

PRECIPITATION OF INTERMETALLIC COMPOUNDS IN CERTAIN
STAINLESS ~~IR~~AGING STEELS.

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by

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ABSTRACT

A study has been made of the precipitation reactions in a stainless maraging steel. The high strength obtained in the alloy was found to be due to a precipitation hardening reaction involving R phase precipitates obtained by ageing in the range 500-700°C. Electron microscopy revealed that the lath martensitic structures of the alloy gave rise to a very fine and uniform distribution of precipitates which nucleated only on dislocations. Dilatometry and hardness data showed that the transformation was diffusion controlled and that the rate-controlling process was different for temperatures above and below 570-580°C. In the early stages of ageing the kinetic data indicated that rods of precipitate were growing radially and later they formed spherical particles; this was confirmed by electron microscopy studies.

At temperatures above 650°C the R phase still precipitates but after an incubation period, in which R-phase precipitates coarsen, the more stable Chi-phase is precipitated at high angle boundaries. As these particles grow the R phase in the surrounding areas dissolves, allowing the remaining dislocation structure to recover. The precipitation of the Chi - phase leads to a sharp drop in the hardness values as there is no longer a favourable precipitate distribution to harden the matrix.

Directly quenching specimens to 600° and 700°C, (i.e. well above the M_s temperature of 400°C), gives rise to a discontinuous precipitation process producing ferrite and an $(Fe\ Cr)_2\ Mo$ precipitate. On prolonged ageing at 700°C the more stable sigma phase nucleates at grain boundaries and grows at the expense of the $(FeCr)_2\ Mo$ precipitate.

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CHAPTER 1

INTRODUCTION

High strength materials were in everyday use long before a clear understanding was available of the strengthening mechanisms that can result from the precipitation of a second phase in the alloy matrix. Since the importance of precipitation was realised much effort has been devoted to finding ways of controlling precipitate morphology so as to obtain good combinations of properties, not only at room temperature but also for high temperatures.

In steels this has led from the tempered carbon martensites, to the use of alloy carbides, until some of the present generation of high strength steels are strengthened by the precipitation of intermetallic compounds from a low carbon martensite. The maraging alloys fall into this latter class and the intermetallic compounds are precipitated on the dislocations present in the lath martensite formed in this type of alloy. The intermetallic compounds are usually formed, and are therefore stable, at higher temperatures than the carbides.

The normal type of maraging alloy is based upon the iron-nickel system which means that the service temperatures are comparatively low due to the lack of oxidation and corrosion resistance. To overcome this, the Stainless Maraging alloys have been developed, based upon the Fe 12% Cr alloys. The required martensitic structure is obtained by additions of cobalt and an element to give intermetallic compound precipitation.

At the present time there is one commercially produced alloy, known as AEC-77, ~~and is~~ produced by

The Crucible Steel Company. Its composition is

Fe	Cr	Co	Mo	C	V	wt%
BALANCE	14.5	13.0	5.0	0.15	0.35	

This type of alloy finds application as disc and blade material for steam turbines as well as in the cooler sections of gas turbines, as a structural and skin material in supersonic vehicles and as hot working components e.g. extrusion dies and mandrels.

Although there have been a few investigations carried out on stainless maraging alloys a complete understanding of their structure is not available. It is difficult to compare them directly with the iron-nickel maraging alloys as there is still controversy over the identification of the precipitates responsible for the hardening.

The present work sets out to study the transformations involved and to identify the precipitating phases in a stainless maraging alloy of composition

Fe	Cr	Co	Mo	C.		
BALANCE	9.9	12.8	4.8	0.01	wt%.	

The composition differs somewhat from that of APC-77 and was selected so as to eliminate the complicating effects of delta-ferrite formation, and the precipitation of carbides, and to minimise the amount of austenite present in the structure at room temperature and ageing temperatures.

The structures before and after heat treatment were studied by several methods which have been successfully used on the iron-nickel alloys. They were, thin foil electron microscopy, X-ray and electron probe analysis of extracted precipitates as well as of the matrix, hardness measurements and magnetic measurements.

In addition the kinetics of precipitation were studied using a differential dilatometer as it was thought that a kinetic study of the principle precipitation process would help in understanding why this type of alloy is able to give such good properties. Hitherto, there has been no data reported on the kinetics of precipitation in stainless maraging alloys; moreover the data obtained on iron-nickel type alloys have not yet been able to be explained satisfactorily by theoretical models.

The present work has not included measurements of mechanical properties or corrosion and oxidation resistance; the alloy studied was selected with the aim of elucidating the structural and kinetic features rather than optimising the properties just mentioned. The results obtained have provided new information on the structural and kinetic aspects of precipitation in stainless maraging steels, and are of significance in relation to the behaviour of these alloys in high temperature service.

CHAPTER 2

REVIEW OF PRESENT KNOWLEDGE.

2.1. INTRODUCTION

This chapter reviews certain limited aspects of the general field relevant to the steel being studied. Only a brief survey of some of the precipitation hardening theory will be given as a much fuller review is already available¹. A summary is given of the analysis of precipitation kinetics and some literature on high strength steels particularly relevant to the present work is discussed.

2.2. PRECIPITATION HARDENING

In a system showing decreasing solid solubility of one component with fall in temperature, a supersaturated solid solution can be obtained by quenching the material from a high temperature to some temperature below the solvus. The degree of supersaturation depends on the difference in solubilities at the two temperatures and, for any one composition, on the amount by which the second temperature is below the solvus.

The supersaturated solid solution is unstable and tries to reduce its free energy by decomposing to form the equilibrium products. This takes place by the diffusion of one or more component in the solid solution which allows nucleation and growth of the precipitate particles. The variation of the rate of transformation with temperature depends on a balance between the increase in supersaturation and the decrease in diffusion rate as the

temperature is lowered.

The formation of a precipitate of the equilibrium structure will give the greatest decrease in free energy; however it has been shown that the precipitation follows the path of minimum activation energy so giving a sequence of metastable phases ending with the equilibrium structure.

Decomposition by long range transport can occur by either a continuous or a discontinuous reaction. In a continuous reaction the transformation takes place throughout the matrix and gives a structure which produces precipitation hardening. In a discontinuous reaction the transformation proceeds by the growth of duplex regions which have a definite interface between the transformed and untransformed regions.

Continuous precipitation occurs in the alloys studied so that it will be considered further.

2.2.1. HOMOGENEOUS PRECIPITATION

It was first shown thermodynamically by Gibbs² that precipitation can occur by either of two processes

a) SPINODAL DECOMPOSITION - On a free energy vs composition curve for two stable phases differing in composition but similar in structure there is a point at which $\frac{\partial^2 G}{\partial C^2} = 0$, (G = free energy, C = concentration).

If this term is negative, any fluctuations in composition lead to a decrease in free energy so that there is no nucleation barrier to decomposition. The solid solution generally forms a periodic array of solute rich zones, throughout the matrix, which

are continually changing in composition until the equilibrium structure is reached.

b) NUCLEATION AND GROWTH - When $\frac{\partial^2 G}{\partial c^2}$ is positive,

slight variations in composition lead to an increase in free energy; while greater variations produce a decrease i.e. there is a definite free energy barrier, which must be overcome before a stable nucleus can form and grow.

There is no evidence for a spinodal decomposition in the maraging type alloys so that only the nucleation and growth mechanism will be considered here.

The nucleation energy in terms of the classical nucleation theory can be written as

$$\Delta G_{\text{NUCL}} = \Delta G_{\text{VOL}} + \Delta G_{\text{STRAIN}} + \Delta G_{\text{SURF}}$$

Where ΔG_{NUCL} is the free energy, per unit volume, of formation of the nucleus, ΔG_{VOL} is the difference in free energy of the phases before and after transformation, ΔG_{STRAIN} is due to the differences in density of the precipitate and matrix and ΔG_{SURF} is the free energy of the interface formed.

ΔG_{VOL} must be negative, as the supersaturated solid solution is unstable, and depends on the degree of supersaturation. Both ΔG_{STRAIN} and ΔG_{SURF} are positive so that for nucleation to occur ΔG_{VOL} must be greater than ΔG_{STRAIN} plus ΔG_{SURF} .

All three terms are functions of the nucleus size, and assuming a spherical nucleus, it can be shown that there is a critical nucleus radius, r_{CRIT} , which must be attained before the nucleus can grow with decreasing free energy. The value of ΔG_{NUCL} gradually rises with increase in radius until a value of ΔG_{CRIT} , corresponding to r_{CRIT} , is reached

It is assumed that embryos are constantly being formed by fluctuations in solute distribution due to thermal agitation. If the size of these embryos is below r_{CRIT} they will redissolve, but if they are greater than r_{CRIT} they will be stable and form nuclei which can grow with a decrease in overall energy of the system. This type of precipitation is known as "homogeneous" as it occurs uniformly throughout the matrix.

Any means of reducing the values of ΔG_{SURF} and ΔG_{STRAIN} will make nucleation easier, and numerous investigations have shown precipitates which have nucleated on grain boundaries, dislocations, vacancy clusters, stacking faults and twin boundaries.

2.2.2. PRECIPITATION ON DISLOCATIONS

Cahn³ has given a theoretical treatment for nucleation on dislocations in which he made the following assumptions.

- a) The nucleus lies along the core of the dislocation.
- b) Its cross-section at right angles to the dislocation is circular.
- c) It is a non-coherent precipitate.
- d) A value of grain boundary energy can be assigned to the precipitate-matrix interface.
- e) The matrix is elastically isotropic.
- f) The sign of the strain energy is reversed due to the strain field of the dislocation.

He derived an equation.

$$G = A \log r + 2\pi\gamma r - \pi r^2 \Delta G_{VOL}$$

where $A = \frac{Gb^2}{4\pi(1-\nu)}$ for edge dislocations

$$= \frac{Gb^2}{4\pi} \quad \text{for screw dislocations}$$

G = shear modulus

b = Burgers vector

ν = Poisson's ratio

γ = interfacial energy

r = particle radius

Fig I represents the relationship of ΔG and for two different supersaturations. At low supersaturations $\frac{2A\Delta G_{VOL}}{\pi\gamma^2}$ is less than 1 which results in a minimum in the free energy curve A in Fig. 1; this occurs before r_{CRIT} and has been correlated to a Cottrell atmosphere. There is still a nucleation barrier which is equivalent to the difference between the minimum and maximum values of free energy.

At higher supersaturations $\frac{2A\Delta G_{VOL}}{\pi\gamma^2}$ is greater than 1 and there is no such minimum, B Fig 1, so that there is no nucleation barrier to a phase transformation.

Cahn also showed that edge dislocations were better sites than screw dislocations and that increasing the Burgers vector and supersaturation favoured dislocation nucleation. However, this theory was unable to explain all the observations on dislocation nucleation and diffusional effects must then be taken into account.

In this theory the dislocation-nucleated and matrix-nucleated precipitate have the same structure and it is simply the reduction in the free energy barrier which determines the nucleation sites.

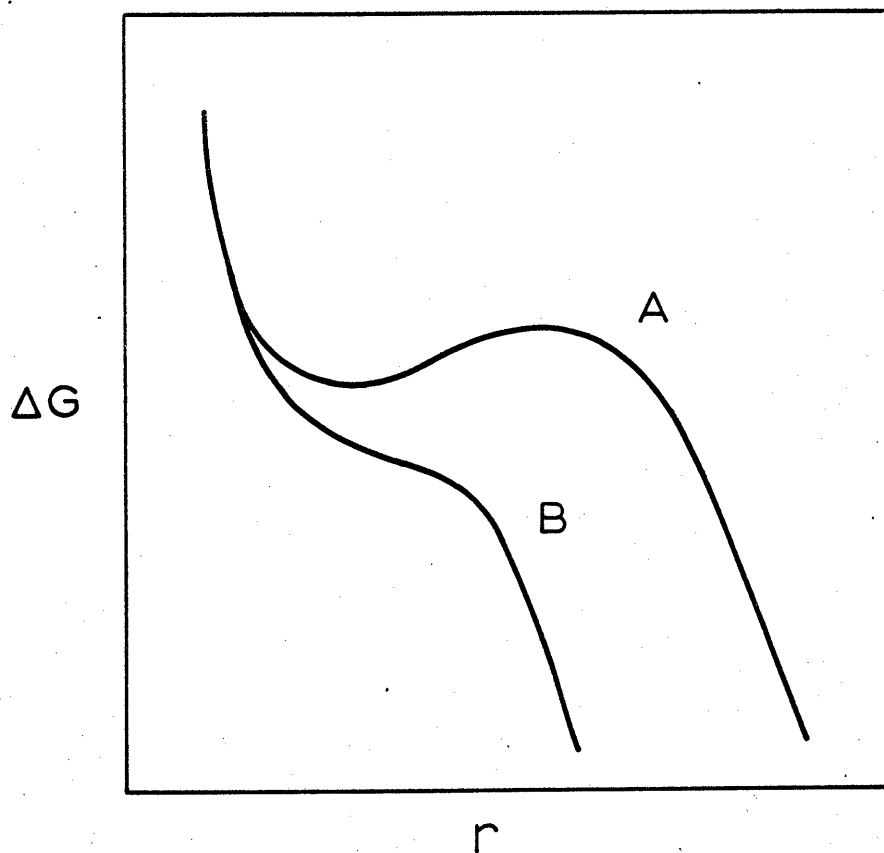


FIG.1. Variation of Free energy as a function of the radius of a spherical nucleus

22.3 PRECIPITATION ON GRAIN BOUNDARIES

A grain boundary is a region of disorder which can give rise to an alteration in the ΔG_{SURF} term when precipitates nucleate on it. This will give an overall reduction in ΔG_{NUCL} which makes it possible for the stable precipitates to form. These can then grow at the expense of a metastable matrix or dislocation nucleated precipitates.

2.2.4. MECHANICAL PROPERTIES

The mechanical properties of a precipitation hardening material depend on the degree of hindrance the second phase exerts on the movement of dislocations.

