt as it is in the 0.4C, 2.5Cr, 0.5V% steel, with the increase in tungsten equivalent (1W+2Mo). The tempering parameter becomes almost independent of tungsten equivalent at (1W+2Mo)=5, and at that composition the rate of improvement in wear properties falls sharply and any further additions of tungsten or molybdenum has very little effect. This correlation between tempering parameter and wear properties is not observed in cobalt containing No. 5 die steels. The rate of improvement in wear properties with the increasing amount of cobalt is very similar to that with the increasing amount of tungsten equivalent. The rate in both the cases falls exponentially and in a very similar way at 5% cobalt the improvement becomes insignificant.

4. DISCUSSION OF THE RESULTS

The existing literature and all the experimental observations so far made of the effect of cobalt on different types of steel fail to reveal that any general principles govern the effect of cobalt on low alloy steels. Unlike all other alloying elements generally added to steels, which usually influence a particular property of steel in a consistent way, e.g. hardenability, impact transition temperature etc., cobalt shows a marked discontinuity in its behaviour, and reports from different research workers differ so widely that, instead of proceeding towards a conclusion, it seems that more illusions are being created as more and more experimental data are accumulated. From the study of the equilibrium diagram of iron-carbon-cobalt system one can hardly infer that the effect of cobalt on alloy steels would be so inconsistent apart from being a simple diluent. Not only the actual mechanism of the effect of cobalt on steels remains unexplained but also no systematic generalisation of the effect has yet been possible. Moreover, various explanations offered from different sources have made the situation even more complicated. Under these circumstances it seems reasonable to discuss the effect of cobalt on the particular steel investigated and try to correlate the results, as far as possible, with the similar results obtained from different sources on different steels.

In No. 5 die steel, AC_1 and AC_3 are raised almost linearly with the increasing amount of cobalt and the difference between AC_1 and AC_3 is virtually independent of cobalt content. From the schematic vertical section of Fe-Co-C diagram (36) one would expect that cobalt would exert no fundamental effect on $Fe-Fe_3C$ equilibria. Over the entire range of cobalt content studied, through the ternary phase diagram parallel to the iron-carbon side, it shows (36) that at a very small concentration of carbon AC_3 is raised from 900^{o}C. to 910^{o}C. by 10%Co., and no appreciable rise in AC_3 was noticed at 2 to 3%Co. At eutectoid carbon content where AC_3 and AC_1 almost coincide, the effect of cobalt on transformation temperature is appreciable, rising from 715^{o}C. at 2%Co. to 770^{o}C. at 10%Co. This is in agreement with the present experiments where AC_3 rises from 764^{o}C. at 0%Co. to 805^{o}C. at 7%Co., and AC_1 rises from 721^{o}C. at 0%C to 778^{o}C. at 7%Co. It is advantageous in this respect that cobalt increases the limiting operating temperature of the No. 5 die steel by about 40°C. at 5%Co. Therefore during tempering of quenched specimens at a constant temperature the specimens with cobalt are being tempered at a temperature which is further away from the equilibrium transformation temperature. In other words, the cobalt containing No. 5 die steels are slightly high temperature materials in comparison with the steels without cobalt.

The Ms temperatures show a linear increase from 209°C. to 260°C. as the amount of cobalt is increased and take a steady value of 260°C. above about 3%Co. This is a rise of approximately 16°C. per %Co. There is evidence that Co. raises the Ms temperature(36, 27) but no quantitative information, as to what extent Co. influences the Ms temperature of low alloy steel, is given. Strangely, this fact coincides with the fact that the diffusion coefficient of carbon in iron achieves a maximum value at 3%Co. Martensitic transformation is a diffusionless process and cannot be related directly with increased diffusion coefficient of carbon. The theory offered for this 3%Co. peak diffusion coefficient does not account for the steady Ms temperature after 3%Co.

Chiswik and Greninger(57) determined the effect of cobalt on the Ms temperature (from 3.31 to 7.57%Co.) on a series of plain carbon steel containing 1.12%C. that there was a uniform rise of 19°C. per 1%Co. They extrapolated their results to 0%Co. and found a value which was 43°C. below that reported before for a 1.12%C. steel. To account for this discrepancy they considered three possibilities: a) the cobalt alloy they made contained 0.10%Mn; b) at lower cobalt contents the influence might not be uniform; c) small addition of cobalt might lower the Ms temperature. They did not find any break in the uniformity at any amount of cobalt up to 7.57%Co. alloy studied. The observed discontinuity and steady value of Ms temperature at 3%Co. may be ascribed to the comparatively low carbon content of No. 5 die steel. The other alloying elements may also have some effect, but it is not possible to generalise without further specific experimental evidence.

It is fairly certain that the amount of retained austenite in No. 5 die steel is well below the detectable amount (0.5%) and that the cobalt additions do not promote retention of austenite in quenched specimens. This observation agrees with the conclusion of Trusculescu(41) that cobalt additions decrease the retained austenite in 9%Ni. steel, increase the austenite decomposition rate especially in the bainitic field and a decrease in the decomposition rate of the residual austenite during tempering. So, in high nickel steels cobalt increases the decomposition rate of austenite during quenching cycle, and decreases the decomposition rate during tempering. The reason for stabilisation effect on any residual austenite is unknown. The increase in carbon activity with the addition of cobalt should have influenced the austenite in opposite direction, and furthermore the decrease in retained austenite during quenching from austenite to martensite, is independent of carbon diffusion.

Chandhok et. al.(6) tentatively tried to explain the effect of cobalt on this issue as the increased activity of carbon in austenite containing cobalt, the carbon diffuses more rapidly to any available sinks, e.g. carbide nuclei provided by auto-tempering of martensite as a result of increased nucleation rate due to cobalt, thus locally raise the Ms and Md (the temperature where martensite becomes thermodynamically possible) temperatures of the carbon depleted zones and increase the amount of martensite.

If the rise of Ms temperature is the only factor responsible for reducing the retained austenite then, without the above explanation cobalt would reduce the retained austenite. However, the reduction of retained austenite content by cobalt is independent of alloying elements like Si, Mn(71).

Isothermal transformation diagrams (fig. 8a-c) agree with previous observations that cobalt reduces the incubation period for pearlitic and bainitic transformations.(5, 36, 20) Fig. 28A shows qualitatively, the structural changes that takes place in air cooled conditions as the amount of cobalt is increased. Cobalt-free steel has almost entirely martensitic structures with a few autotempered martensite areas that gives a structure which is very similar to lower bainite. As the amount of cobalt is increased massive area of bainite appears, and at 7% Co. upper bainite and pearlite are the two structures present.

The classical 'bracketing' technique for the determination of T. T. T. curve was not very successful especially at a higher cobalt content, because of the autotempering of the martensite, makes it virtually impossible to discriminate it from the lower bainite. This is another reason why the dilotometric method had to be used for Ms determination.

Hawkes and Mehl(36) observed that there was no change in the shape of the 'knees' nor any additional 'bay' produced by addition of cobalt in the plain carbon steel. This agrees well with the present experimental results on No. 5 die steel where, both pearlitic and bainitic hardenability were reduced with the increasing amount of cobalt. It seems that the effect on pearlitic hardenability is very pronounced. Cobalt does not seem to depress or raise the temperature of the noses of the pearlite or bainite curves, nor does it seem to affect the total reaction time. The only effect of cobalt on the T.T.T. curve is to shift the whole system towards the left of the diagram. The only change in the diagram caused by the cobalt is to alter the AC_1, AC_3 and M_s lines.

The hardenability experiments confirmed that the rate of austenite decomposition in the pearlitic and bainitic range is greatly increased with the additions of cobalt. Although there is no doubt that cobalt lowers the hardenability, the effect seems to be rather discontinuous. The addition of five percent cobalt causes an abrupt fall in hardenability. Steels containing more than 5%Co. do not harden at all under the test conditions and maintain a pearlitic structure of varying fineness along the length of the test piece.

Increase in carbon activity and consequent increase in the austenite decomposition rate as proposed by Chandhok et al(6) is one of the explanations of decrease in hardenability with the addition of cobalt. The other explanation(24, 25) is the increase in nucleation rate by increasing the dislocation density in the matrix which subsequently provides more nucleation sites for the precipitates. The suggested influence of the strengthening of austenite by the alloying elements on hardenability is quite convincing. As the temperature of transformation is reduced both the volume change associated with transformation as well as the flow strength of the austenite increase to resist the transformation. Stronger alloys transform less rapidly it is true, but cobalt addition in no way softens the matrix to reduce the hardenability, although the solid solution hardening effect of cobalt is not significant.

"No partition temperature" concept was introduced by Aaronson(22), which is a modified A_3 temperature below which alloying element partition does not occur. Co., Al. and Si. raise the no partition temperature above AC_3 and lower the hardenability, whereas, most elements lower the no partition A_3 and increase the hardenability. This concept does not satisfy the effect of carbide forming elements, eg. Mo. No present theory accounts fully for the observed effect of cobalt.

Effect of cobalt on tempering characteristics have been investigated by various authors and all the conclusions are unanimously in agreement that cobalt increases the resistance to tempering. The present tempering test results also confirm this. As shown in Fig.10 the tempering experiment on No. 5 die steel shows two additional effects of cobalt, firstly the steel is divided into two specific groups, above and below 5%Co. The resistance to tempering is very significant above 5%Co., secondly, the resistance to tempering at a low parameter value (Fig.11). No secondary hardening is exhibited by the system.

The solid solution hardening effect of cobalt is very small, and it is very unlikely that cobalt forms any carbides or precipitates to exert the observed influence.

Chandhok et al(6) proposed that the nucleation rate of the alloy carbides are increased and their rate of growth and agglomeration are decreased. The extracted carbides in quenched and tempered No. 5 die steel containing 3%Co. show no evidence of any alloy carbides (Fig. 19 Table 9) except cementite with other alloying elements dissolved into the Fe_3C type lattice (Table 8), causing a small amount of lattice expansion. The electron micrographs of the carbide extraction replica of quenched and tempered steels confirm that the addition of cobalt increases the number of carbide particles and reduces their growth considerably (Fig. 16). The rate of agglomeration is definitely decreased (Fig. 17). Lower temperatures and longer times of tempering (Fig. 17) show that the carbides which initially grew in one direction in the form of needles have agglomerated more in cobalt free steel than that in 3%Co. steel. The number of nucleation sites are also less in cobalt free steel. This effect certainly seems to have an influence on the decrease of the rate of softening during tempering of No. 5 die steels containing cobalt. The mechanism invoked(6) to rationalise the effect of cobalt, which decreases the agglomeration of carbide, is supported by subsequent investigators. The cobalt did not partition in any temperature(23), studied during the early stage of transformation. The present investigations on No. 5 die steel support the view that the cobalt does not partition, and the interface control mechanism to reduce the agglomeration of carbide remains still debatable. Qualitative spectrographic analysis (Fig. 18A) gives no evidence of cobalt being dissolved into the cementite lattice and influencing the carbide behaviour in any way. The experimental evidence that Co. increases the dislocation density by reducing the stacking-fault energy of the matrix of maraging steel(25), may also occur in No. 5 die steel. This theory is only able to explain the increase in carbide precipitation by providing the nucleation sites by the dislocations, but neither can it explain the reduced rate of agglomeration nor the fact that in the region of 4-5% Co. in No. 5 die steel a sudden change in the tempering resistance occurs.

The carbide formers like Mo., W., V., and Ti increase resistance to tempering by their secondary hardening reactions. Increasing amounts of Cr., Mn and Ni are found to reduce the tempering resistance of steel.(72) The way the cobalt affects tempering resistance seems to be very intimately connected to the other effects of cobalt, e.g. rise of Ms temperature, lowering of hardenability etc. Considering all the effects of cobalt on No. 5 die steel only, it is difficult to generalise because the interaction of cobalt with other alloying elements may play a significant part.

Chandhok et al(30) established from the concentration penetration curve of diffusion couples that the activity of carbon is increased by the addition of cobalt. These calculations were based on the activity concentration data of Smith(38) for plain carbon steel. Dividing the activity by the atom fraction of carbon at the interface for each side of the couple, the activity coefficient of carbon for both the high and low cobalt side was calculated. The results show that at 1038°C. 0.23% carbon steel and 0.27% carbon plus 10%Co. steel give a ratio:

$$\frac{\gamma \text{c on high-co. side}}{\gamma \text{c on low-co side}} = 1.15$$

Smoluchowski(54) had performed similar experiments on welded specimens with 4%Co. and another with no cobalt, both with 0.80% carbon. He found no change in the carbon distribution at the weld.

However, the activity coefficient of carbon is increased as the concentration of carbon in solution becomes less and reaches unity at a very dilute solution. The most probable effect of cobalt seems to be its diluent action on the most potent alloying element carbon. Although no quantitative experiment has been done, the effect seems to be equivalent to 10 times as much as iron. In other words, the "effective" amount of carbon is reduced with the cobalt additions. This diluting effect on carbon may increase the activity coefficient of carbon and the steel behaves exactly in the same way as if the carbon is being lowered with the increasing amount of cobalt. When the carbon content of the steel is of the order of 0.005% the activity coefficient reaches almost unity andthe diluent action of cobalt becomes almost negligible. Under this circumstance cobalt behaves like other alloying elements, and gives a slight increase in the hardenability. The reason for this effect is not clear but it explains all the observations, eg. the rise in Ms temperature, decrease in hardenability, increase in AC_3 and AC_1 transformation temperatures, and no fundamental change in the shape of the T.T.T. diagram. The retained austenite is also reduced. When quenched from austenite to martensite all the carbon atoms trapped in the distorted lattice produce lattice distortion proportional to the carbon atoms present, but during tempering, the behaviour is almost like lower carbon steel of similar composition. The carbide growth is slow at low tempering parameter and agglomeration is less, but at high tempering parameters the carbides which previously formed on situ without much diffusion tend to agglomerate and equilibrium structure results. The increase in dislocation density with the addition of cobalt may also be responsible for this dilution of carbon, by providing low energy sites for the interstitial atoms to be fixed. The formation of carbide during tempering is encouraged by the cobalt because it fixes the carbon and helps the dilution effect, but the subsequent behaviour afterwards is retarded by the cobalt.

The effect of carbide formers to fix the carbon as carbide may have an important effect on the properties of cobalt. This may reduce the carbon available to cobalt to such an extent that the usual behaviour of cobalt may be completely suppressed and only solid solution hardening effect will predominate. This is what happens in high chromium (14%Cr.) cobalt steels. The effect of 2-3%Mo. is not very significant in this respect. The anomolous effect of No. 5 die steel may be due to the saturation of cobalt at 4-5% ranges, above this concentration the effect of cobalt on the remaining carbon drops significantly. The interaction of cobalt with other alloying elements are not clearly known.

Impact test results show a slight decrease in impact strength but no effect on the transition temperature observed with the addition of cobalt. This is in agreement with results on plain carbon steel.(20) There is some evidence(5) that cobalt increases the impact strength of the steel, but the experimental results are not sufficient to make a definite statement.

The die wear test results, as given in Fig. 22 and Table 12, show that a remarkable improvement in wear properties occurs by increasing the amount of cobalt. The amount of wear has been assessed by the volume of metal removed after the forging test and descaling the surface. The mean die wear results give an improvement of 35% at about 4%Co., and then the rate of improvement falls off exponentially with further cobalt additions. The wear on the bottom die is more than that on the top die (Fig. 21), which is expected because the hot slug is in contact with the bottom die for a longer period. Fig. 23 shows a relation between mean die wear and tempering parameter at HV400 in No. 5 die steel with increasing amount of cobalt. This effect has been observed on other steel, e.g. a 0.4C., 2.5Cr. 0.5V% steel. Fig. 24 shows the same relationship with increasing amount of tungsten equivalent (1W+2Mo) in a 0.4C., 2.5Cr., 0.5V% steel. The comparison between the two diagrams indicates that the effect of cobalt on the die wear is not fully accounted for by the increase in tempering resistance and consequently, some other possible mechanisms need to be considered. It has been shown (19) that if the bulk temperature of the No. 5 die steel is approximately 130°C. there is a partial transformation on the die surface due to the momentary rise of the surface temperature above AC_1 temperature and the rate of wear increases to its maximum. The rate falls steadily as the bulk temperature is lowered from that value. The bulk temperature for the present investigation is approximately 150°C. and 3% cobalt rises the AC_1 temperature by about 30 °C. This effect may keep the die surface temperature below the AC_1 and reduce the rate of wear quite significantly after 3-4%Co. by preventing austenite formation during the cycle. Thermal conductivity of the die material should play an important role in this connection. Cobalt is known to increase the thermal conductivity of steel(56, 27) and will reduce the surface temperature build-up. The oxidation resistance is also improved by cobalt. All these effects contribute to the complex wear resistance property. The die wear test under identical heat treatment conditions (ie. under different hardness conditions, the difference in hardness between 0% and 7% Co. steel is about HV50), shows a similar type of improvement, (table 10). It would therefore, appear that hardness in cobalt containing No. 5 die steel is not the most important factor which determines wear resistance in this situation. Although it is not possible at this moment to single out the dominant cause of the improvement in the die wear properties, the improvement is really promising and it is worth considering whether the use of such an alloy might yield economic advanttages. The reduction in die costs per forging is again a very difficult matter to determine. A simple example, quoted from an unpublished private communication(18), will show how the material cost compares with the cost per forging.

	No. 5 die steel	2.5Ni. 3Mo% steel
Cost of inserts	10.0 units	21.0
Cost of sinking	36.6	36.6
Total die cost	46.6	57.6
Mean die life	12,000	19,000
Mean die cost per forging x 1000	$\frac{46.6\text{x}1000}{12,000}$ = 3.88	$\frac{57.6\text{x}1000}{19,000}$ = 3.03
Ratio of labour to material cost	$\frac{36.6}{10}$ = 3.66	

Die sinking cost depends on the machinability of the material and it can be assumed that cobalt addition will not increase the sinking cost of No. 5 die steel. The cost of No. 5 die steel is increased by approximately 71% with the 4% addition of cobalt. The 35% decrease in wear would be expected to give a 50% increase in mean die life.

Cautiously assuming a 35% increase in mean die-life, mean die cost per forging can be calculated and compared with the given data:

	No. 5 die steel	No. 5 die steel + 4%Co.
Cost of inserts	10.0 units	17.1 units
Cost of sinking	36.6	36.6
Total die cost	46.6	53.7
Mean die life	12,000	16,200
Mean die cost per forging x 1000	3.88	3.31

This costing gives a reasonable improvement. Unfortunately at 4% Co. level the hardenability is reduced to such an extent that it would be virtually impossible to heat treat large die blocks for industrial application. Die inserts which can be hardened after machining and do not need re-sinking can be profitably used. At present the tendency is to use higher alloy steel for the increased labour cost and consequently No. 5 die steel is losing its market. If this single problem of hardenability could be solved by cheap alloying additions like chromium, it seems probable that this steel would retain its present position for another few years. A thorough understanding of the problem of interactions of alloying elements in steel is sadly lacking and the experimental data on this problem is also insufficient.

5. CONCLUSIONS

The effect of cobalt on No. 5 die steel may be summarised as follows :

a) Cobalt raises transformation temperatures. Both the AC_1 and AC_3 are raised equally in proportion to the Co. content as far as 10% Co.

b) Ms temperature rises with the increase up to 3%Co. and then becomes steady up to5%Co. Mf temperature follows approximately the same pattern as Ms.

c) T. T. T. diagrams indicate that the pearlitic and bainitic transformation times are both affected and cobalt greatly reduces the incubation periods. The pearlitic transformation time seems to be affected more severely than the bainitic transformation time.

d) Hardenability tests reveal a gradual lowering of hardenability as the amount of cobalt increases and at about 3%Co. a drastic fall in hardenability occurs.

e) There is always a rise in hardness at a particular tempering parameter value with the increase in cobalt content. This increase is more pronounced at low parameter values. The resistance to tempering is raised significantly when the cobalt content of the steel is about 4 to 5%. This difference in hardness brought about by the addition of cobalt at a single value of parameter falls, and vanishes at a parameter value of 19×10^3.

f) Impact tests show a small decrease in impact value as the amount of cobalt is increased but the transition temperature (-5 to -15°C) is unaffected.

g) No retained austenite is detected in either oil or water quenched conditions at any amount of cobalt content up to 10%Co.

h) No evidence of partitioning of cobalt is obtained at either ferrite-austenite or martensite-carbide interfaces in a 5%Co. steel.

i) No secondary hardening effect is observed with the addition of cobalt.

j) Analysis of the extracted carbide/reveal the presence of only one type of carbide, i.e. cementite with some alloying elements dissolved in the cementite lattice. No cobalt is found to be dissolved in the lattice.

k) Electron micrography of the extraction replica of the tempered specimens show that the carbides are finer and more numerous as the amount of cobalt is increased and less agglomeration of carbide particles with the addition of cobalt.

1) Die wear test results show an improvement in the wear properties of the die as the amount of cobalt is increased. The improvement is quite significant as the amount of cobalt is increased up to 4%. At the present moment it is not possible from metallographic or mechanical property data to explain the great improvement that takes place up to this critical value of 3-4%Co.

The results of the other tests show that the influence of cobalt on No. 5 die steel has a marked discontinuity at 3 to 4% level. The repeated coincidence of 3-4% cobalt as a value of significance suggests that this optimum value of cobalt must be considered.