The strength of the supersaturated alloy depends on the solid solution strength which can be increased by the presence of a dislocation structure introduced either by cold working or in some systems by a martensitic transformation. On ageing coherent precipitate particles form and dislocations are able to pass through them. The yield stress now depends upon,

- a) the elastic coherency stresses set up by the precipitate
- b) the difference in slip distances between the matrix and precipitate
- c) the amount of new interface formed after slip
- d) the shape of the particles; at constant volume, particles of different shape intersect different numbers of slip planes.
- e) the matrix strength.

The work hardening rate will still be similar to that of the original matrix.

Ageing for longer times will increase the size of the precipitate until it is energetically more favourable to form non-coherent precipitates. Dislocations now find it more difficult to pass through the non-coherent precipitates and so they can

- a) form dislocation pile-ups at the precipitate until there is sufficient stress to shear the precipitate.
- b) cross-slip or climb around the precipitates and leave behind dislocation segments
- c) bow between the particles. This has been treated by Orowan⁵ who showed that the stress required to bow a dislocation between particles was inversely proportional to the interparticle distance.

The work-hardening rate with semi-coherent and non-coherent precipitates is increased by the dislocation segments and **loops** left behind after a dislocation has passed since these further hinder the movement of other dislocations.

It is now possible to show that the criteria for high strength precipitation hardening materials are

- a) The matrix should be as strong as possible, an ordered structure giving the best results.
- b) There should be a large volume fraction of second phase.
- c) The second phase should be evenly distributed throughout the matrix.

Conditions b) and c) are to ensure that the greatest number of slip planes are influenced by the second phase.

- d) The second phase should be at least partially coherent to ensure small precipitate particles and a good dispersion for a given volume fraction. Non-coherent precipitates have high interfacial

energies which encourages coarsening and interfacial cracking.

- e) The precipitates should be in the form of long plates or rods to cut as many slip planes as possible. However the precipitate shape is determined by the strain energy, surface energy and orientation relation with the matrix⁶

2.3. PRECIPITATION KINETICS

Continuous precipitation by the nucleation and growth mechanism can be treated theoretically if the two parts can be separated. However, they usually occur at the same time and in such a way that it is only for the simplest processes that a theoretical treatment can be applied.

It has been found that the kinetics of most solid state reactions can be described in terms of an empirical equation which was first used to account for the growth of pearlite in austenite⁷.

$$\frac{dy}{dt} = k^n t^{n-1} (1-y)$$

where "y" is the fraction transformed in a time "t" and "k" is a rate constant with dimensions of (time)⁻¹. The term (1-y) was an arbitrary factor taking into account the impingement of different transforming regions.

Integrating gives

$$y = 1 - \exp(-kt)^n$$

which is known as the Johnson-Mehl equation.

The values of "k" and "n" give an unambiguous description of the reaction kinetics at any given temperature. The actual value of n has been shown to provide useful information in determining the

rate-controlling steps.

2.3.1. DIFFUSION CONTROLLED TRANSFORMATIONS.

The Johnson-Mehl equation was applied by Wert⁸ to the precipitation of carbides and nitrides in steels. Zener⁹ applied a more theoretical approach to the experimental results obtained by Wert when he studied the transformation in terms of a diffusion controlled process. He solved a one dimensional problem and applied it to three dimensions resulting in an expression which could be reduced to the Johnson-Mehl form with an "n" value of $3/2$.

Zener's assumption of a diffusion limited transformation has also been used for more complex treatments^{10,11}. The work by F.S. Ham¹² was a rigorous mathematical treatment which evaluated the solute precipitated as a function of position and time. He found that there was no fundamental justification in using a Johnson-Mehl equation, but it provided a good approximation to his rigorous equation for times up to $y = \frac{1}{2}$.

Ham first considered the growth of spheres, of initially small dimensions, from a slightly super-saturated solid solution and found that the radius increased in proportion to $t^{1/2}$ and the volume as $t^{3/2}$. He later applied his solution to the growth of oblate and prolate spheroids with constant eccentricity and found the same results. In the growth of long rods where the growth at the ends can be neglected the "n" values should be 1, and similarly for the thickening of discs. However, if the initial volume of the precipitates is substantial, i.e. 1/10 final volume, then the "n" value will be between 1 and 1.5.

In a later paper Ham¹³ applied his diffusional analysis to the growth of rods and discs in preferential

directions where there were specified limits on the diffusion of solutes to the surfaces. For a disc of constant thickness but with solute capture over its entire surface a time dependence of t^2 was obtained. A similar result was obtained if capture occurs only at the edge but in this case the constant in the rate equation is altered. A rod of constant diameter with capture only at the ends increases in proportion to "t", however if capture occurs over its whole length an increasingly rapid growth is predicted.

In all cases considered so far, the initial particles have been assumed to form relatively easily and the rate of transformation is then controlled by diffusion.

2.3.2. STRESS ASSISTED PRECIPITATION ON DISLOCATIONS

Cattrell and Bilby¹⁴ first obtained expressions for the drift of solute atoms to a dislocation in order that the strain field of the dislocation could be partially accommodated by these atoms. An edge dislocation was considered in the original derivation but a screw dislocation will have a similar although smaller effect on a substitutional atom.

An expression was derived for the stress assisted drift of atoms to a dislocation and was incorporated in an expression for the fraction of solute precipitated

$$y = 3L \left(\frac{\pi}{2} \right)^{1/3} \frac{(ADt)^{2/3}}{kT}$$

y = fraction transformed

L = dislocation density

A = constant

t = time

Harper¹⁵ modified this expression by incorporating an impingement factor (1-y) due to the dislocation arrays

competing for solutes

$$\text{i.e. } \frac{dy}{dt} = 2L \left(\frac{\pi}{2} \right)^{\frac{1}{2}} \left(\frac{AD}{KT} \right)^{\frac{2}{3}} t^{-\frac{1}{3}} (1-y)$$

$$y = 1 - \exp \left[-3L \left(\frac{\pi}{2} \right)^{\frac{1}{2}} \left(\frac{ADt}{KT} \right)^{\frac{2}{3}} \right]$$

This is a Johnson-Mehl type equation with $n = \frac{2}{3}$. As precipitation proceeds chemical diffusion will become more important and a number of investigations have tried to take it into account^{16,17,18,19}.

Bullough and Newman¹⁷ considered the problem and found solutions for the precipitation of discrete particles and continuous rod-like precipitates. If the binding energy in a precipitate is greater than the energy of elastic interaction of a dislocation and a solute atom, then discrete particles will form on the dislocations. If the solute atoms can drift to the dislocations and travel along them relatively easily, the rate controlling step will be the transfer of atoms from the dislocation core to the precipitate. Bullough and Newman used several different rates of transfer but in all cases found that the results could be represented by a Johnson-Mehl type equation with $n = 1$.

In the other extreme, where the elastic interaction energy is greater than the chemical binding energy a continuous rod of precipitate is formed. However this leads to an increase of "pressure" in the core region which results in local hydrostatic compression. By choosing suitable values of the hydrostatic compression and binding energy the kinetics observed by Harper can be predicted.

Recent work by Meisel²⁰ on the kinetics of carbide precipitation has shown that provided both the dislocation density and interaction energy are

sufficiently large, the Harper type kinetics of $n=\frac{2}{3}$ can be predicted.

2.3.3. INTERFACE CONTROLLED TRANSFORMATION

Turnbull²¹ considered the case where the rate controlling step was the transfer of atoms across the precipitate-matrix interface. He provides a theoretical solution where the concentration gradient in the matrix is eliminated and the difference in the activity of solute in the precipitate and matrix provides the driving force. The result can be reduced to a Johnson-Mehl equation with $n = \frac{2}{3}$.

If the transformation is controlled by both interface and diffusion then in the initial stages the interface control can be expected to predominate. As the matrix is depleted, concentration gradients form and diffusion becomes the controlling step. This will result in n values varying from $\frac{2}{3}$ to 1.5.

2.3.4. NUCLEATION AND DIFFUSION CONTROLLED TRANSFORMATIONS

Up till now it has been assumed that nucleation has been completed before ageing has started, and in most cases this is acceptable. The classical nucleation theory predicts a nucleation rate which is dependent on ΔG_{VOL} which is itself dependent on composition, and therefore on transformation time. In general ΔG_{VOL} decreases rapidly as the solute supersaturation is decreased so that nucleation ceases in the early stages of transformation.

If this is not the case, some method of combining the nucleation rate with the growth rate must be used. So far no theoretical treatment has been completely successful and only empirical equations have been produced. In these, a known time dependence of nucleation is used in conjunction with a diffusion

controlled transformation. The results are expressed in terms of a Johnson-Mehl equation with values of "n" ranging from $1\frac{1}{2}$ to $2\frac{1}{2}$.

A summary of the "n" values in the Johnson-Mehl equation is given in Table 1.

2.3.5. ACTIVATION ENERGY ANALYSIS

In all these transformations the rate of reaction increases will rise in temperature and the temperature dependence can be shown to obey an Arrhenius type equation.

$$K = A_A e^{-\frac{E_A}{KT}}$$

where A_A and E_A are the apparent frequency factor and activation energy of the system. In certain cases the value of E_A can be related to the basic atomic processes and this enables the reaction to be more fully understood. In most transformations it has been assumed that the diffusion is the rate-controlling step so that the apparent activation energy values in these cases should be close to those of diffusion.

Not a great deal of work has been carried out on the diffusion in b.c.c. alloys but the general principles are the same as for f.c.c. materials.

Atoms may diffuse in a matrix by

- 1) Volume diffusion
- 2) diffusion along surfaces
- 3) diffusion along grain boundaries
- 4) diffusion along dislocations

Most work carried out on volume diffusion shows that the exchange of atoms and vacancies is the controlling step. However, interstitial movement and 2 or 4 ring exchange mechanisms can be shown to be possible. If it is assumed that the activation energy for vacancy and interstitial diffusion is the sum of the

Table 1

VALUE OF THE CONSTANT "n" IN THE JOHNSON-MEHL EQUATION

Condition	"n"	Reference
Diffusion Controlled Growth.		
a) Particles with constant eccentricity	$3/2$	12,13.
b) Discs of constant thickness	2	13.
c) Rods of constant diameter with capture and growth at the ends only	1	13.
d) Thickening of long plates after complete edge impingement	$\frac{1}{2}$	22.
e) Radial growth of rods after complete end impingement	1	22.
f) Needles and plates of finite long dimensions small in comparison with their separation	1	22.
g) Growth on dislocations	$\frac{2}{3}$	15.
All shapes growing from small dimensions		
a) Increasing nucleation rate	$> 2\frac{1}{2}$	22.
b) Constant nucleation rate	$2\frac{1}{2}$	22.
c) Decreasing nucleation rate	$1\frac{1}{2}-2\frac{1}{2}$	22.
Growth on dislocations of spheres and rods	1	17.
Growth of a fixed number of particles with interface control	3	21.
Growth of eutectoid nodules with a constant nucleation rate.	4	7.

formation and migration energies for the vacancy and interstitial then it is possible to calculate the activation energies for the different diffusion mechanisms. These have been calculated for copper²³

- a) Vacancy control - energy of formation =
26.6-27.5 Kcal/mole
energy of migration = 13.8-23.0 Kcal/mole
Activation Energy of Diffusion = 34.4-50.5
Kcal/mole
- b) Interstitial diffusion - energy of formation
= 115-206 Kcal/mole
energy of migration = 4.6-11.5 Kcal/mole
Activation Energy of Diffusion = 119.6-217.5
Kcal/mole
- c) 2 atom ring Activation Energy of Diffusion
230 Kcal/mole
- d) 4 atom ring Activation Energy of Diffusion
92 Kcal/mole.

These results show that the vacancy mechanism is the most favourable method for the self diffusion of copper and the experimentally determined value is in close agreement being 48.4 Kcal/mole²⁴.

In b.c.c. materials it can be expected that the activation energy values for the various mechanisms are nearer to one another²⁵.

In b.c.c. iron experimental evidence²⁶ on the recovery of point defects gives a migration energy of 12.6 Kcal/mole and a formation energy of 47.2 Kcal/mole. This gives a value of 60 Kcal/mole for the self diffusion of iron by a vacancy controlled mechanism, and as experimental values for diffusion of iron are approximately 60 Kcal/mole it must be assumed that a vacancy controlled mechanism operates.

A great deal of work has been carried out on impurity diffusion in both austenite and ferrite and

a summary of relevant data is given in Table 2. However, in the present work the chemical diffusion of substitutional solute atoms must really be considered, and as yet no satisfactory theory has been able to account for this and very little experimental information is available.

So far only volume diffusion has been considered but materials of high dislocation density or small grain size will show significant contributions from these defects. They provide regions of relatively loose atomic packing so that diffusivities can be expected to be higher and activation energies lower. Values of volume and grain boundary diffusion are given in Table 2. Christian²⁷ states that the activation energies for grain boundary and dislocation diffusion are approximately equal and are about half the value for volume diffusion.

2.4. HIGH STRENGTH STEELS.

Nearly all high strength steels are based on quenched and tempered structures. The quenched structure is a tetragonal martensite whose properties are very dependent on the carbon content; the higher the carbon, the greater is its strength but also the more brittle the material becomes which leads to problems with machining and fabrication. The martensite crystals have a high dislocation density and large internal stresses. An improvement in ductility whilst retaining some of the strength is obtained by tempering to precipitate carbides.

In high strength plain carbon steels, low ageing temperatures are used to produce iron carbide precipitates. The strength can be increased by increasing the volume fraction of carbide by raising the carbon content. This is undesirable as it not

TABLE 2 ACTIVATION ENERGIES FOR DIFFUSION

DIFFUSING SPECIES.	MATRIX	ACTIVATION ENERGY Kcal/mole	REFERENCE
Fe	Fe b.c.c. paramagnetic	57.2	28
	b.c.c. ferromagnetic	60.0	28
Fe	Fe b.c.c. ferronagnetic BULK	60.7	29
	GRAIN BOUNDARY	41.5	29
Mo	Fe b.c.c.	57.7	30
Co	Fe b.c.c. BULK	62.3	29
	GRAIN BOUNDARY	41.5	29
Cr	Fe 25% Cr.	50.0	32
Fe	Fe 9.13% Cr.	55.1	31
Ni	Fe b.c.c. BULK	58.7	29
	GRAIN BOUNDARY	43.3	29

only increases the brittleness and susceptibility to quench cracking but also increases the rate of coarsening of the carbides.

A development from the plain carbon steels was to make alloy additions in order to produce alloy carbides which generally form at higher temperatures. These carbides are also less susceptible to coarsening but once again the extent of strengthening depends on the carbon content. Increasing the alloy content still further makes it possible for intermetallic compounds to form. It is this approach which appears promising as there is no longer a dependence on the carbon content.

In all the high strength steels based on martensite it has been the precipitate distribution, due to nucleation on dislocations, which has given the alloy its high strength and good ductility. It would therefore be reasonable to assume that any method of producing a uniform dislocation distribution would be a good basis for high strength alloys.

Cold working has been used to produce high precipitation hardening strengths but it is limited in its practical applications and also due to the dislocations tending to form cell structures.

It is known that the martensite produced in low carbon alloys (0.1-0.3 wt% C) is different from that produced in the higher carbon steels. Instead of being tetragonal, it is cubic and consists of untwinned laths with a very high, uniform, dislocation density. Since it is cubic the internal stresses are not so severe so that it is not so strong as the tetragonal martensite but it has much more ductility. This matrix can then be used as a basis for the precipitation of intermetallic compounds to form a high strength steel.

24.1 MARAGING ALLOYS

Work at the International Nickel Company³³ produced a series of high strength alloys, known as Maraging Steels, based upon the above ideas. It was found that a lath-type martensite could be produced in Fe-Ni alloys with Ni contents in the range 10-25 wt% and this martensite could be produced even by air cooling. Additions of Mo, Ti, Al etc. were used to give intermetallic compounds on ageing and these were nucleated on dislocations which produced very high strength and toughness values.³⁴

It is appropriate at this point to describe the lath martensite in more detail. This martensite has been found in other systems both ferrous, FeCr³⁵, FeSi³⁶, FeCrNi³⁷ and non ferrous, Ti based alloys³⁸, and in many papers is referred to as massive martensite. At present there is controversy over this term and so the structure will be referred to as lath-type martensite.

The morphology in an Fe-Ni alloy was investigated by Marder and Marder³⁹ and they came to the following conclusions

- a) The prior austenite grains are split into a number of packets which have no specific orientation relation with one another.
- b) Each packet is divided into a series of blocks which are separated by high angle boundaries, or in certain cases they are twin related.
- c) The blocks consist of laths which have essentially the same orientation and which are generally separated by low angle boundaries. There may also be sets of laths within a block

which are twin related or separated by a high angle boundary.

The dislocation density does not vary across the lath; Deter⁴⁰ has put the density as high as $10^{10}/\text{cm}^2$ and they are predominantly screw in nature⁴¹

Floreen carried out investigations into the mechanical properties of Fe-Ni⁴² and Fe-Ni-Cr⁴³ lath type martensite. He found that the alloys studied all appeared to have similar yield and ultimate tensile strengths with good ductilities. He interpreted the apparent independence of strength with composition as a balance between the increase in solid solution strengthening and the decrease in residual stress as the amount of alloying elements is increased. The fact that on relieving the residual stresses the expected variation of strength with composition is obtained supports his view. In general the mechanical properties were found to be those which could be expected from a highly alloyed b.c.c. iron matrix. Typical values obtained by Floreen are given in Tables 3 and 4.

The impact values were found to be dependent on composition only at sub zero temperatures where an empirical relationship

Impact value = $4\text{Ni}(\text{wt}\%) + 1\text{Cr}(\text{wt}\%) - 25\text{ ft-lb}$ could be fitted to the results. This suggests that, although Ni provides the greatest benefit, chromium is also helpful. The superior toughness properties (resistance to crack propagation) were explained in terms of the ability of the dislocations to move in this structure more easily than in other high dislocation density structures.

Precipitation hardening in the maraging alloys is carried out in the range 425°C to 550°C which

TABLE 3. MECHANICAL PROPERTIES OF Fe 6.2%Ni, 5.2% Cr 0.009C (ALLOY A) and Fe 11.3%Ni, 9.3% Cr 0.015% C (ALLOY B)

ALLOY AND TEST TEMPERATURE		0.2% P.S. k.s.i.	U.T.S. k.s.i.	% ELONGATION	CHARPY VALUE ft lb.
A	20°C	116	139	13	50.5
B	20°C	103	135	13	56.0
A	-77°C	122	156	17	36.0
B	-77°C	115	155	15	42.2
A	-196°C	161	192	17	7.0
B	-196°C	160	194	16	28.1

TABLE 4. MECHANICAL PROPERTIES OF ALLOYS A AND B AFTER STRESS RELIEVING FOR 1 HOUR AT 425°C.

ALLOY AND TEST TEMPERATURE.		0.2% P.S. k.s.i.	U.T.S. k.s.i.	% ELONGATION	CHARPY VALUE ft lb.
A	20°C	120	140	15	53.2
B	20°C	124	146	15	49.5
A	-77°C	130	158	19	28.6
B	-77°C	142	164	19	40.7
A	-196°C	163	194	16	4.7
B	-196°C	180	205	17	29.2

results in precipitates of a number of compounds formed from one or more substitutional elements. Floreen⁴⁴ classifies them as giving

- a) Strong age hardening - Be, Ti.
- b) Moderate age hardening - Al, Nb, Mn, Mo, Si, Ta, V, W,
- c) Weak age hardening - Co, Cu, Cr.

In the original alloys⁴⁵ Ti and Al were used to provide the hardening but Decker et al³³ noted that on adding both Co and Mo a much greater hardening took place than would be expected by summing the individual effects. Floreen and Speich⁴⁶ carried out a survey to see if this effect could be produced with other elements, but were unable to find any such elements. The reason why a combination of Co and Mo should give the effect is still unknown although results from electron microscopy indicate that a finer distribution of precipitates is produced in a cobalt bearing alloy. At present there are two theories

- a) the cobalt lowers the solubility of molybdenum in the matrix and so a greater volume fraction of precipitate than expected forms^{47,48}
- b) the cobalt lowers the stacking-fault energy of the alloy which restricts cross-slip and so increases and stabilises the dislocation structure which is then able to provide more nucleation sites for precipitates⁴⁹.

At the present time there is no complete agreement as to the precipitates responsible for hardening in these alloys since identification is very difficult, due to their small particle size at peak hardness. Identification is carried out by one or more of a number of methods which include, electron diffraction examination of thin foils or of extracted precipitates, (specimens must be in the

overaged condition). X-ray diffraction of extracted precipitates, microprobe analysis and Mossbauer spectroscopy⁵⁰. In the cases where an analysis has been made little or no cobalt was found in the precipitates; this suggests that cobalt mainly provides solid solution hardening.

Floreen⁴⁴ gives a fairly comprehensive list of precipitates identified in various maraging alloys after different heat treatments and from these a trend can be seen for the molybdenum-bearing alloys. Initially an A_3B type compound is formed, usually Ni_3Mo or $Ni_3(Ti,Mo)$ but with further ageing a more stable compound is produced. This is usually Fe_2Mo or Fe_7Mo_6 depending on the composition and temperature range.

The equilibrium structure after ageing is austenite, ferrite and intermetallic compound, ~~the~~ austenite being formed by a nucleation and growth process, and Peters and Cupp⁴⁷ have shown this to take place at the same time as the intermetallic forms. However, they say that the amount formed is very small and so does not affect the precipitation reaction, although it does set a limit on the ageing temperature that can be used.

Electron microscopy, together with hardness values, internal friction⁵¹, resistivity⁴⁷, magnetic measurements⁵² and Mossbauer techniques⁵² have been used to follow the kinetics of precipitation. Microscopy shows that peak properties are obtained either just before or just after precipitate particles are visible, usually $100\text{\AA}$ in the martensitic matrix.

The precipitates appear to form on dislocations and not on grain boundaries or sub-grain boundaries,

this resulting in a uniform but dense distribution of particles.

Isothermal data have been expressed by the general equation

$$y = 1 - \exp(-kt)^n$$

and values of the exponent "n" found to be in the range 0.2-0.5^{47,53,54}. Arrhenius plots give apparent activation energies of 30-45 Kcal/mole. The low values of "n" and activation energy have been attributed to the high dislocation density altering the diffusion rates.

Several workers^{51,47}, following isothermal ageing by internal friction and resistivity have noted quite large changes in these properties in the very early stages of ageing. They associate these with a dislocation recovery process which is terminated by the nucleation of precipitates which pin the dislocations.

Recently, two pieces of work have shown entirely different kinetics from those generally found in the maraging alloys. The first by Marcus, Peistrup and Fine⁵² gave a value of 60 Kcal/mole for the activation energy of precipitation in an Fe-17Cr-7Ni 1.2 Al alloy. This was attributed to the bulk diffusion of either Ni or Al, as the first precipitates were deduced to be ordered Ni Al. This result suggests that the lath type martensite only plays an important role in the nucleation of the precipitates and not in altering the diffusion rates.

The second piece of work was carried out by Peters and Floreen⁵⁵ on an Fe-18Ni-13 Mo alloy, this composition being chosen so that a ferritic or martensitic matrix could be produced by altering the

solution treatment temperature. They compared the kinetics of precipitation in both conditions and also in a cold worked ferrite matrix. Ageing was carried out at temperatures between 480°C and 590°C and its progress was followed by electrical resistivity and hardness measurements. An incubation period was found using hardness measurements for all three conditions; however the resistivity measurements showed an incubation period only for the ferritic condition. The isothermal curves for the martensite and cold worked structures showed that the rate of change of resistivity was much less than those reported in the normal maraging steels. Plots of $\log \left(\log \frac{1}{1-y} \right)$ VS $\log t$ gave

segmented curves with "n" values from 2.0 to 0.5. The activation energy plots are shown in Fig. 2 and a value of 60 K cal/mole was obtained by Peters and Floreen.

In both cases the activation energies of the process can be taken as being equal to that for substitutional diffusion in b.c.c. ferrite and not for enhanced diffusion along dislocations. This would suggest that the lath martensite structure is not dictating the ageing of these particular alloys; whether a similar assumption can be made for other maraging alloys is still in doubt. Peters and Floreen suggest that the nucleation rate determines the kinetics in maraging alloys. If there was a low free energy of nucleation the temperature dependence of the reaction would be controlled by that of the nucleation rate which could give low values of "n" and activation energy. If the free energy of nucleation was high there would be a limit on the

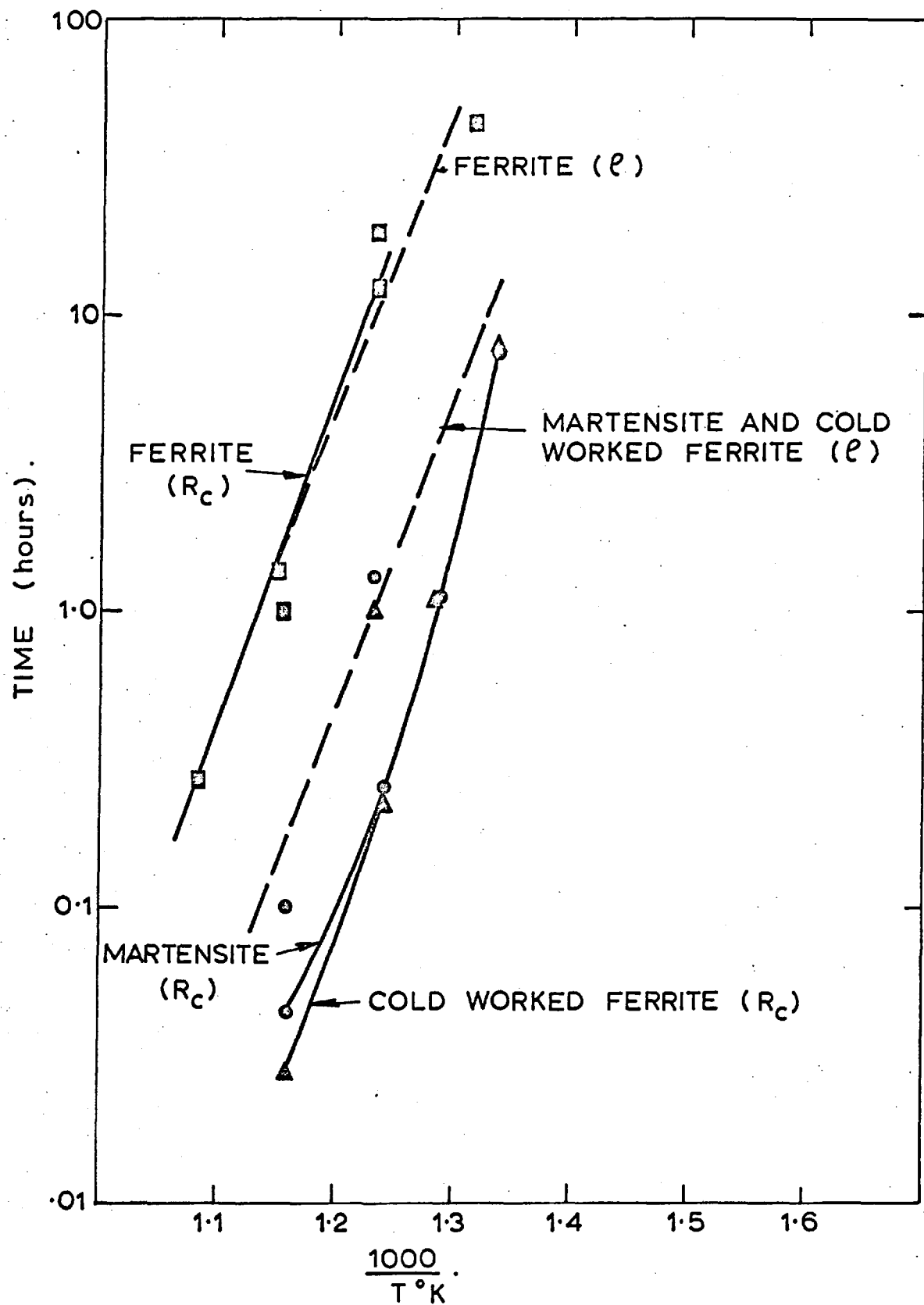


FIG.2. Activation energy plots for an Fe, 18%Ni, 13%Mo alloy⁵⁵.

number of sites so that the nucleation rate would be relatively independent of the temperature. The ageing kinetics would then be controlled by the diffusion of solutes which would give the higher activation energy values. A change in nucleation rate could be brought about by changes in the precipitating phase and as already shown there is some uncertainty about which precipitates form. If the A_3B type precipitate nucleates it should do so relatively easily whereas the Fe_2Mo type should find it much harder.