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APPENDIX

STEEL No.O. HEATING CURVE Cold junction 18°C

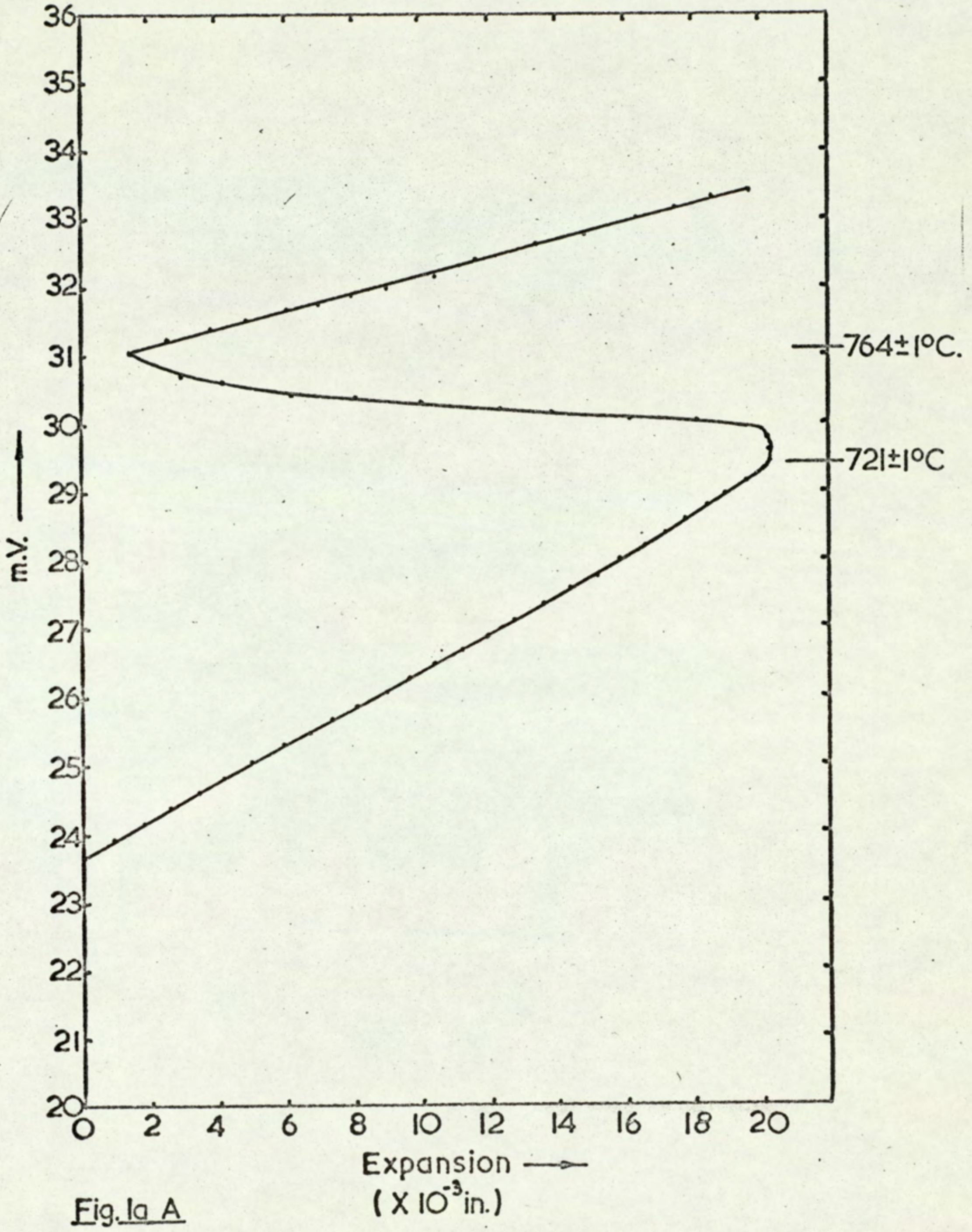


Fig. Ia A

STEEL No. 1. HEATING CURVE Cold junction 18°C

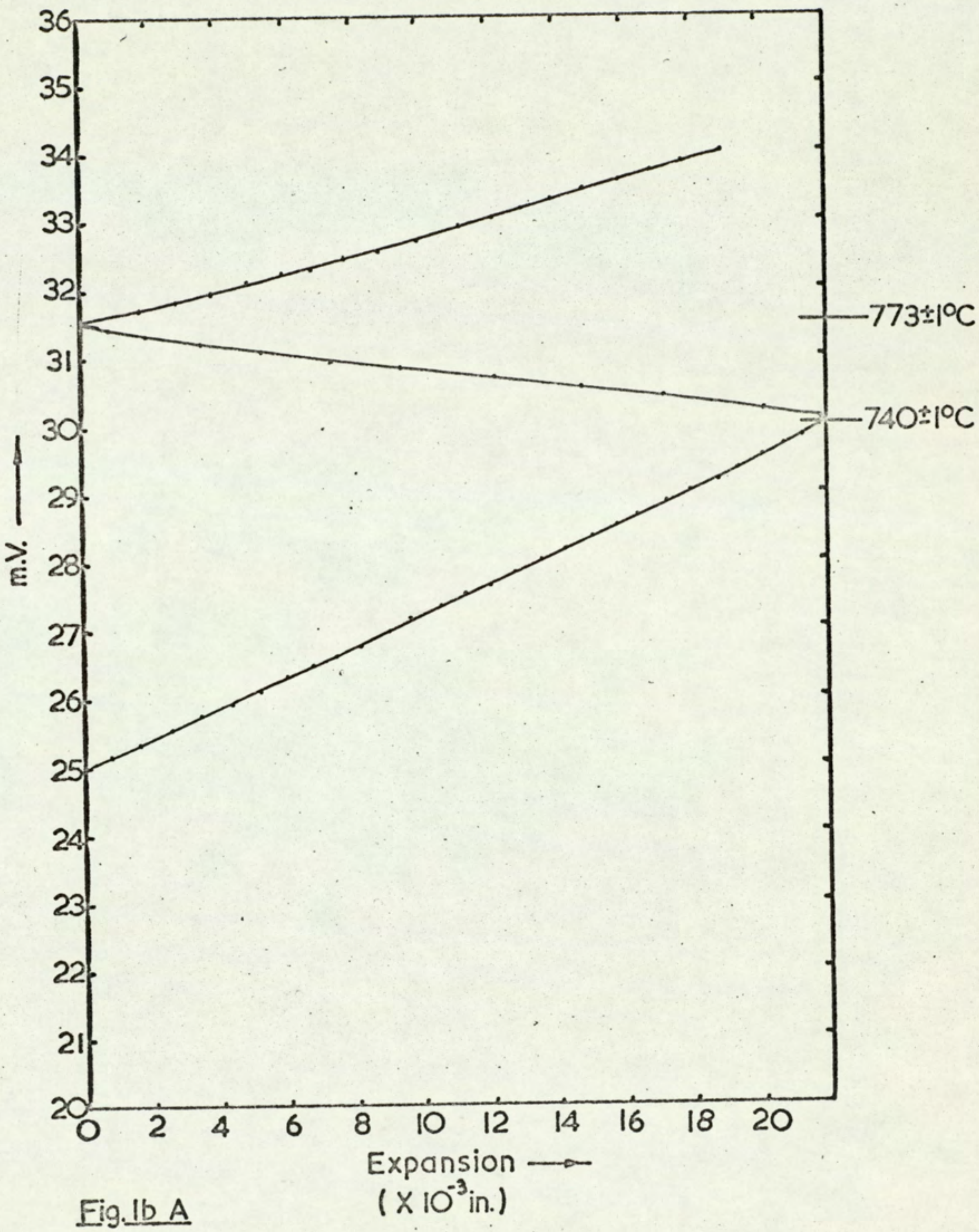


Fig. 1b A

STEEL No. 2. HEATING CURVE Cold junction 18°C