Peters and Cupp⁴⁷ and Peters⁵⁴ found evidence of two types of precipitates in both Fe-18 Ni-5Mo and Fe-18Ni-5Mo-8Co with a definite precipitate reversion taking place. They concluded that a molybdenum rich matrix precipitate was forming at low temperatures, its tendency to form increasing with molybdenum supersaturation or cobalt content. Preaging above $450^{\circ}C$ reduced the supersaturation and prevented the matrix precipitate forming, resulting in just the dislocation nucleated precipitate. However, activation energy values for the reaction, from resistivity and hardness measurements, were found to be 43 Kcal/mole and 26.3 Kcal/mole respectively. Values of n equal to $\frac{1}{2}$ at high temperatures and $\frac{1}{3}$ at low temperatures were interpreted as the thickening of plates ($n=\frac{1}{2}$) and as precipitate dissolution ($n = \frac{1}{3}$).

2.4.2. STAINLESS MARAGING STEELS

The maraging alloys discussed so far have very poor high temperature oxidation and corrosion resisting properties, which has resulted in a number of attempts to try to combine the excellent strength properties of the maraging steels with the corrosion resisting properties of the high chromium steels. The most promising results are found by starting with a basic

12% Cr steel and balancing the structure with cobalt so as to give a lath martensite, precipitation hardening being accomplished by using molybdenum to produce a series of intermetallic compounds.

One of these alloys has the basic composition Fe-12% Cr-13% Co-4% Mo 0.01%C and was chosen for the present work to study the kinetics and structural changes during transformation. The effects of the various alloy additions are given below,

Chromium 1) It is essential to impart corrosion and oxidation resisting properties. The composition can be varied only slightly since above 12% Cr δ -ferrite tends to form and below 10% the corrosion and oxidation properties are affected.

2) It is a ferrite stabiliser.

3) There is a possibility that it promotes zone formation.

Cobalt 1) The Fe-Co phase diagram has an extended austenite field which is used to balance the effect of chromium.

2) It appears to be the only alloying element which does not affect the M_s temperature^{57,58} and it only slightly alters the A_s temperature⁵⁰

3) It has a strong solid solution hardening effect as shown in Fig. 3, and is virtually absent from the precipitates

4) Co and Mo have been shown to produce an additional hardening effect in the Fe-Ni maraging alloys. This effect could also be present in the stainless type of alloy.

5) It has been reported to lead to ordering⁵⁹

Molybdenum 1) It is a ferrite stabiliser.

2) It shows decreasing solid solubility

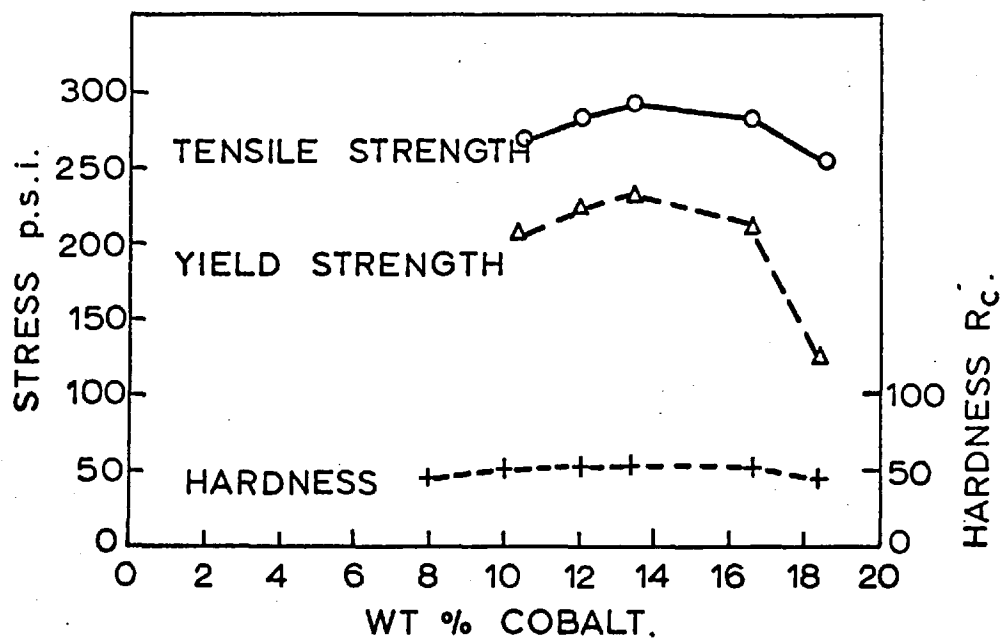


FIG.3. Variation of cobalt on the properties of 0.15% C 14% Cr 0.4% V 5% Mo Steel⁶³

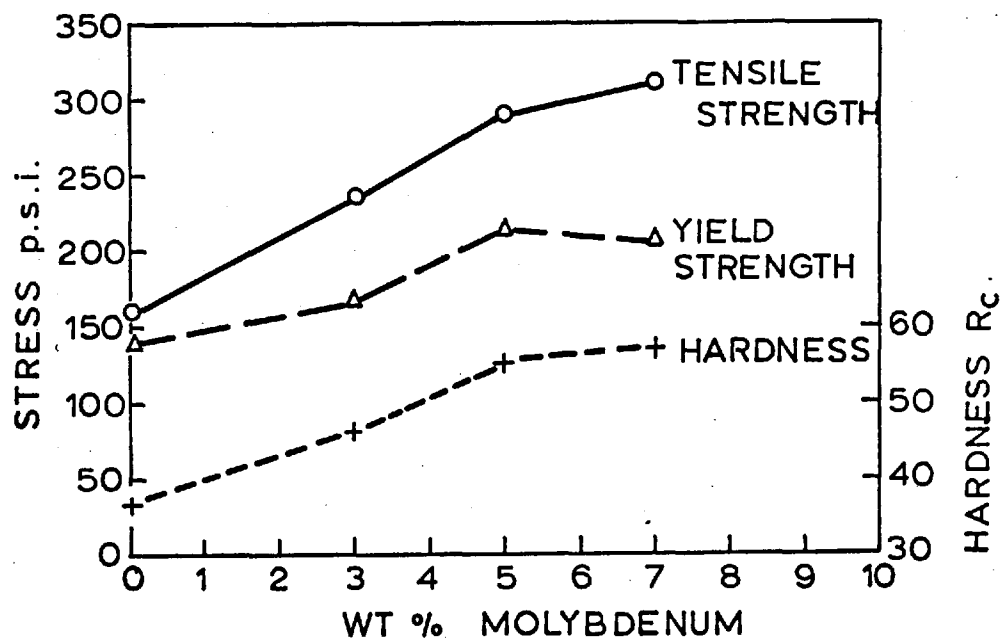


FIG.4. Variation of Molybdenum on the properties of 0.15% C 14% Cr 0.4% V 13% Co Steel⁶³

and is known to form intermetallic compounds with Fe, Cr and Co.

3) It shows good substitutional solid solution hardening.

4) There appears to be an optimum amount of molybdenum in these alloys. Fig. 4.

Low Carbon

1) To form lath martensite and to keep the matrix ductile

2) It is not needed as a precipitate forming agent

3) This avoids problems due to decarburisation and in welding.

This alloy can be cooled relatively slowly to produce a lath type martensite, but a refrigeration treatment is given to provide the maximum amount of transformation to martensite. The equilibrium structure both at room temperature and ageing temperatures appears to be ferrite and intermetallic compounds as no austenite is formed even after prolonged ageing treatments at 700°C.

The precipitate identification is in even more doubt than that of the Fe-Ni maraging alloys. Once more the trouble lies in the size of the precipitate particles at peak hardness and in the number of precipitate types with very similar "d" spacing. West⁶⁰ has reviewed the constitution of this type of alloy and the likely precipitates are listed below.

a) Fe₂Mo - A laves phase with C₁₄ type structure $a = 4.745\text{\AA}$, $c = 7.734\text{\AA}$ $\frac{c}{a} = 1.63061$. It has been reported in Fe-Ni based alloys, in 12% Cr steels^{62,79}, in Fe-14Cr-15Co-5Mo⁶³ and in Fe-13Cr-10-20Co-0-8Mo⁶⁴.

b) Sigma - A tetragonal structure with $a = 8.8\text{\AA}$ $c = 4.5\text{\AA}$ $\frac{c}{a} = 0.51$. This phase appears in binary

Fe-Cr, Co-Cr, Co-Mo, ternary Fe-Cr-Mo, Fe-Cr-Co, Co-Cr-Mo and complex alloys. It was reported after 500 hours at 600°C in Fe-13Cr-20Co-2Mo⁶⁴.

c) Chi - A complex b.c.c. structure isomorphous with α Mn. $a = 8.920\text{\AA}$. Kasper⁶⁵ has shown it to occur in the Fe-Cr-Mo system and to contain 58 atoms per unit cell, $\text{Fe}_{36}\text{Cr}_{12}\text{Mo}_{10}$. It has been identified in a number of alloys in the higher temperature range^{63,64,66}.

d) R - A hexagonal structure $a = 10.903\text{\AA}$ $c = 19.342\text{\AA}$ $\frac{c}{a} = 1.77$ with 159 atoms per unit cell⁶⁷. This phase has been reported as stable at high temperatures in the Fe-Mo system⁶¹, as well as in Cr-Mo-Co⁶⁸. Recent work by Dyson and Keown⁶⁹ has shown the R phase to be present in an Fe-12Cr-10Co-6Mo-0.1C steel.

e) Fe_3Mo_2 , Fe_7Mo_6 - these were tentatively identified by early workers as occurring in Fe-Mo, Fe-Mo-Cr and Fe-Mo-Cr-Co systems⁶²

f) Cr rich zones - Zones of Cr rich ferrite have been reported by several investigators in Fe-Cr alloys and it is believed to give rise to the 475°C embrittlement. In general, spherical zones have been found in Fe-Cr alloys in the range 10.5-50% Cr aged at temperatures up to 500°C^{70,71} Lagneborg⁷² working on Fe-30% Cr showed that at 550°C disc shaped particles were formed while at 475°C they were spherical. The difference, he suggests, is due to the lower ageing temperature being within a spinodal.

Zones have also been reported in more complex alloys. Abson⁷³ reported them in a martensitic Fe-15Cr-20Co alloy aged at 500°C and 550°C and in a ferritic Fe-15Cr-20Co-8Mo alloy aged at 550°C. Coutsouradis et al⁶⁴ showed a spherical precipitate in Fe-10-20Co-13Cr and Fe-10-20Co-13Cr-0-8Mo alloys aged at 500°C and 600°C; although they were not

identified it is possible that they were Cr-rich zones

g) Mo rich zones - Hornbagen⁷⁴ has reported the formation of Mo-rich zones on collapsed vacancy clusters in a Fe-20 at % Mo alloy aged at 500°C. He showed that they were discs with a 100 habit plane. Work on Fe 12at% Mo alloy by Higgins and Wilkes⁷⁵ showed Mo-rich zones forming during the initial stages of ageing in the range 525°-575°C. Abson⁷³ also reported their occurrence in an Fe-15Co-18Mo alloy aged at 500°C.

As can be seen, the range of possible precipitates is quite large and great care must be taken before a definite identification can be made.

Structural observations, by electron microscopy, of stainless maraging alloys have shown a very dense precipitate dispersion with some precipitation on sub-grain boundaries. In certain cases two types of precipitates were observed, one spherical which was identified as intermetallic compound and the other ribbon-shaped which was explained as being a carbide^{69,63}. The work by Coutsouradis et al⁶⁴ showed an even more complex series of precipitates starting with spheres, less than 100Å in diameter, which were found to increase in size and volume fraction with increase in cobalt content of the alloy. Further ageing produces a coarse spherical precipitate identified as Fe₂Mo while at higher molybdenum or higher temperatures sigma phase is formed.

The kinetics of the transformation have not been studied; however workers noted a lack of incubation period and a very rapid rise to peak properties. Diderrick, Coutsouradis and Habraken⁷⁶ suggest that the value of "n" is 0.25 and the kinetics are similar to the maraging alloys.

The mechanical properties are comparable with those for the Fe-Ni based alloys with the exception that the toughness properties are not quite as good. However, the stainless maraging alloys are able to retain these properties to higher temperatures. Typical properties are shown in Fig 5 for a commercially available alloy, AFC-77⁶³

To make the full use of this type of aged structure a detailed knowledge of the ageing characteristics must be obtained. The present research has been aimed at determining these characteristics for a particular alloy composition.