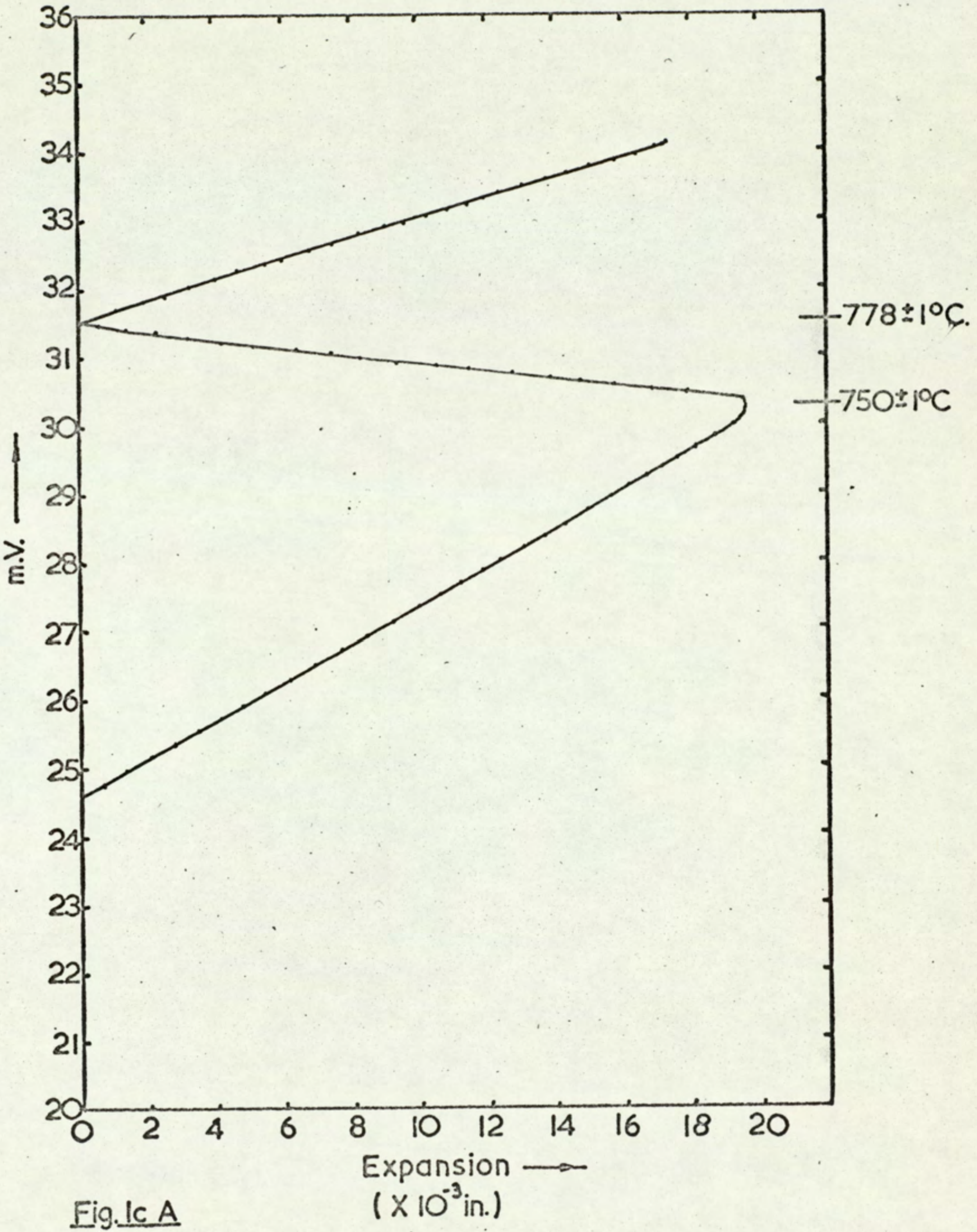


Fig. Ic A

STEEL No. 3. HEATING CURVE Cold junction 18°C

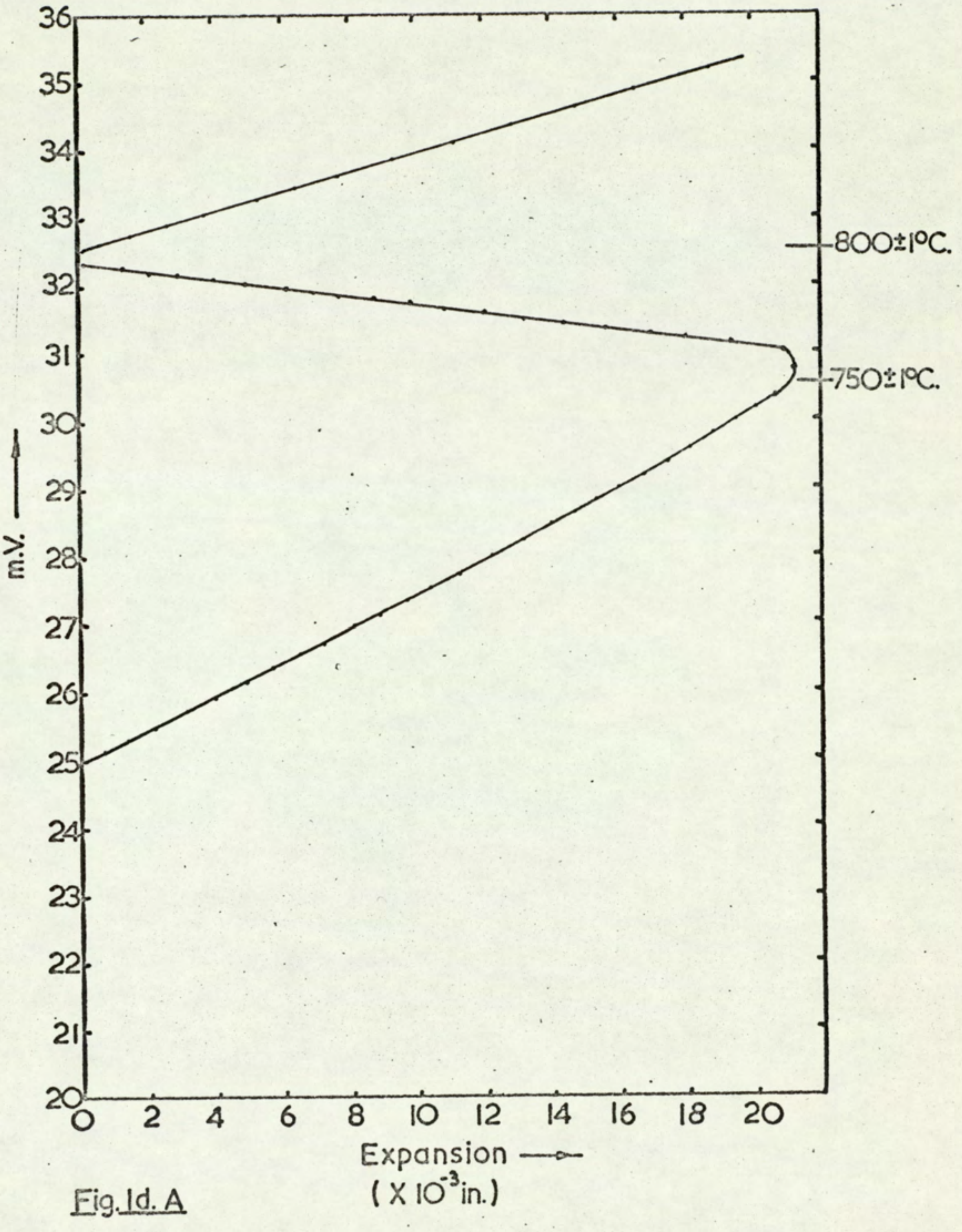


Fig. Id. A

STEEL No. 5. HEATING CURVE Cold junction 18°C

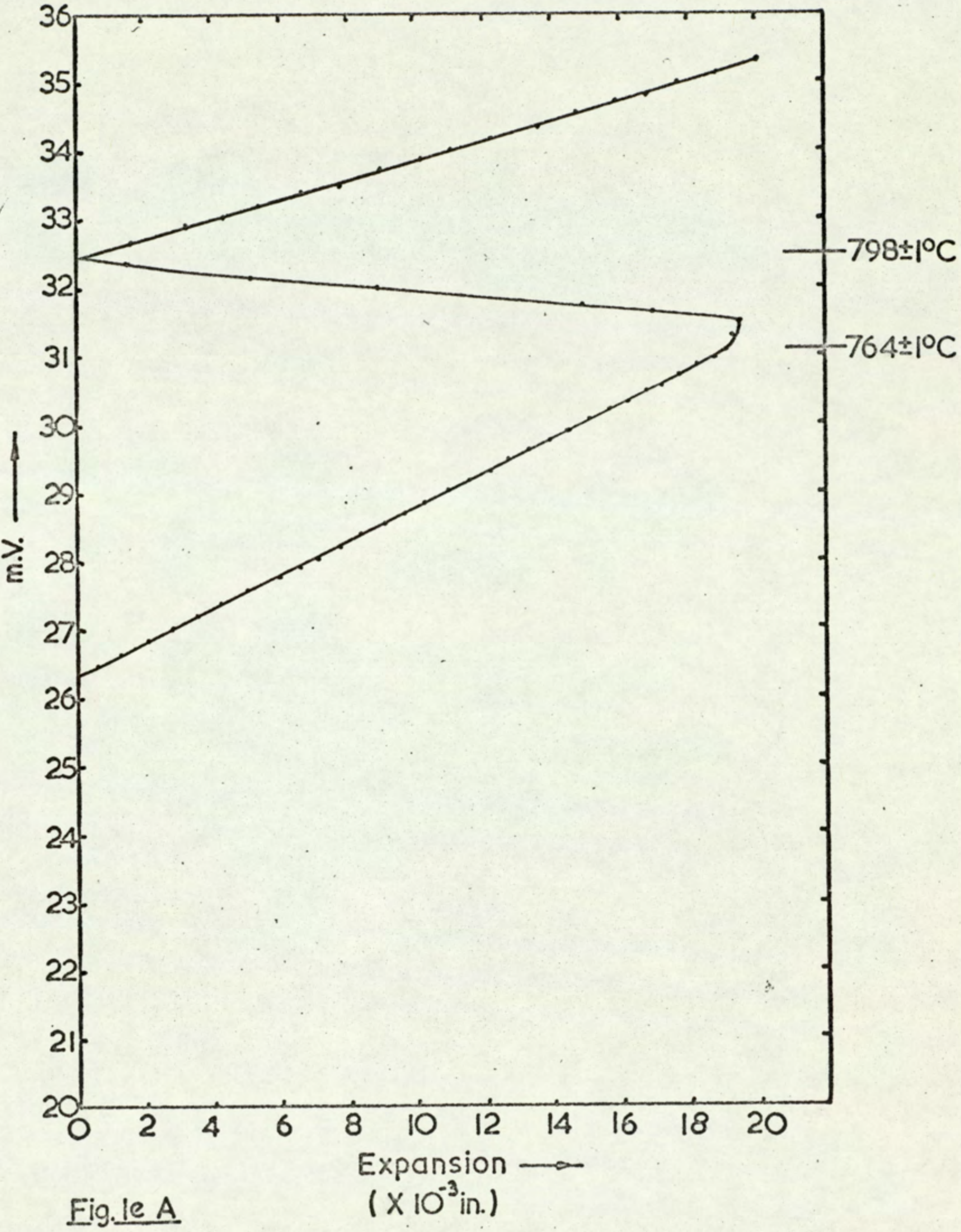


Fig. 1e A

STEEL No.7. HEATING CURVE Cold junction 18°C

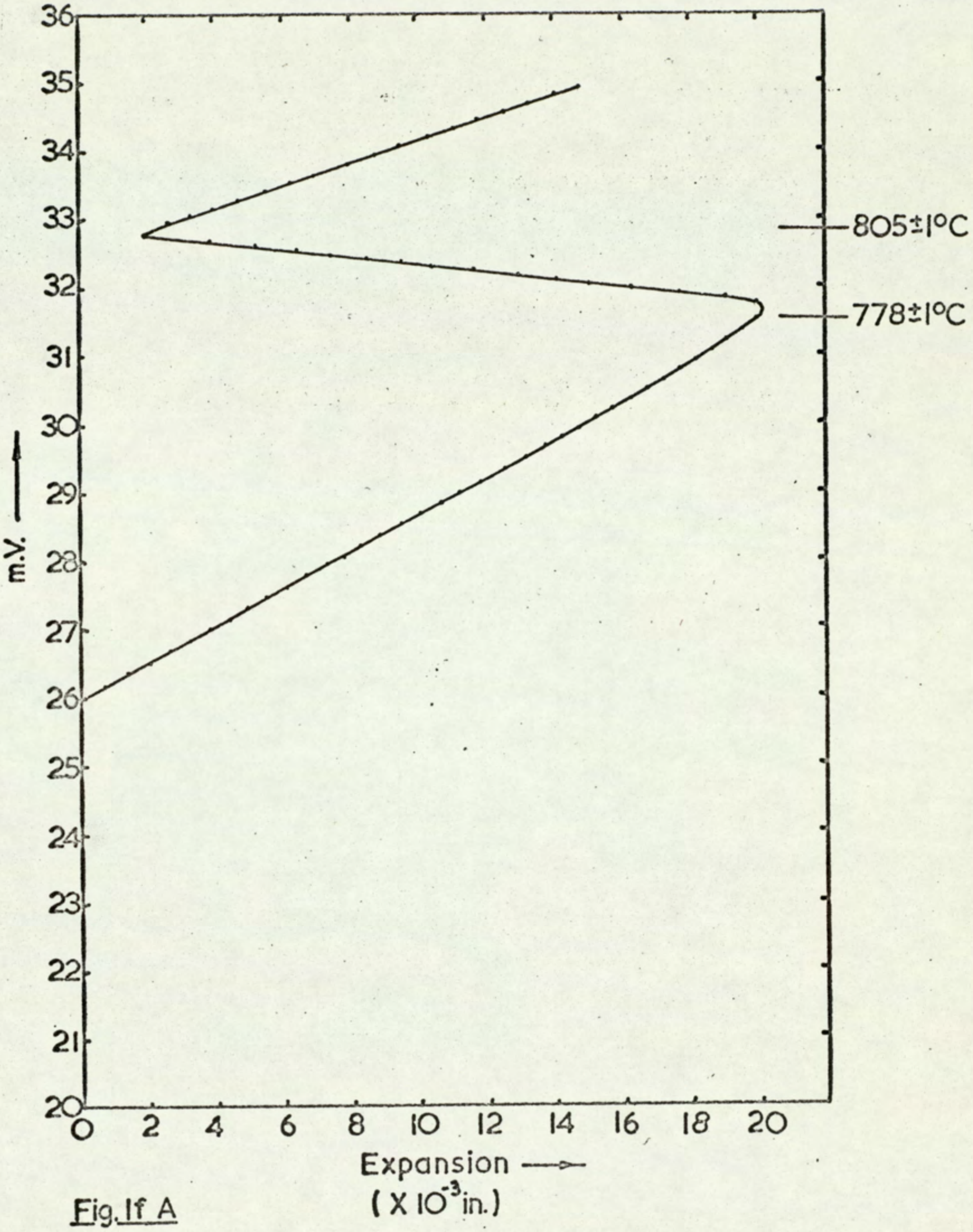


Fig. 1f A

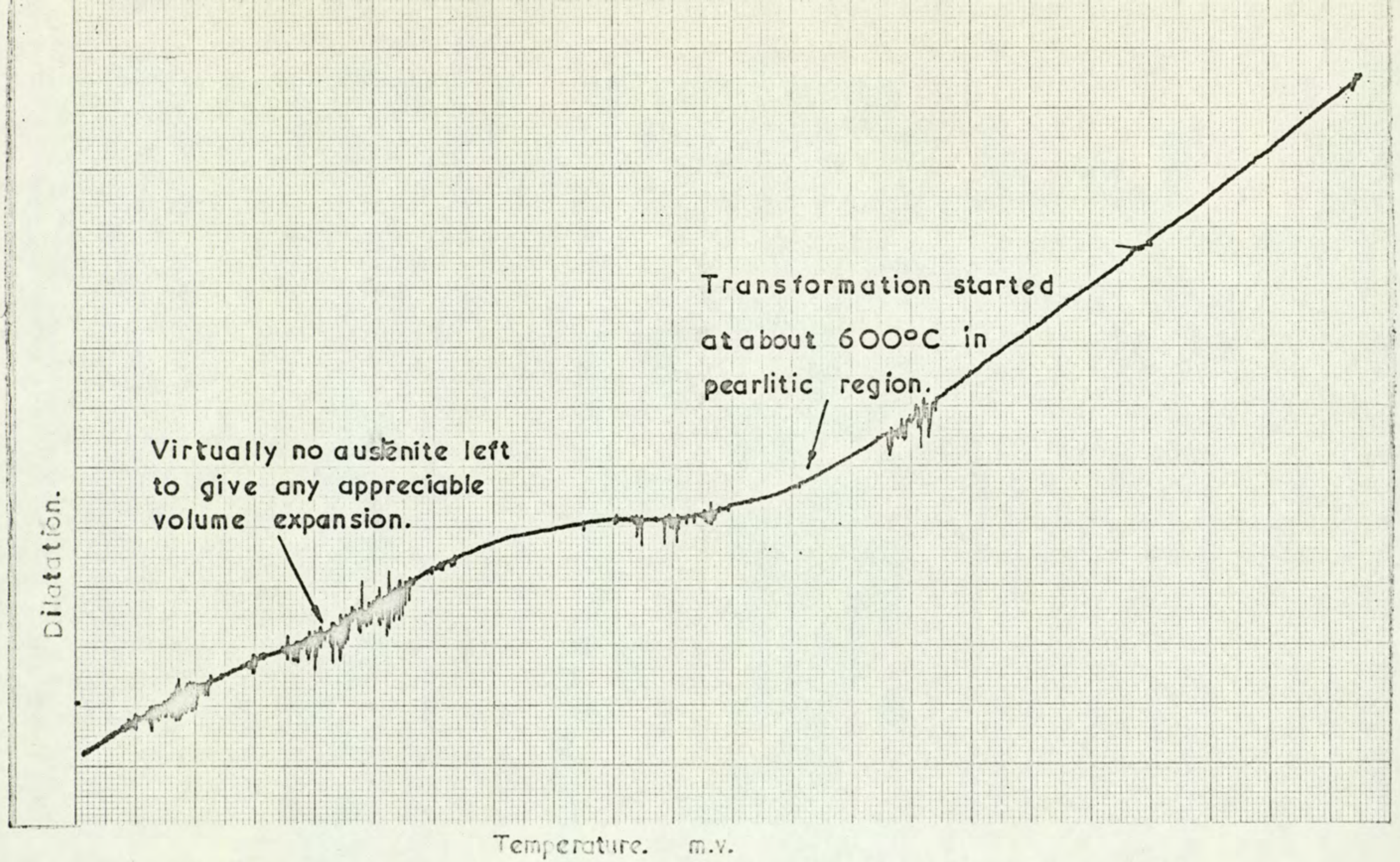
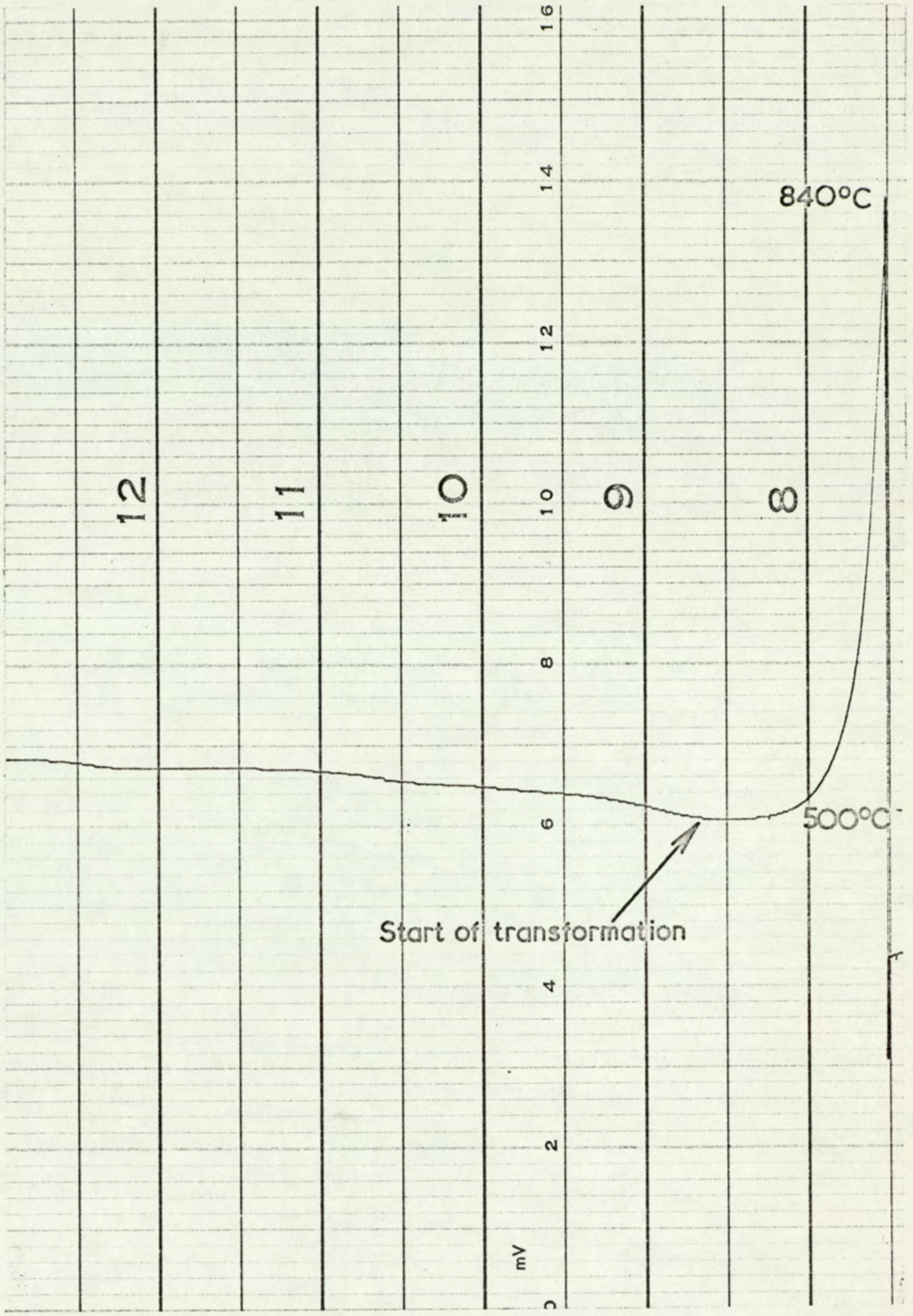
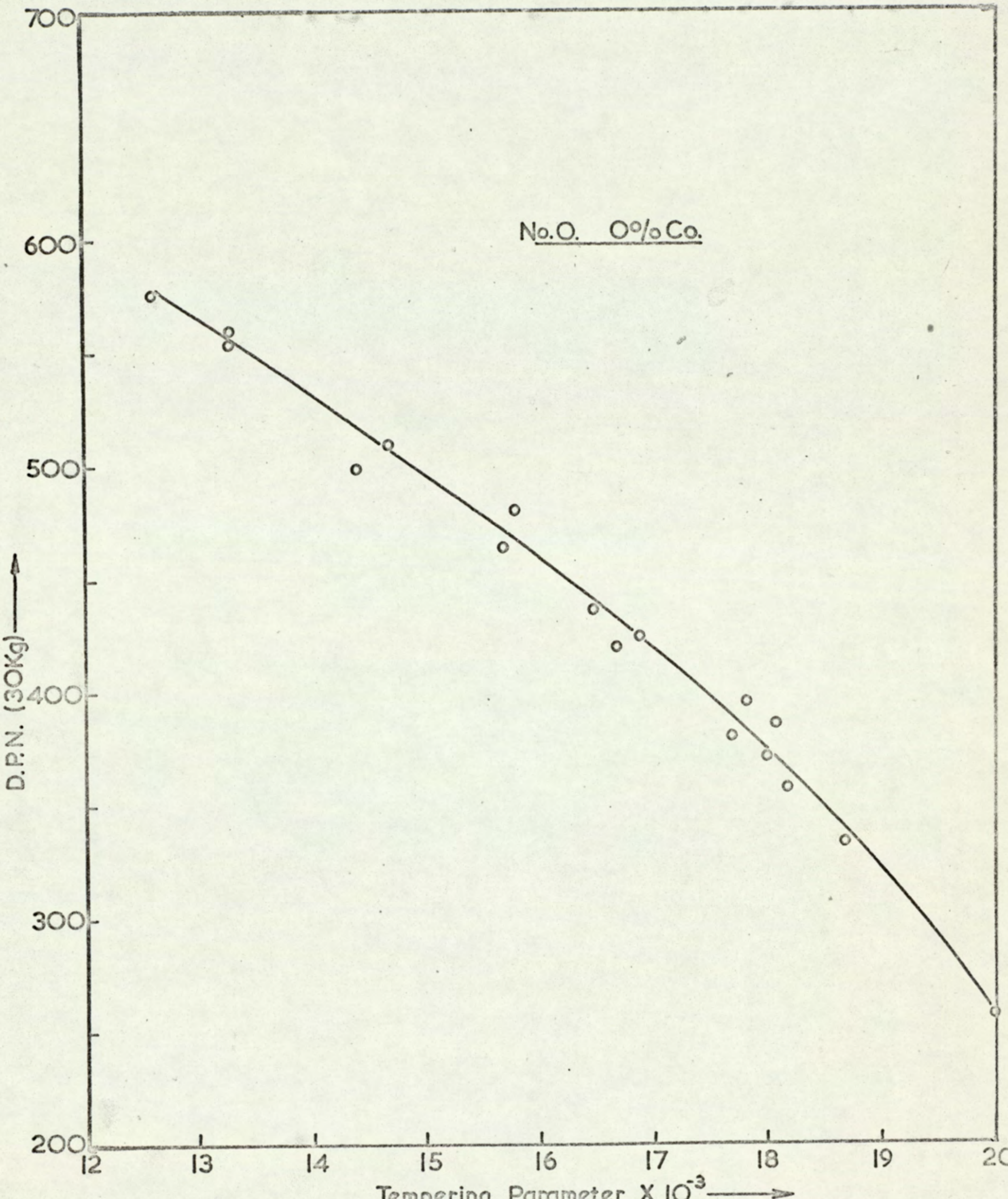


Fig. 5c.A. A typical X-Y recorder trace for the determination of the martensitic transformation temperatures, showing the failure at a higher cobalt content. Steel No. 7. (7% Co) Room temp. 23°C.