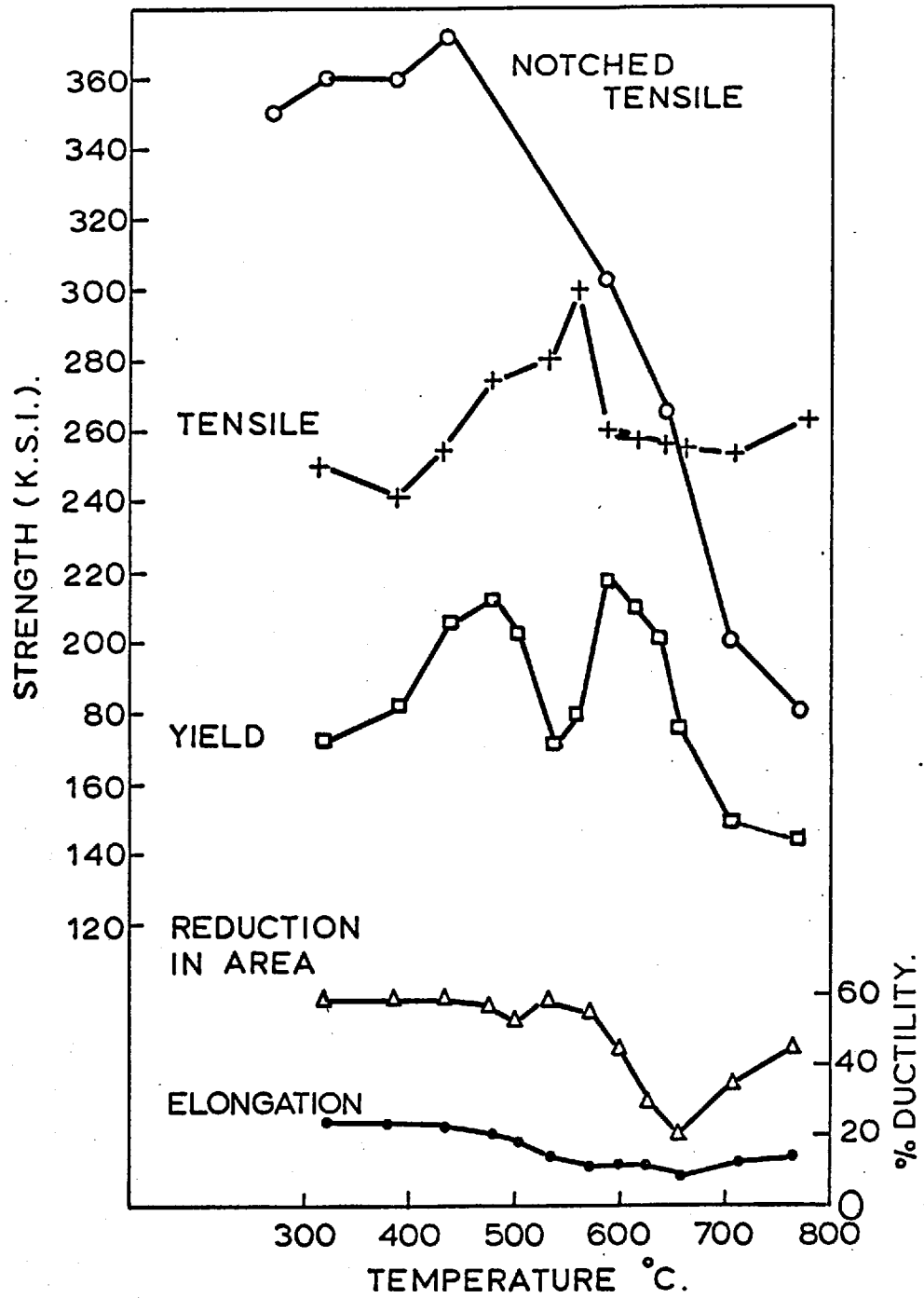


FIG.5. Properties of AFC - 77

CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1. ALLOY PREPARATION

A series of 50 gm. alloy ignots was prepared by high frequency induction melting, in order to determine the optimum composition with which to work. The requirements for the alloy were that it should be fully austenitic at a suitable solution treatment temperature and transform to martensite on quenching. It should also undergo a precipitation hardening reaction on ageing in the range 500 - 700°C.

The composition finally chosen was 13 wt % Co, 10 wt% Cr 4½ wt % Mo with the balance of Fe. A 60 lb ingot was prepared by induction melting, under vacuum, Japanese electrolytic iron, Murex high purity Cr and Mo and electrolytic cobalt.

The analysed composition of this ingot was

	Co	Cr	Mo	C	Fe
wt%	12.8	9.9	4.8	0.01	BALANCE

The ingot was forged and hot rolled to lengths of plate 4 inches wide by ¼ inch thick. Pieces of this plate were then surface ground to a depth of 0.01 inches on each side and homogenised at 1200°C for six hours before being cold rolled to 0.1 inches for hardness specimens and 0.020 inches for dilatometry and electron microscopy specimens.

3.2. HEAT TREATMENTS

Solution treatment was carried out in a vertical tube furnace employing crusilite rods as heating elements. It was found that the quenching rate was not critical but the same quenching procedure was used for all samples. The samples were sealed

in silica capsules with $1/3$ atmosphere of high purity argon. On quenching into water the capsules were broken open as soon as they were below the surface.

A solution treatment of 2 hours at $1100^{\circ} \pm 5^{\circ}\text{C}$ followed by water quenching and refrigeration at -196°C for 15 hours gave a structure which was over 95% martensite.

Ageing treatments were carried out in horizontal nichrome wound furnaces giving temperatures in the range $500-700^{\circ}\text{C} \pm 1^{\circ}\text{C}$, the specimens once more being encapsulated in silica or pyrex glass with $1/3$ atmosphere of high purity argon. Also some direct quenching experiments were carried out by replacing the water beneath the solution treatment furnace by a salt bath. Specimens without the silica capsules were suspended in the furnace in an atmosphere of argon. After solution treatment the specimens were quenched into the salt bath, held at the predetermined temperature and given the required treatment after which they were water quenched.

3.3. HARDNESS AND OPTICAL SPECIMENS

Aged samples of dimensions $\frac{1}{2} \times \frac{1}{4} \times 0.1$ inches were surface ground to remove 0.01 inches and were then polished on successive grades of water lubricated silicon carbide papers to a final 600 grade.

Hardness specimens were given a final polish on a 7 micron diamond wheel before being tested on a Vickers Diamond Pyramid hardness tester using a load of 30 Kg. An average hardness value was taken from at least 8 impressions.

Optical microscopy specimens were carefully polished on 7 and 1 micron diamond wheels before etching for 5 seconds in a solution of 30% glycerol, 30% hydrochloric acid, 10% nitric acid and 30% hydrogen peroxide. Optical micrographs were taken on a Reichert microscope.

3.4. MAGNETIC BALANCE MEASUREMENTS.

Magnetic balance readings to determine the percentage of ferromagnetic phase in a sample were obtained on a Sucksmith type balance. The samples used had the dimensions $\frac{1}{4} \times \frac{1}{4} \times 0.02$ inches.

3.5. X-RAY DIFFRACTION.

Diffraction patterns were obtained from powdered specimens by the Debye-Scherrer method using a Straumanis Camera.

Lattice parameter measurements of the alloy matrix in the solution treated and the aged conditions were determined using filings which had been annealed and then passed through a 300 mesh sieve before mounting them in a 0.3 mm glass capillary tube. As the lattice parameter was known to be approximately $2.87\text{\AA}$, nickel-filtered copper radiation was used. The resulting fluorescent radiation was removed by an aluminium foil 0.001 inches thick which was placed directly over the X-ray film.

Samples of precipitates were obtained from the matrix by electrolytic extraction in a solution of 10% hydrochloric acid in ethyl alcohol using a current density of 0.1 amp/cm^2 . The matrix was dissolved away leaving the precipitate particles to collect in the bottom of the cell. These were centrifuged and washed several times before being dried and mounted in a glass capillary tube. Vanadium-filtered chromium radiation was used and the resulting diffraction patterns were analysed using Cohen's method.⁷⁷

In all cases, except those for precipitates extracted from samples aged below 700°C , sharp lines were obtained so that an accuracy for the lattice parameters of $\pm 0.0005\text{\AA}$ could be obtained. In the remaining patterns more diffuse lines were obtained and an accuracy of only $\pm 0.01\text{\AA}$ could be achieved.

3.6 ELECTRON MICROSCOPY.

Specimens used were in the form of 3mm diameter discs which could be fitted directly into the specimen cartridge of the microscope. The discs were punched out from 0.02 inches thick sheet and then solution treated and aged. Preliminary work had shown that there was no difference in structure between specimens prepared by this method and specimens aged in hulk (e.g. 0.1 inches thick) and then thinned.

The specimens were magnetic in all conditions examined so that to reduce to a minimum the interaction with the electron beam a final specimen thickness of not more than 0.005 inches was required.

The aged discs were chemically thinned to 0.007 inches in a hot solution of 5% orthophosphoric acid, 50% hydrochloric acid, 10% nitric acid and 35% water. The specimens were then ground to 0.005 inches on 600 grade silicon carbide paper.

A two stage electro-thinning technique was employed to produce suitable foils, the first stage providing a profile on the disc. The specimen was made the anode and held in lacomited tweezers while a jet of 40% hydrochloric acid in water impinged on the side of the specimen and completed the circuit by having a stainless steel tube, as the cathode, incorporated into the jet. A jet diameter of 1 m.m. using 50 volts at a current of 0.6 amps for 8 seconds was found to give the best profile. This treatment created a depression on one side of the specimen which was then reproduced on the reverse side resulting in an outer rim of approximately 0.005 inches with a small area at the centre of less than 0.001 inches.

The second stage was the careful electropolishing to produce a small hole at the centre of the disc around which an area thin enough for study in the microscope was obtained. The electrolyte used was a saturated solution of chromium trioxide in orthophosphoric acid which was kept at 0°C. The specimen was once more held in protected tweezers and made the anode, the cathode being a pair of

stainless steel plates.

It was found that the stability of the power supply was far more important than in the jetting stage. A Heathkit transistorised regulated power supply was used at 12 volts giving a current of approximately 0.3 amps. Due to the opaqueness of the electrolyte the specimen had to be removed every 5 seconds to see whether a hole had appeared, which usually took $1\frac{1}{2}$ minutes. As soon as it had perforated, the specimen was washed thoroughly in water, distilled water and finally alcohol.

The specimens were studied in an A.E.I. E.M.6.G. electron microscope operating at 100 KV.

The disc technique was chosen in preference to a window method for several reasons.

- a) Ease of preparing and heat treating discs.
- b) The speed of preparing thin foils enabled several of the same condition to be studied in the microscope so giving a representative picture of the particular treatment.
- c) The specimens were self-supporting and so not easily deformed.
- d) The discs fitted straight into the A.E.I. specimen holder.

3.7.1. DILATOMETRY

In order to study the kinetics of the precipitation process a more accurate method, than hardness values, of following the transformation was needed. Differential dilatometry was chosen and the equipment was constructed as part of the project, a full account of which is given in the Appendix.

Dilatometry was chosen for the following reasons

- a) A definite value of 100% transformation can be obtained. Fig. 6 shows both hardness and dilatometry data plotted for the same temperature. It can be seen that peak hardness does not correspond to 100% transformation so that hardness measurements should not be used to determine fractions transformed for substitution in the Johnson-Mehl equation.
- b) The transformation can be studied using one specimen at a constant temperature. The length change is plotted continuously and there is no need to quench to some lower temperature to obtain a reading.
- c) The specimens used are in a form which can be readily prepared for examination in the electron microscope.
- d) Due to the very small length changes involved, the percentage transformation can be taken as being directly proportional to the length change.

The specimens used were in the solution treated condition having the dimensions 5 x 1 x 0.05 cms with a gauge length, between jig-drilled holes, of 4.5 cm.

3.7.2. ISOTHERMAL TREATMENTS

The change in length of a solution treated specimen on ageing at the required temperature was compared with a control specimen which was in the fully aged condition. The resulting chart recordings were transferred to percentage transformation v. $\log$ time plots from which the kinetic results were obtained.

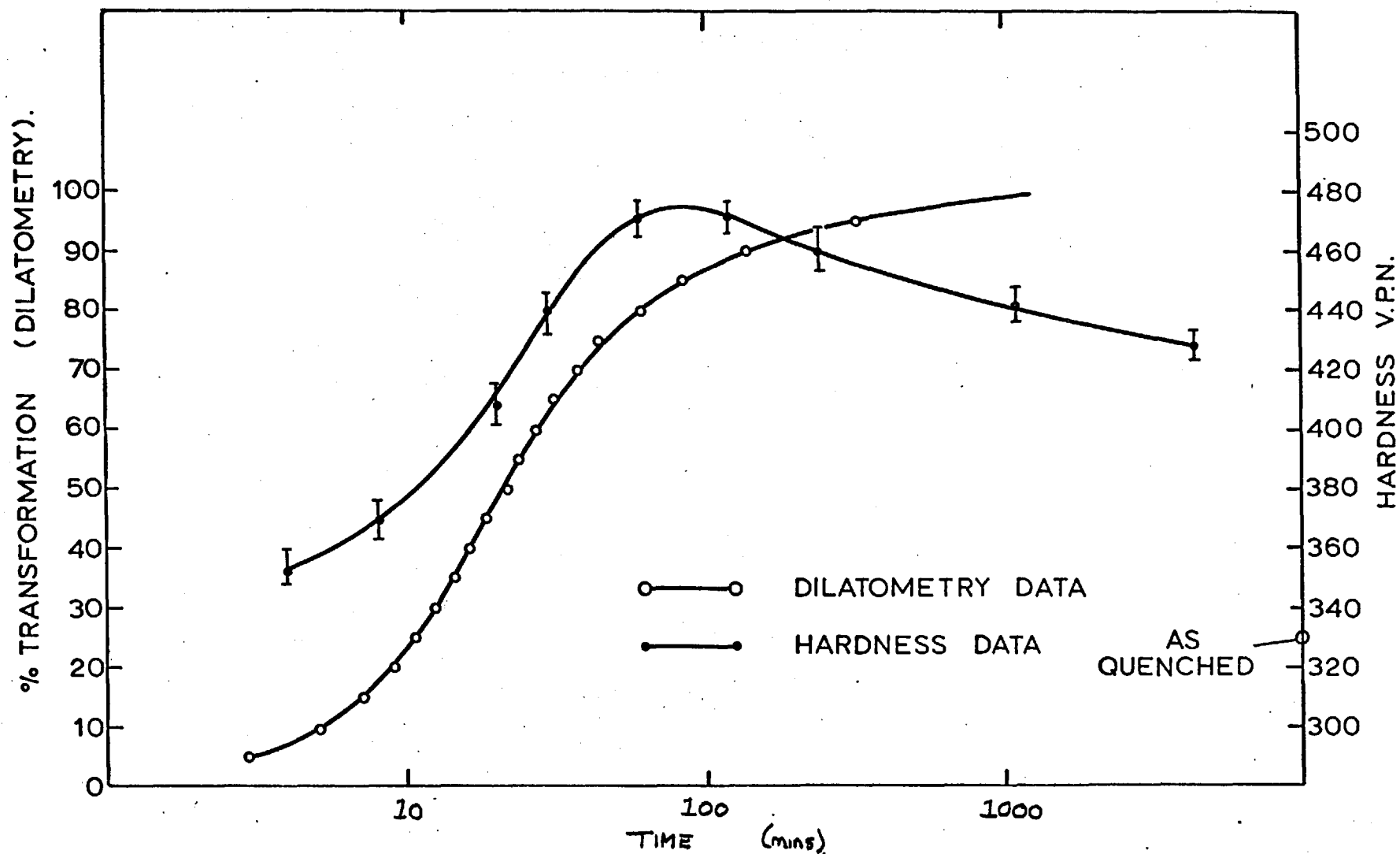


FIG.6. Ageing curves at 605°C using hardness and dilatometry data

Activation energy analysis was carried out from these plots and also from a method involving measurements of rates of transformation at two different temperatures.⁷⁸ A specimen was isothermally treated to a predetermined fraction of transformation and then the temperature was altered. Knowing the change in temperature and the rates of transformations immediately before and after the change, the activation energy after a known amount of transformation could be calculated.