Typical chart record showing start of transformation for T.T.T. curve of steel No.3 at 500°C. chart speed ½in./min.

FIG. 7. A.



No.O. 0% Co.
700
600
500
400
300
200
D.P.N. (30Kg)
12
13
14
15
16
17
18
19
20
Tempering Parameter X 10^{-3}

Fig.9a.A.

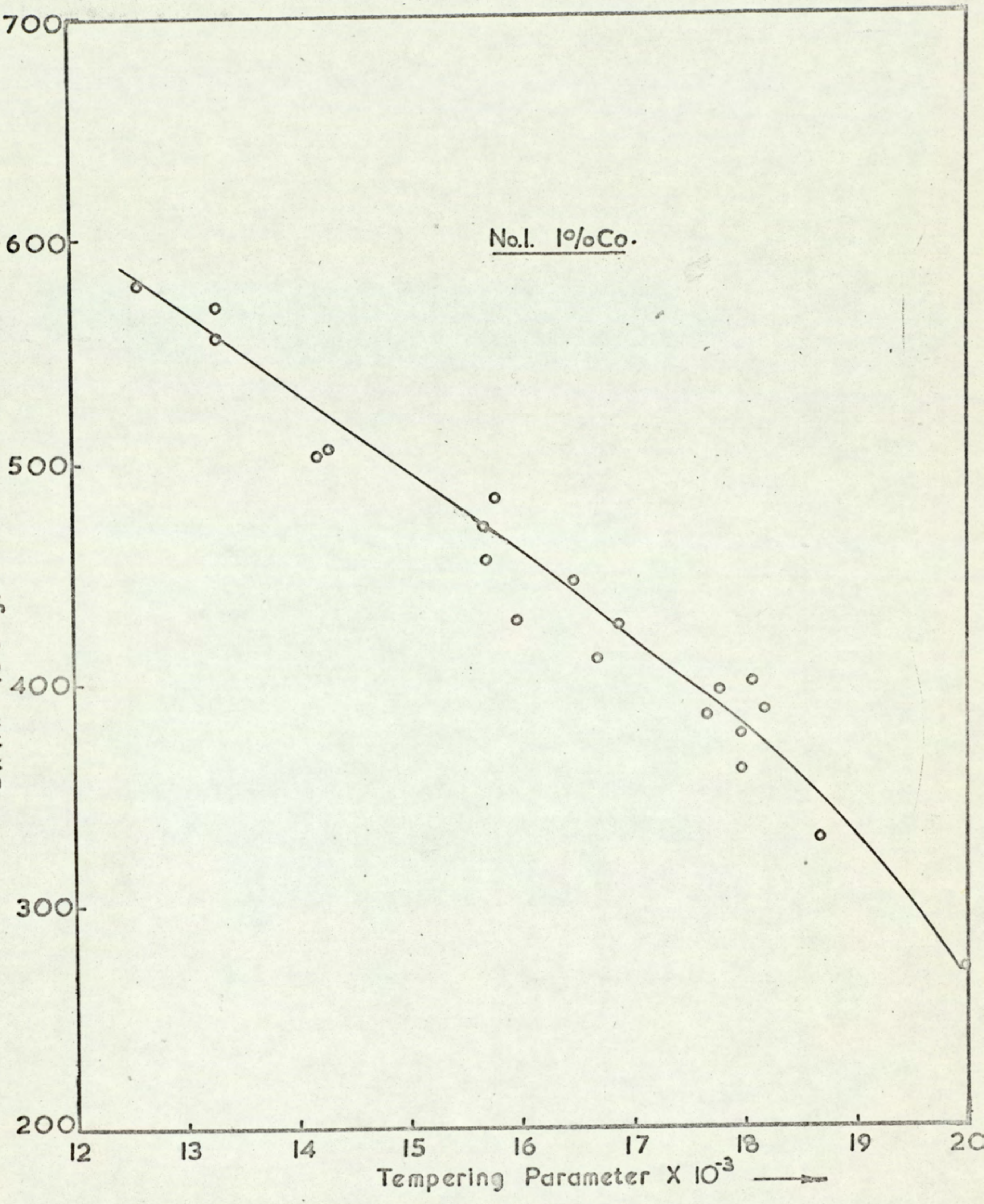
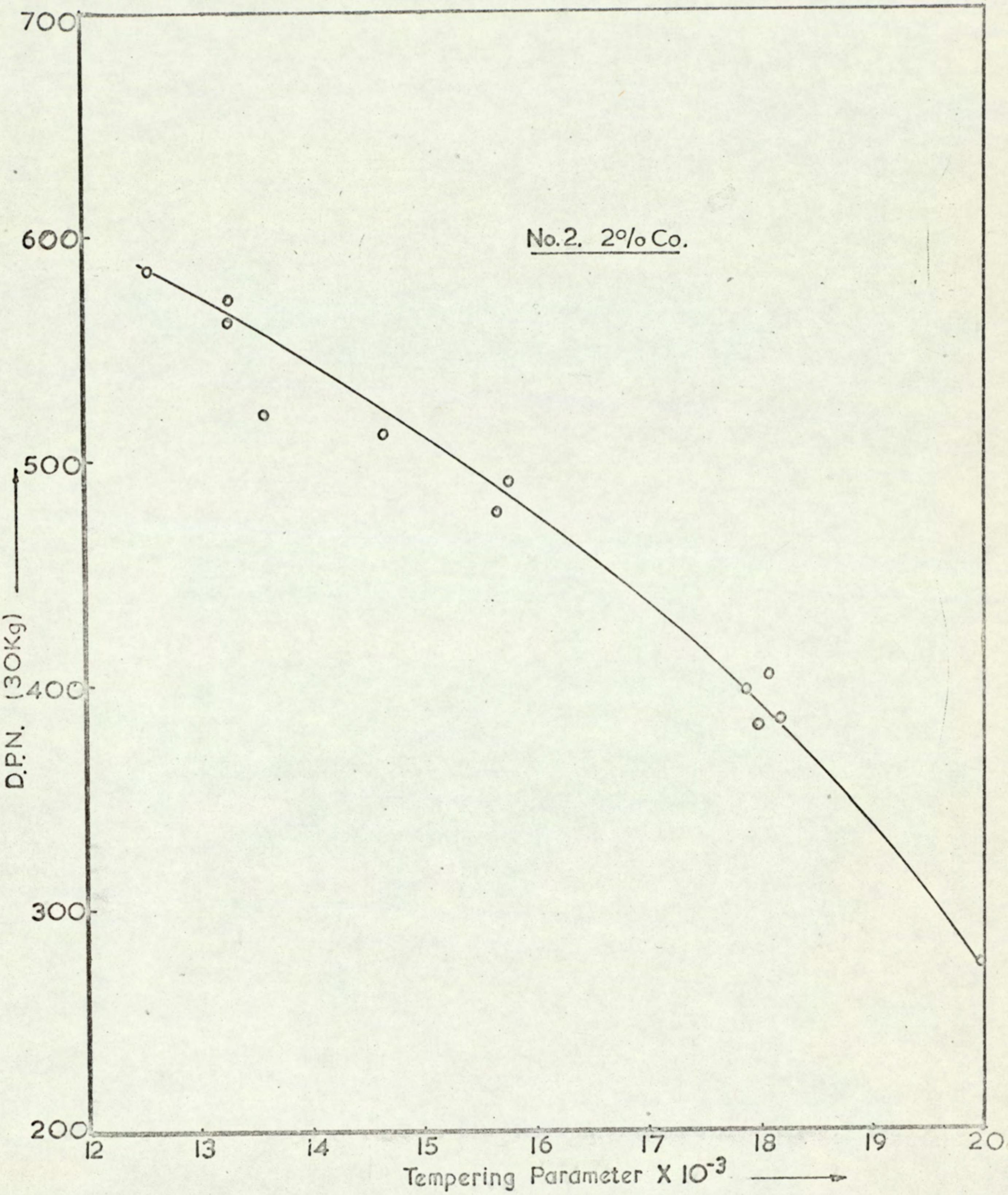
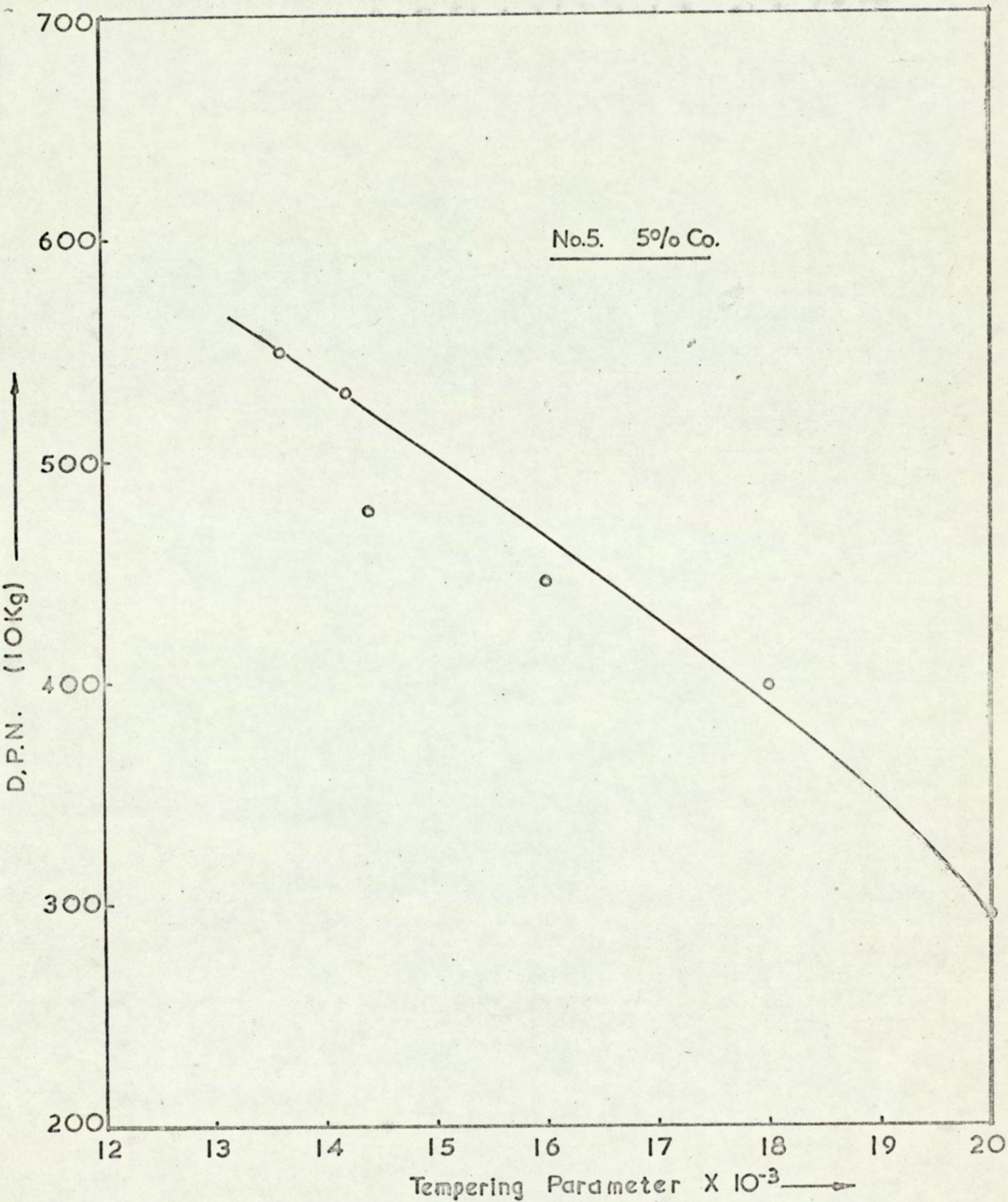

No.1. 1%Co.
700
600
500
400
300
200
D.P.N. (30Kg)
12
13
14
15
16
17
18
19
20
Tempering Parameter X 10^{-3}

Fig.9b A.