3.7.3. CONTINUOUS HEATING AND COOLING

The dilatometer was set up to record the length change of one specimen as the temperature was raised and lowered. No control specimen was used so that the true length change of the specimen and the silica support rod was recorded.

CHAPTER 4

RESULTS

4.1. INTRODUCTION

The ageing results in the temperature range 500°C - 700°C for times up to 100,000 minutes will be considered in two main sections. In the first, changes in structure will be considered using the results of optical and electron microscopy, X-ray analysis and chemical analysis. The second section will then deal with the kinetics of the precipitation reaction by analysis of hardness and dilatometry data. The final part of the chapter will give the results of some direct quenching experiments.

Isochronal hardness results, Fig. 7, show that this particular alloy undergoes a precipitation hardening reaction with a 1 hour peak hardness at just over 600°C .

A. STRUCTURAL RESULTS

4.2. OPTICAL MICROSCOPY

In the solution treated condition the microstructure was typical of the lath martensite (massive martensite) structures obtained in the Fe-Ni maraging alloys. The prior austenite grains could be seen and these were divided into a number of packets which were subdivided into blocks³⁹ (Fig. 8). No definite substructure could be seen within the blocks although the etching response differed from block to block within any one packet. Microhardness tests on these areas showed that they were in fact the same phase, and the difference in etching response was due to the difference in orientation of the blocks.

On ageing to peak hardness at 550°C no change in microstructure could be observed. Overageing produced the same type of structure but it was more

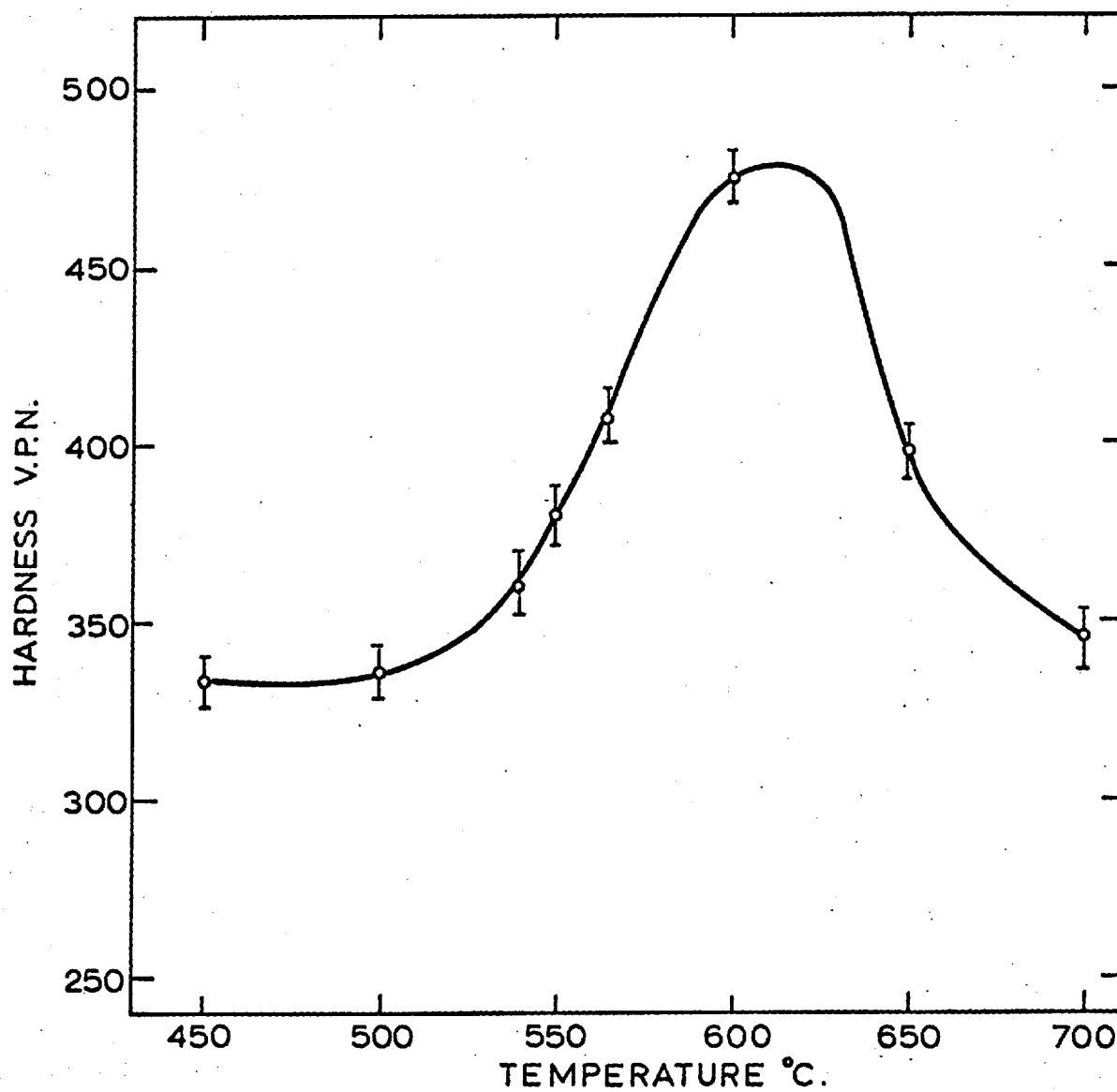


FIG.7. Isochronal ageing curve (1 hour at temperature)

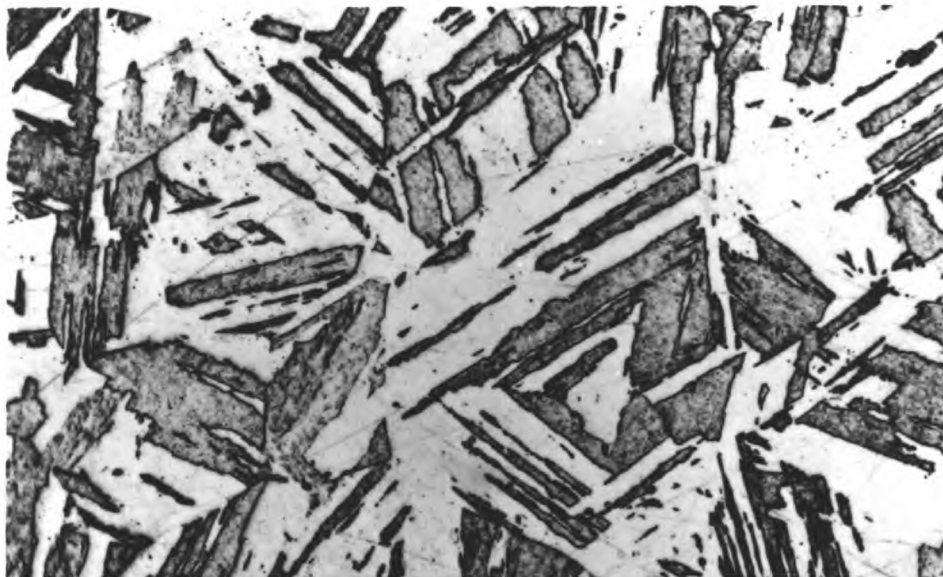


FIG 8. Solution treated 2 hrs. 1100°C + Liq. N_2 .
(X200)

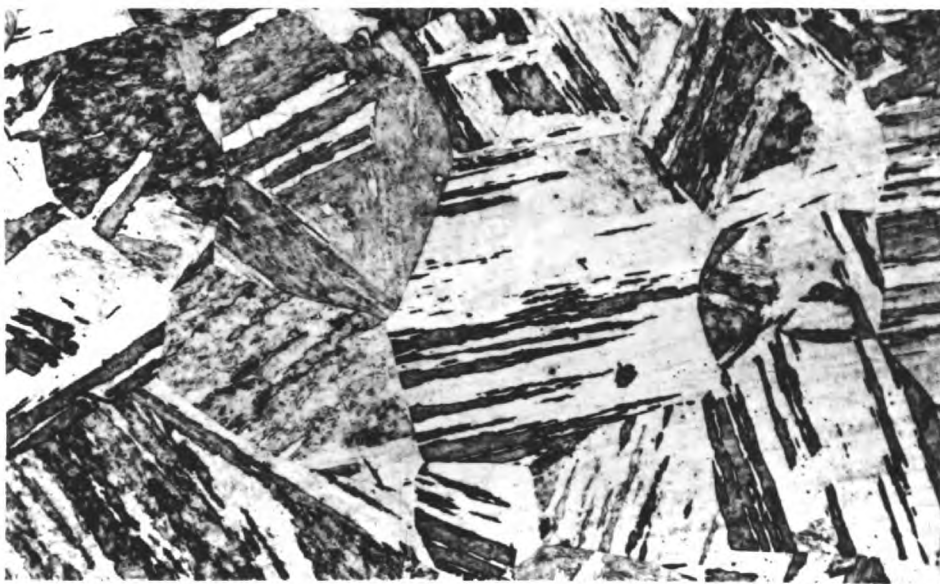


FIG 9 Solution treated 2 hrs. 1100°C + Liq. N_2
Aged 50,000 mins. at 550°C (x200)

rapidly attacked by the etching solution (Fig 9).

Raising the ageing temperature to 600°C produced no change up to peak hardness. Overageing, Fig. 10, produced darkening similar to that in the 550°C treatment and also discrete precipitate particles could now be seen. No estimate could be obtained of the particle size since the particles were still very small and the etching tended to distort their size. The particles could be seen to be distributed uniformly throughout the structure and there was no apparent preference for precipitate formation on grain boundaries or sub-grain boundaries.

On ageing at 650°C , results similar to those for 600°C ageing were obtained in the early stages; however, on prolonged overageing large particles appeared at the prior austenite grain boundaries and also at a few points within the grains. The difference in nucleating site for these large particles suggests that they could be of a different phase from that observed in the earlier stages of ageing (Fig 11).

At 700°C , ageing for short periods produced the darkening, but after 30,000 minutes, Fig. 12, the larger particles observed at 650°C were seen to occur at prior austenite grain boundaries as well as on sub-grain boundaries within the packets. Further ageing produced a decrease in the area showing the darkening while there was an increase in the size of the larger particles. After ageing for 60,000 minutes, Fig. 13, only the larger particles were visible and they were irregular in shape but of the order of 5-10 microns in size.