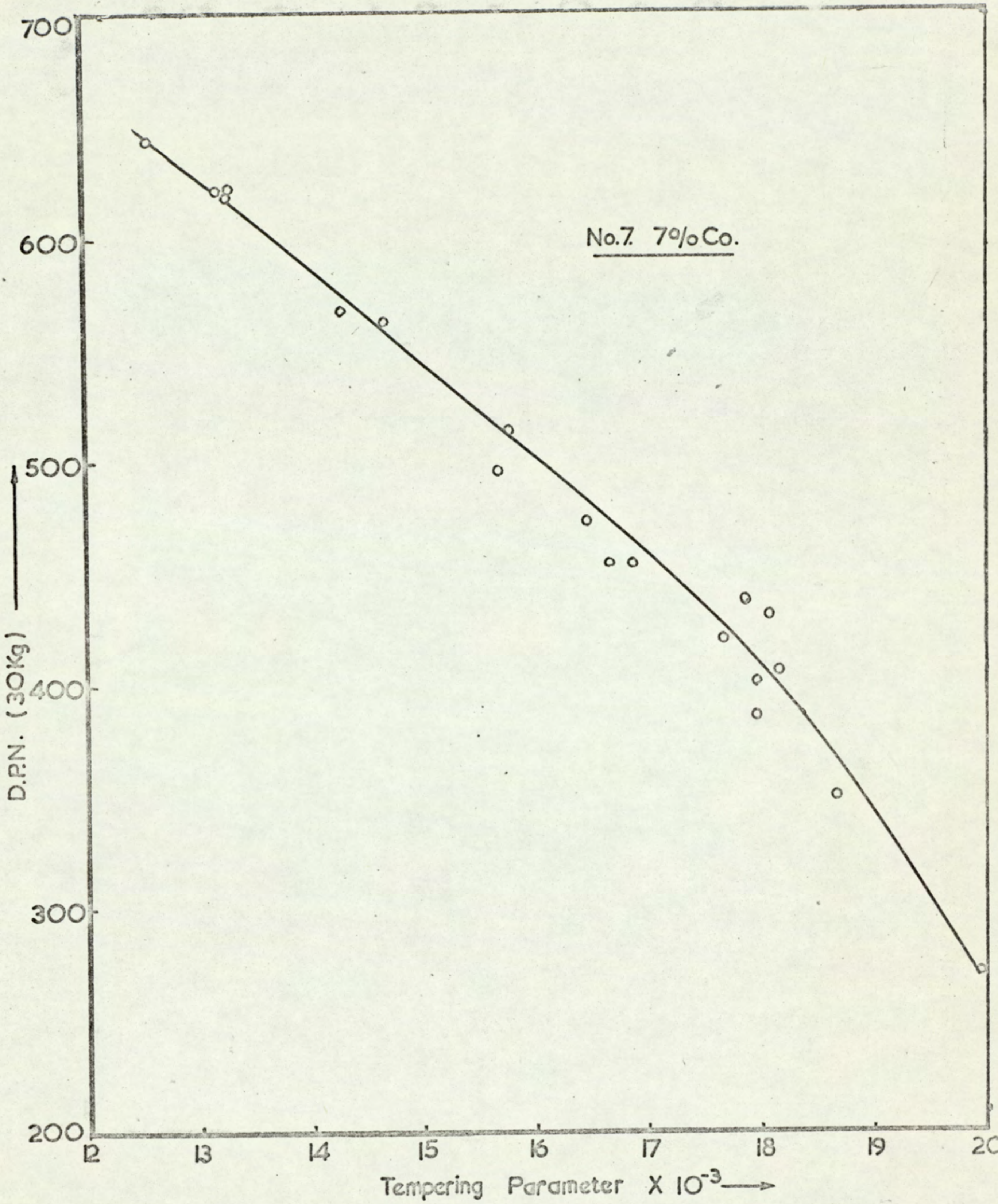
700
600
500
400
300
200
D.P.N. (30Kg)
No. 2. 2% Co.
12
13
14
15
16
17
18
19
20
Tempering Parameter X 10⁻³

Fig. 9c A.



No.5. 5% Co.
700
600
500
400
300
200
D.P.N. (10Kg)
12
13
14
15
16
17
18
19
20
Tempering Parameter X 10^{-3}

Fig.9d.A.



700
600
500
400
300
200
D.P.N. (30Kg)
No.7 7% Co.
12
13
14
15
16
17
18
19
20
Tempering Parameter X 10⁻³

Fig. 9e. A.

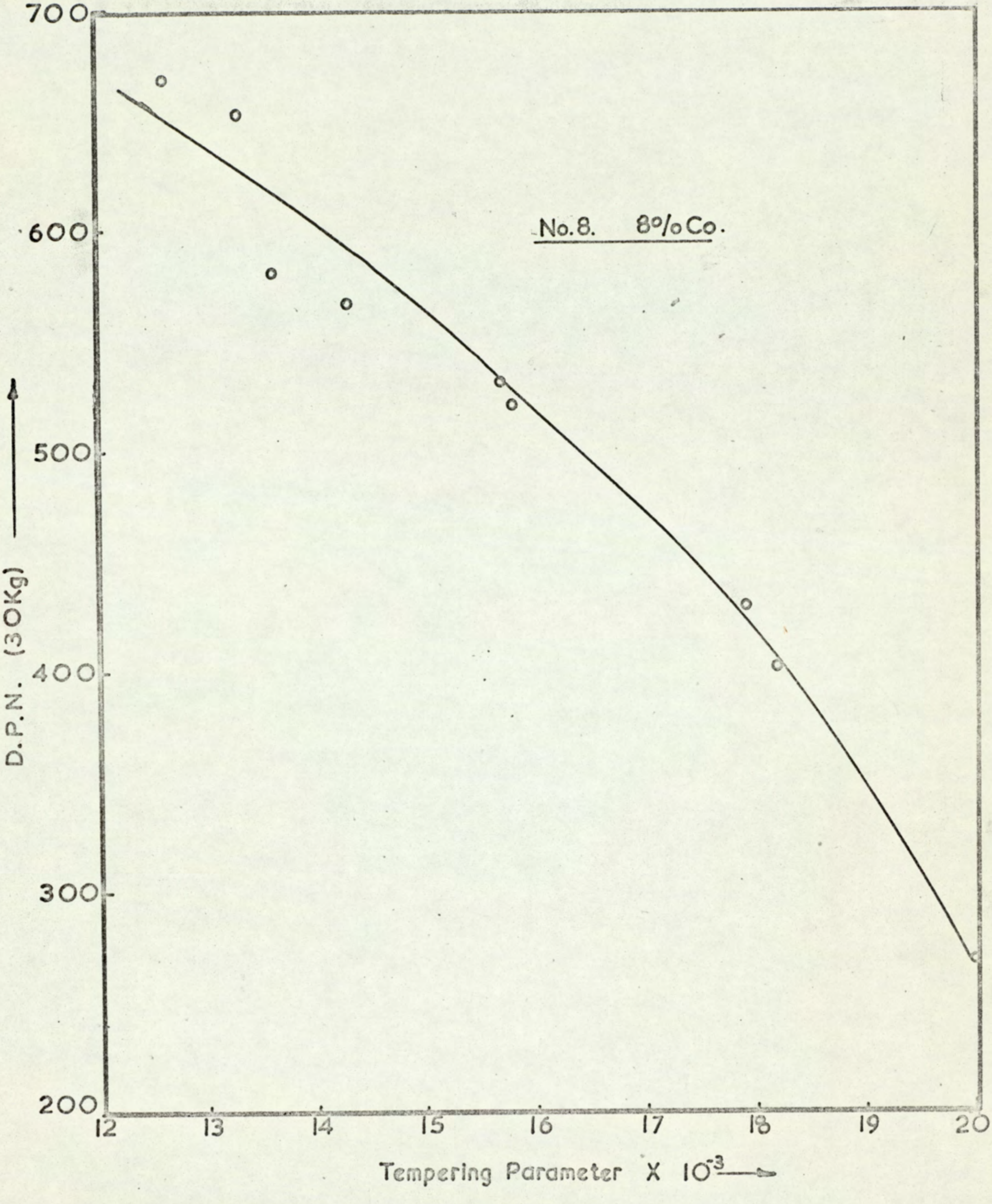

700
600
500
400
300
200
D.P.N. (30Kg)
12
13
14
15
16
17
18
19
20
Tempering Parameter X 10^{-3}
No.8. 8% Co.

Fig.9f.A.