FIG.10 Solution treated 2 hrs. 1100°C + Liq N_2 .
Aged 30,000 mins. 600°C (x350)

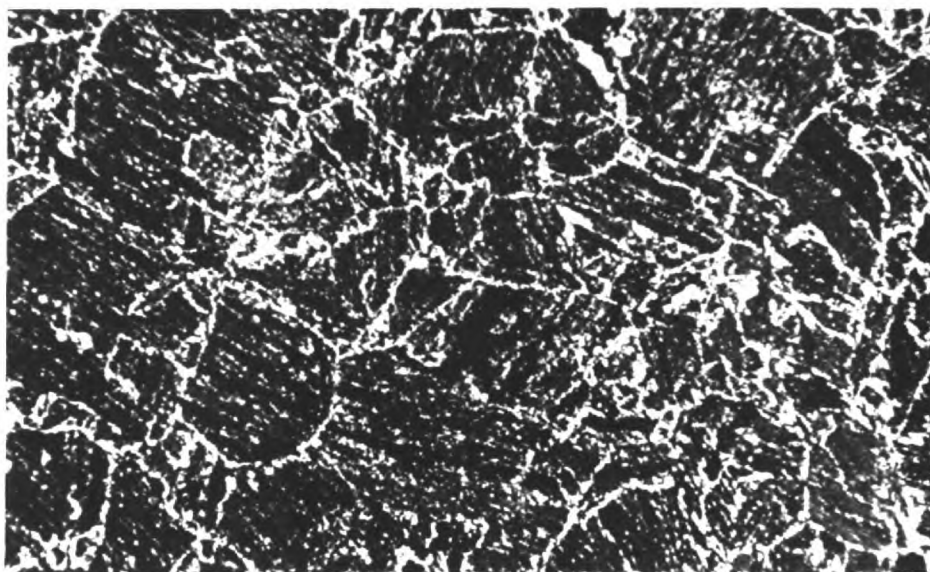


FIG.11 Solution treated 2 hrs. 1100°C + liq. N_2
Aged 9,000 mins 660°C (x350)



FIG 12 Solution treated 2 hrs: 1100°C + Liq N_2
 Aged 30,000 mins. 700°C . (x350)

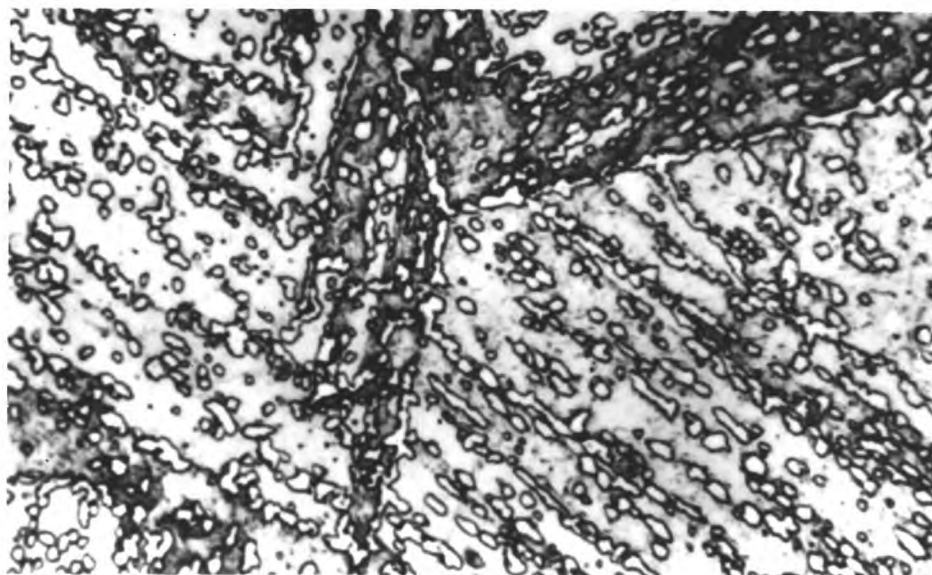


Fig 13 Solution treated 2 hrs 1100°C + Liq. N_2
 Aged 60,000 mins 700°C (x1200)

4.3. X-RAY ANALYSIS

At all temperatures, ageing to peak hardness produced precipitate particles which were of the order of 300-400 Å in diameter, which are too small to produce meaningful results from X-ray diffraction. Identification of precipitates was carried out on precipitate particles extracted from samples overaged to give a size of between 500 and 700 Å.

4.3.1. OVERAGEING AT 600°C

The resulting X-ray diffraction pattern contained 13 lines which are shown in TABLE 5. Also in this table are the values for R-phase⁶⁸ and Fe₂Mo⁷⁹. It can be seen that all the lines can be accounted for by the R-phase precipitate. The h.k.l. values were calculated and the lattice parameters were determined as $a=11.00\text{Å}$ $c=19.36\text{Å}$ $\frac{c}{a} = 1.76$.

4.3.2. OVERAGEING AT 500°C AND 550Å

Slightly broader lines were obtained for these conditions due to the smaller size of precipitate particles; also some of the weaker lines were absent. However, all the lines present could be accounted for by the R-phase identified for the 600°C treatment.

4.3.3. OVERAGEING AT 700°C

In the early stages of overageing the precipitate particles were identified as R phase. Ageing for 60000 mins produced the larger precipitate particles from which a characteristic set of diffraction lines was obtained. The d - values for these lines are given in Table 6 together with those obtained by Kasper⁶⁵ from a Chi-phase

TABLE 5 'd' SPACINGS OF PRECIPITATES EXTRACTED AFTER
AGEING FOR 1200 HOURS AT 600°C.

PRESENT WORK		R PHASE ⁶⁸		Fe ₂ Mo ⁷⁹	
"d" Å	INTENSITY	d Å	INTENSITY	d Å	INTENSITY
		2.337	30	2.385	M
		2.291	30		
		2.238	20		
		2.186	30	2.198	MS
2.177	S	2.171	100		
2.153	S	2.159	100		
2.114	MS	2.106	70		
2.051	M	2.052	70	2.060	W
2.011	MS	2.005	100	2.037	MS
1.976	M	1.987	70	2.000	MS
		1.966	70		
1.956	M	1.954	50	1.941	MW
1.889	W	1.890	20		
		1.881	30	1.374	W
		1.849	20	1.336	M+
		1.770	40		
		1.291	20	1.298	M
1.286	W	1.280	30		
1.267	S	1.268	40		
		1.263	20		
1.246	MS	1.246	20	1.240	M
1.232	S	1.231	30		
		1.219	30		
1.208	W	1.207	30		

TABLE 6 d SPACINGS FOR PRECIPITATES EXTRACTED
AFTER AGEING FOR 1200 HOURS AT 700 °C

PRESENT WORK		CH1 PHASE IN FeCrMo ⁶⁵	
d Å	INTENSITY	OBSERVED d Å	CALCULATED INTENSITY.
3.5768	VW	3.711	7.1
3.0737	VW		1.2
2.3490	MW	2.405	13.8
2.2816	W	2.239	7.8
2.0796	VS	2.112	320.0
1.9787	VW		3.4
1.8834	S	1.907	51.2
1.8081	MS	1.825	28.1
1.7323	M	1.749	10.9
1.6143	VW		1.9
1.5153	VW		3.1
1.4776	MW	1.490	7.7
1.4363	M	1.448	10.5
1.3681	W	1.376	2.3
1.3367	M	1.344	8.5
1.3108	W	1.315	1.7
1.2807	MS	1.288	16.4
1.2544	S	1.260	22.5
1.2080	VS	1.214	74.1
1.1860	M	1.192	4.7
1.1654	M	1.171	4.0

in Fe-Mo-Cr alloys. It can be seen that all the lines correspond to Chi phase, and the precipitate lattice parameter was calculated as $a = 8.8837\text{\AA}$

4.3.4. MATRIX

A powder sample of the solution treated matrix was examined by X-ray diffraction and the lattice parameter for the b.c.c. structure was found to be $2.8795\text{\AA}$.

4.3.5. MATRIX AFTER AGEING

A powder sample of alloy aged for 30,000 minutes at 550°C was examined and any diffraction from the small quantity of precipitate present was neglected. The resulting lattice parameter of the b.c.c. matrix was $2.8731\text{\AA}$.

4.4 CHEMICAL ANALYSIS

Overaged precipitate particles were extracted and analysed by an electron probe. The results are given in Table 7 together with the analyses reported for precipitates extracted from similar⁶⁴ alloys by Dyson and Keown⁶⁹ and Coutsouradis et al

The precipitate particles after ageing for 1200 hour at 700°C have been positively identified by X-ray analysis as Chi phase. Kasper⁶⁵ reports the presence of Chi phase in the Fe-Mo-Cr system and his results are from alloys of composition 56 wt % Fe, 17 wt % Cr and 27 wt % Mo, which is within the composition range for the Chi phase as reported by McMullin et al⁸² in the FeMoCr system. It could be expected that Co atoms would substitute for Fe atoms and if this were so, then the precipitate found in the present alloy could be assumed to be Chi phase.

TABLE 7

CHEMICAL COMPOSITIONS OF EXTRACTED PRECIPITATES.

ALLOY (wt%)	CONDITION	PRECIPITATE ANALYSIS				IDENTIFICATION	REFERENCE
		(ATOMIC %)					
		Fe	Cr	Co	Mo		
Fe9.9Cr,13Co4½Mo	1200 hrs 700°C	57.4	24.4	10.0	8.1	CHI	PRESENT WORK
	1200 hrs 600°C	41.4	23.2	8.0	27.5	R	
	1200 hrs 500°C	34.9	27.6	6.0	31.6	R	
Fe 11.5Cr,9.6Co 6.05Mo,0.1C.	1 hr 700°C	44.8	27.8	1.8	25.6	R	69
Fe 13Cr 20Co 2Mo	500 hrs 600°C	43.5	34.5	16.8	3.3	SIGMA	64
Fe 13Cr 20Co 5Mo	2,000 hrs 600°C	44.2	30.5	17.3	6.9	SIGMA	64

After ageing for 1200 hours at 600°C and 500°C the extracted precipitates had similar compositions to that reported by Dyson and Keown⁶⁹ which they identified as R phase. The R phase has been reported in the Cr-Mo-Co system by Rideout et al⁶⁸ who give an analysis of 22 at % Cr, 30 at % Mo and 48 at % Co. Therefore Fe and Co also appear to be interchangeable in the R phase.

In none of the three analyses do the compositions approach those reported for sigma phase by Coutsouradis et al⁶⁴ in similar alloys.

4.5. ELECTRON MICROSCOPY

4.5.1. SOLUTION TREATED CONDITION

In the solution treated condition the structure was typical of low carbon and Fe, 10-25 wt% Ni martensites. Fig. 14 shows part of a set of laths with a high dislocation density uniformly distributed. It was found that all the laths in a set had almost the same orientation; however the orientation differed from one set to another within a block.

4.5.2. AGEING AT 550°C

For all ageing times studied, including the overageing period, the lath sub-boundaries were still present even though there was no sign of preferential precipitation upon them. As far as it is possible to tell the dislocation density remains fairly constant until all the transformation has occurred, and it is only in the overaged condition that a definite decrease in density is observed.

Precipitates are first seen after approximately 120 minutes ageing, which, from dilatometry corresponds to approximately 20% transformation.

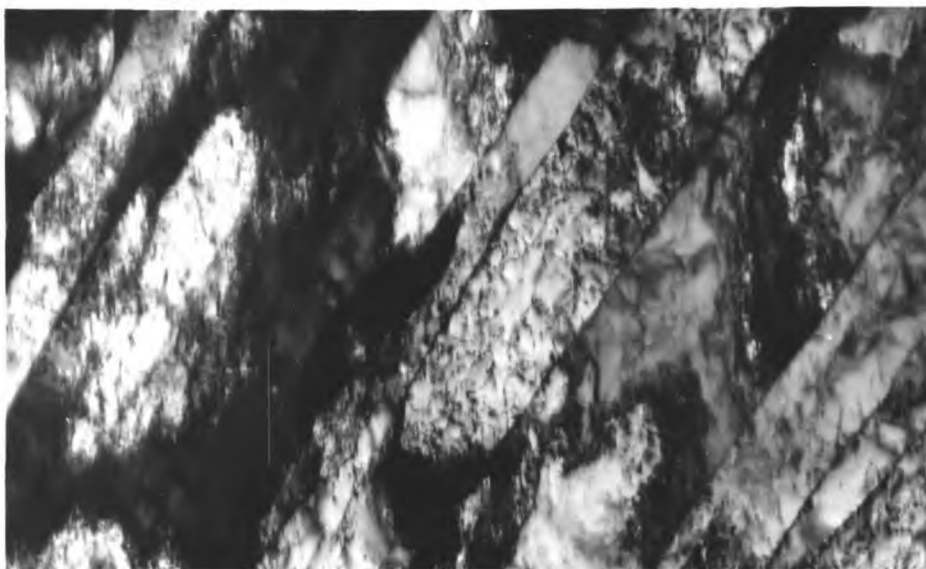


Fig 14 Solution treated 2 hrs 1100°C + Liq N_2
(x45,000)

Figs 15,16 and 17 show the precipitates after ageing for 180 minutes (35% transformation) and it can be seen that they nucleate on dislocations. The dark field micrograph shows that the precipitates appear in the form of rods approximately $120\text{ }\overset{\circ}{\text{A}}$ long by $50\text{ }\overset{\circ}{\text{A}}$ in diameter.

After 300 minutes ageing (50% transformation) a spherical precipitate was also seen which grew on further ageing while fewer rod-shaped precipitates were observed, possibly due to the re-resolution of rods or due to them changing shape. Figs 18 and 19 show both types of precipitates, and after ageing for 1200 minutes (85% transformation) the spheres have reached a size of $300\text{--}400\text{ }\overset{\circ}{\text{A}}$ while the remaining rods are approximately $500\text{ }\overset{\circ}{\text{A}}$ long by $125\text{ }\overset{\circ}{\text{A}}$ in diameter.

In the overaged condition, Fig 20, no rod shaped precipitates were observed, the only ones present being spherical. The number of precipitate particles has also decreased due to coarsening, which results in an average particle diameter of the order of $700\text{ }\overset{\circ}{\text{A}}$.

4.5.3. AGEING AT 600°C

The precipitation sequence at 600°C is similar to that at 550°C . Fig 25 shows precipitates nucleated on dislocations after 20 minutes ageing (30% transformation) and they appear to be rod shaped. Figs. 23 and 24 show the selected area diffraction patterns from the bright field micrograph, Fig. 21; the operating reflection producing Fig. 22 can be indexed assuming that the precipitate is R phase.

After 40 minutes ageing (65% transformation) the spherical precipitates were present and Fig. 26 shows a dark field micrograph with both spherical



FIG 15 Solution treated,
aged 180 mins 550°C
(35% transformation)
(x13,000)

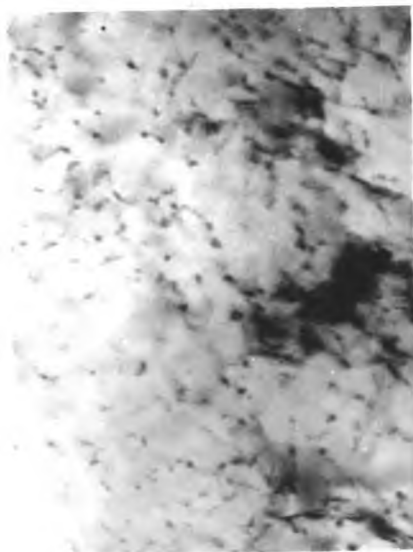


Fig 16 Solution treated
aged 180 mins 550°C
(35% transformation)
(x90,000)



FIG 17 Dark field micrograph
of Fig. 16.