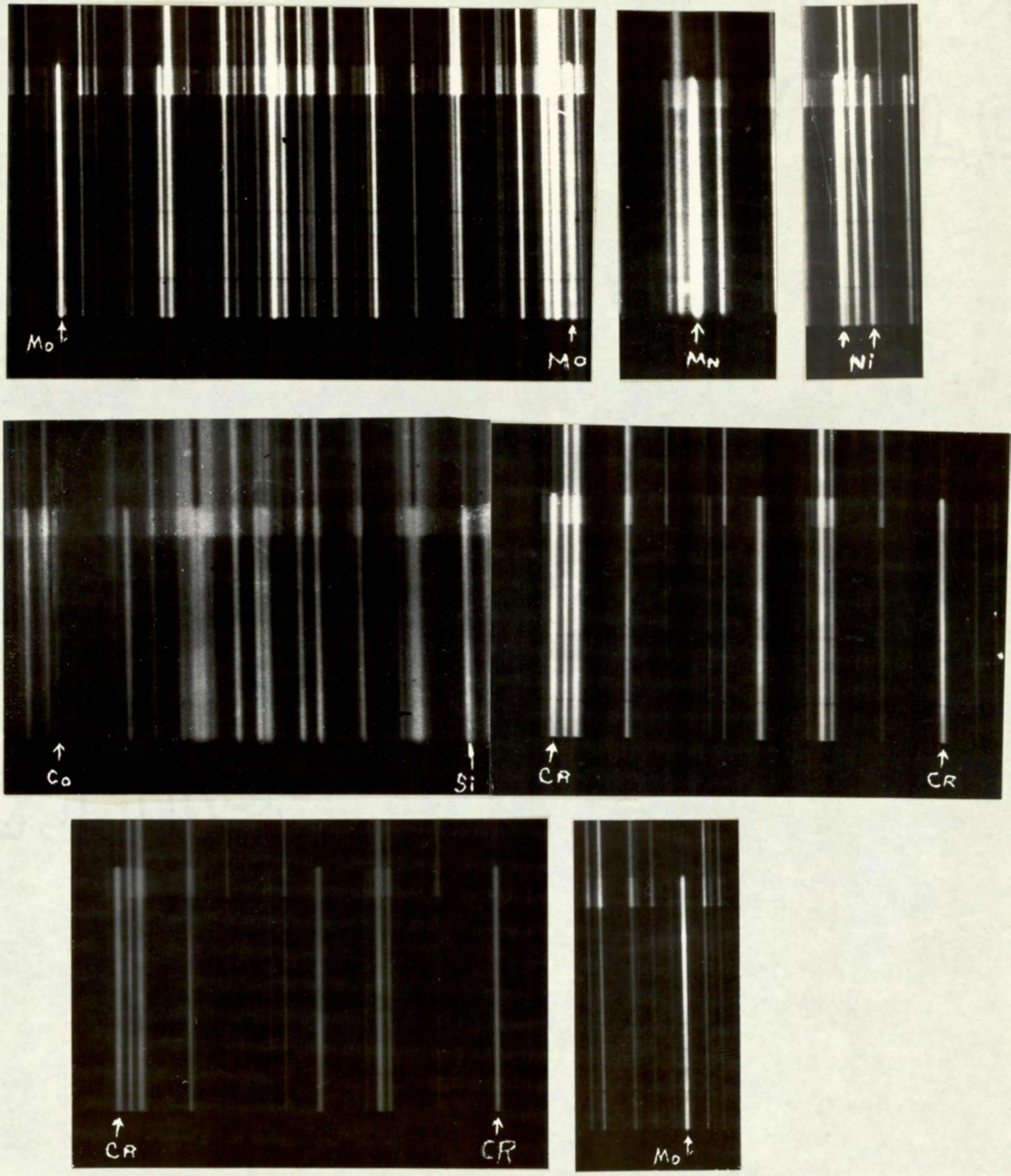


FIG.18.A. Spectrogram of the extracted carbide, showing qualitatively the different elements dissolved in the carbide lattice.

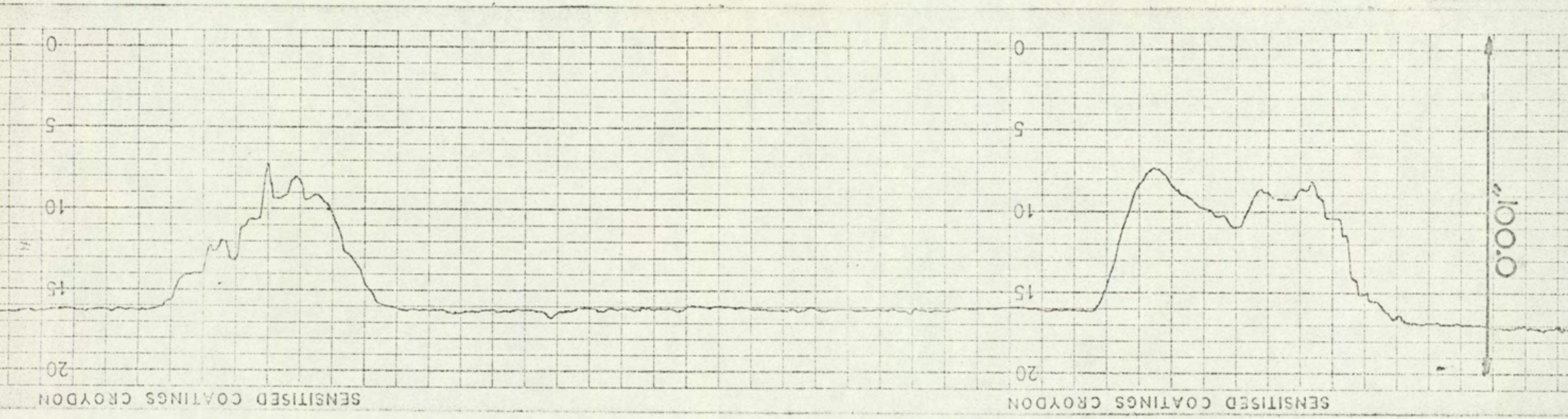
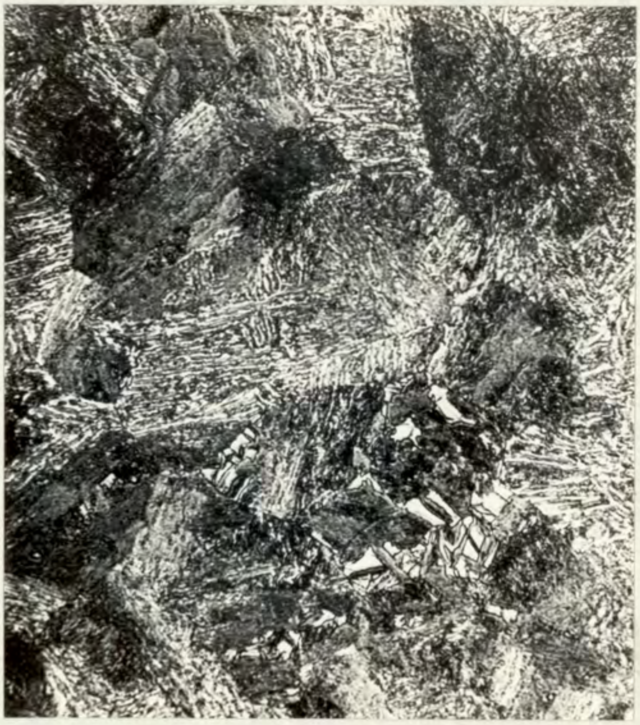


Fig.27.A. A typical 'talylin' rectilinear recorder trace of die-wear.

Steel No.0 0%Co. Steel No. 3. 3%Co.



Steel No.7. 7%Co.

FIG.28.A. Photomicrographs showing the effect of cobalt on the micro structure of 0.5" cube specimens in air cooled condition; austenitised for 30 minutes at 840°C. X 500.

DIE WEAR RESULTS APPENDIX - TABLE IIA

Die	No% Co	No. of Slugs	Slug Temp.	Reduction	Die Temp	Area of Wear	Mean
Set 29	2%Co Top	750	°C 1050-1080	0.75"-0.268"	140 C-175 C	260, 356, 271, 316	275.75
	Bot.				130°C-170°C	303, 281, 280, 285	287.25
Set 30	2%Co Top	750	1050-1080 C	0.75"-0.268"	145°C-175°C	228, 199, 293, 286	251.50
	Bot.				140°C-180°C	312, 294, 243, 269	279.50
Set 25	3%Co Top	650+	1050-1080°	0.75"-0.268"	125°C-160°C	156, 171, 227, 173	181.75
	Bot.				130°C-170°C	151, 152, 158, 158	154.75
Set 26	3% Co Top	750	1050-1080	0.75"-0268"	140°C-185°C	153, 196, 246, 173	192.00
	Bot.				165°C-200°C	251, 246, 183, 257	234.25
Set 27	5%Co Top	750	1050-1080	0.75"-0268"	140°C-190°C	224, 194, 262, 276	239.00
	Bot.				140°C-185°C	275, 289, 263, 237	266.00
Set: 28	5% Co Top	750	1050-1080	0.75"-0.268"	130°C-180°C	189, 259, 233, 200	220.25
	Bot.				140°C-190°C	157, 222, 264, 232	118.75
Set 1	7%Co Top	1100	1000-1020	0.75-0.268"	204°C-260°C	127, 138, 170, 187	155:50 5-10%
	Bot.				240°C-280°C	67, 104, 175, 129	118.75
Set 15	0%Co Top	1000	1050-1080	0.75"-0.268"	120°C	384, 400, 411, 370	391.25
	Bot.				140°C	436, 482, 461, 470	462,25

Table 13aA- Die Wear Test Results

Top Die

Die No	Nominal % Co	Volume x 10^{-5} cu. ins,				Area x 10^{-5} sq. ins.				Diameter in.				Points				Mean Vol. x 10^{-5}
SET		1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	
T	0	16.172	13.670	16.494	-	9.373	8.306	9.632	-	1.0345	1.0502	1.1181	-	341	34	330	-	15.445
29	2	15.998	8.110	16.265	16.434	9.296	4.712	9.430	8.760	0.956	0.762	0.867	1.071	361	349	360	356	13.029
30	2	12.110	8.141	9.681	12.580	7.592	4.402	6.201	7.700	0.893	0.8516	0.836	0.851	349	355	353	358	
25	3	10.330	11.967	12.765	10.600	6.451	7.280	7.651	6.830	0.966	0.836	0.836	0.833	345	348	347	352	10.811
26	3	7.096	11.759	12.120	9.854	4.596	7.261	7.436	6.195	0.815	0.820	0.825	0.820	339	338	343	342	
27	5	8.654	9.568	11.484	9.952	9.982	5.517	6.754	6.341	0.862	0.799	0.809	0.778	342	355	341	333	11.732
28	5	9.880	14.488	16.537	13.296	6.168	7.274	9.562	8.217	0.825	1.086	0.956	0.856	342	347	358	348	
1	7	9.512	7.984	8.317	8.656	5.847	4.726	5.439	5.538	0.799	0.799	0.788	0.809	355	352	356	361	8.467

Table 13bA - Die Wear Test Results

Bottom Die

Die No.	Nominal % Co	Volume x 10^{-5} cu. ins.				Area x 10^{-5} sq. ins.				Diameter in.				Points				Mean Vol. x 10^{-5}
SET		1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	
T	0	23.537	24.100	19.490	18.279	12.577	12.300	11.076	15.036	1.133	1.0606	0.9405	1.065	344	347	338	335	21.701
29	2	18.060	14.830	17.170	18.014	9.402	7.652	9.190	9.427	0.893	0.8778	0.893	0.945	369	366	362	358	13.723
30	2	10.964	7.817	10.246	12.686	5.837	3.741	5.146	6.860	0.856	0.841	0.841	0.856	354	355	346	350	
25	3	10.266	14.946	10.382	17.950	5.614	8.053	5.880	8.324	0.851	0.940	0.867	1.003	350	347	348	340	12.565
26	3	13.005	10.885	12.661	10.427	6.790	5.696	6.818	5.652	0.856	0.867	0.914	0.862	350	347	346	340	
27	5	9.671	9.778	13.230	11.093	5.316	5.919	6.872	5.813	0.841	0.846	1.060	1.233	346	343	344	332	10.007
28	5	10.553	9.853	8.149	7.729	6.004	5.468	4.395	4.447	0.877	0.856	0.856	0.830	342	342	351	337	
1	7	13.084	8.008	9.394	9.452	5.537	3.978	4.907	5.156	1.468	0.851	0.862	0.992	354	353	358	354	9.984