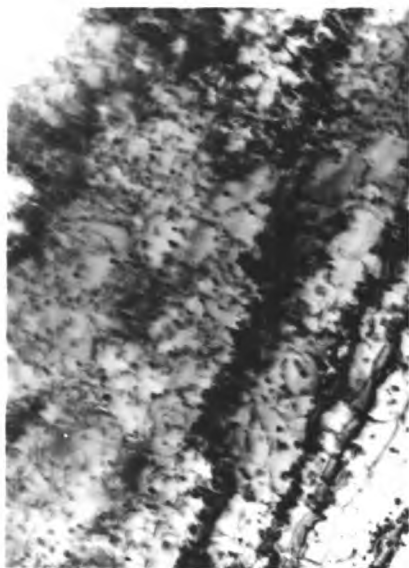


Fig 18 Solution treated,
aged 300 mins.
550°C (50% transformation)
(x45,000)

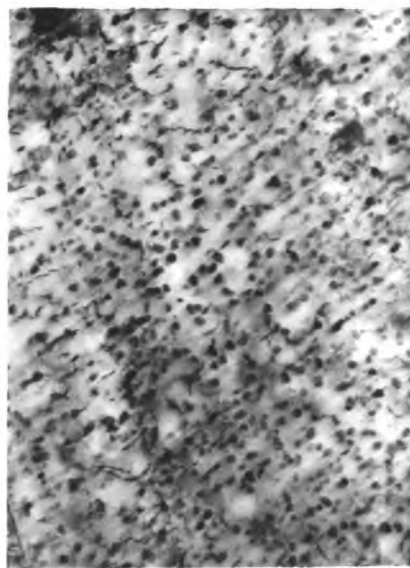


Fig 19 Solution treated
aged 1200 mins
550°C (85%
transformation)
(x45,000)



Fig 20 Solution treated
aged 12000 mins
550°C (x45,000)

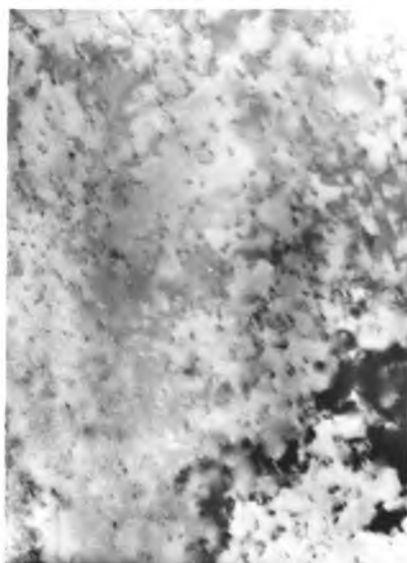


FIG 21 Solution treated,
aged 20 mins 600°C
(30% transformation)
(x45,000)

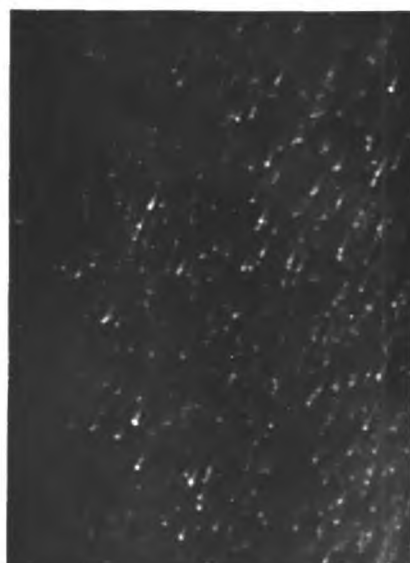


FIG 22 Dark field
micrograph of
Fig 21 .



FIG 23 Selected area
diffraction pattern of
Fig 21.

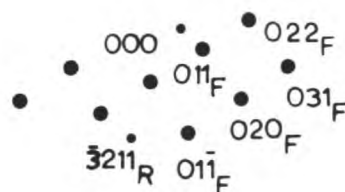


FIG 24 Schematic representation
of Fig 23.

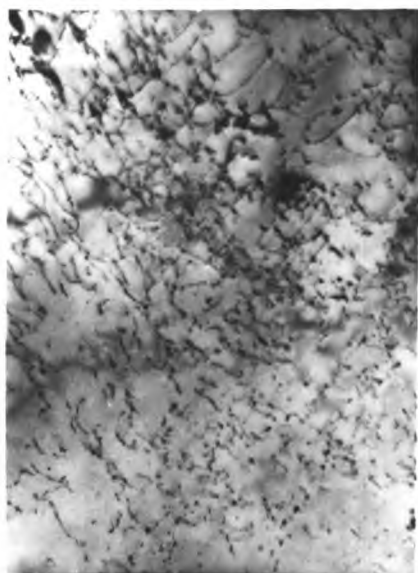


Fig 25 Solution treated aged
20 mins 500°C
(30% transformation)
(x45,000)



Fig 26 Dark field micrograph
of specimen solution
treated, aged 40 mins
 600°C
(65% transformation)
(x45,000)

and rod shaped precipitates visible. The same type of structure was seen after 60 minutes ageing (80% transformation) i.e. Figs 27 and 28; the dark field micrograph was taken using only one reflection and once more both types of precipitates were present. In Fig 29 another view of the structure is shown, the spheres being approximately $400\text{\AA}$ in diameter and the rods approximately $500\text{\AA}$ by $125\text{\AA}$. The corresponding diffraction pattern is given in Fig 31 and the precipitate spots can be indexed assuming them to be from R phase. Fig 30 shows a dark field micrograph from one spot and it can be seen that both spherical and rod shaped precipitates give rise to the same reflection. A general view of the structure at low magnification is given in Fig 33 and the lath boundaries were still present even though there was still no sign of preferential precipitation upon them nor on prior austenite grain boundaries.

In the overaged condition, 24,000 minutes ageing, the rod shaped precipitates have completely disappeared leaving the spherical precipitates which have coarsened; also a decrease in the dislocation density was observed, Fig 34. The precipitates are now of the order of $750\text{\AA}$ in diameter and examination at high magnification, Fig 35, reveals dislocations associated with them.

At both 550°C and 600°C no evidence of clustering was observed in the early stages of ageing. The arcing observed in some diffraction patterns was found to be due to the formation of an oxide on the surface of the thin foil during preparation.

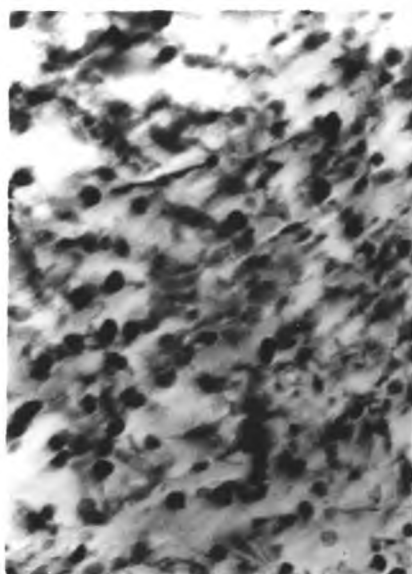


FIG 27 Solution treated,
aged 60 mins 600°C
(80% transformation)
(x90,000)

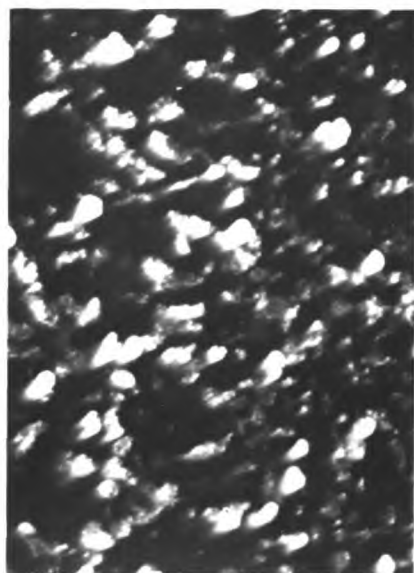


FIG 28 Dark field
micrograph of
Fig 27 using
a precipitate
reflection
(x90,000)

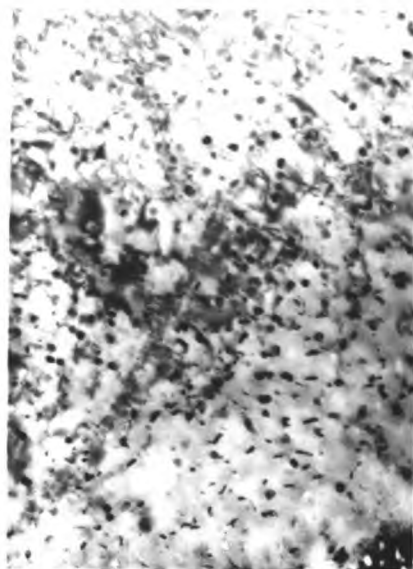


FIG 29 Solution treated, aged 50 mins, 600°C. (80% transformation) (x45,000).



FIG 30 Dark field micrograph of FIG 29 using precipitate reflection (x45,000).



FIG 31 Selected area diffraction pattern of Fig. 29.

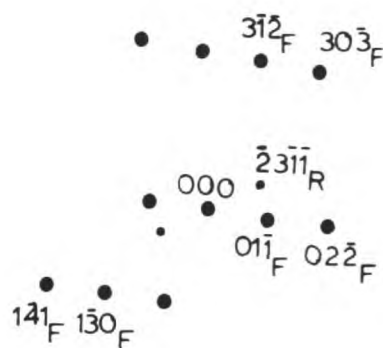


FIG 32 Schematic representation of FIG 31.



FIG 33 Solution treated aged
60 mins 600°C
(80% transformation)
(x13,000)

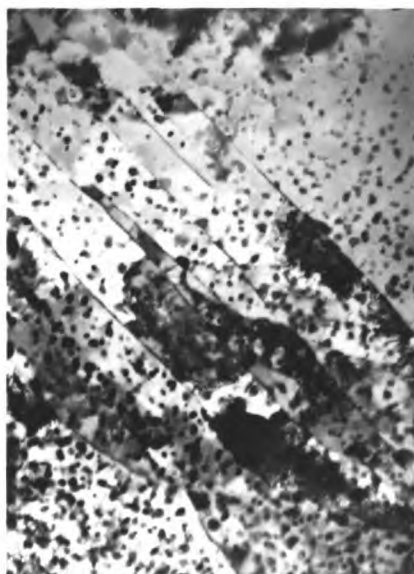


FIG 34 Solution treated
aged 24,000 mins
 600°C (x24,000)

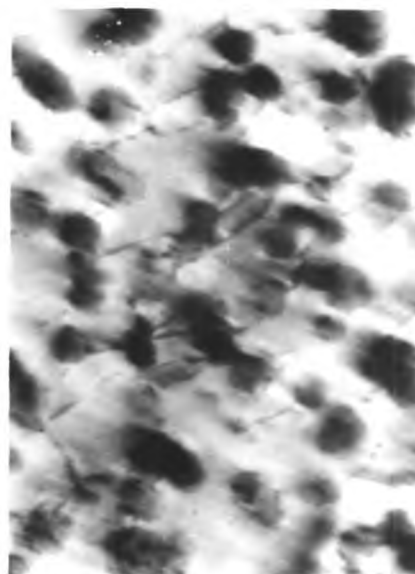


FIG 35 Solution treated
aged 24,000 mins
 600°C (x150,000)

4.5.4. AGEING AT 700°C

Even after very short ageing times at 700°C no rod shaped precipitates could be seen, only spherical ones which had coarsened considerably in times as short as 20 minutes.

Figs 36,37,38 and 39 show a series of micrographs of the structure after ageing for 60 mins; the precipitates are identifiable as R phase and they are approximately 1000Å in diameter. In certain small areas recovery of the dislocation structure had taken place and dislocation networks were visible, Fig. 40.

The precipitates after 1200 minutes ageing were of the order of 1200Å in diameter and it was just possible to obtain single crystal diffraction patterns from an individual particle. These patterns always contained spots which were very close together and there was always more than one zone present. This indicated that the lattice parameter of the precipitate was very large, and in fact all the spots could be indexed assuming the phase to be R. One such pattern is shown in Fig. 43 along with the indexed pattern Fig. 44 and the bright field image, Fig. 42.

Also after 1200 minutes ageing more general recovery had taken place, Fig 41, but more significant is the appearance of another phase. The new phase appears on sub-grain and grain boundaries in regions where a certain amount of recovery had taken place and also in which some of the R phase precipitates had redissolved. An example is shown in Fig. 45 and selected area diffraction enabled the precipitates to be identified



FIG 36 Solution treated
aged 60 mins
700°C (x45,000)

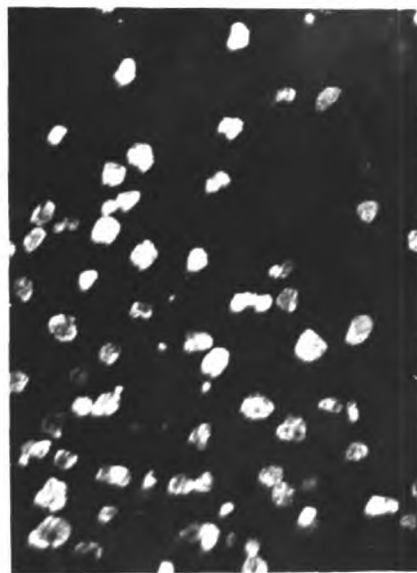


FIG 37 Dark field micrograph
of Fig 36
(x45,000)

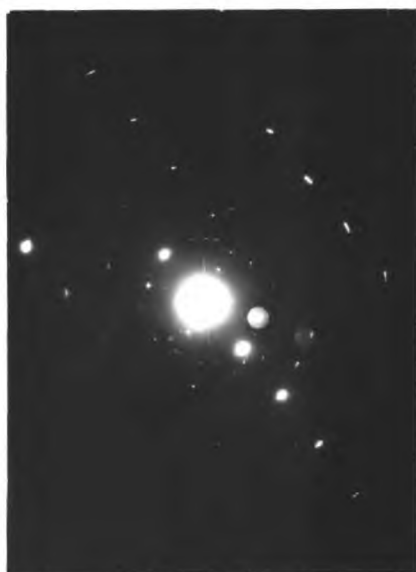


FIG 38 Selected area
diffraction
pattern of
Fig 36.

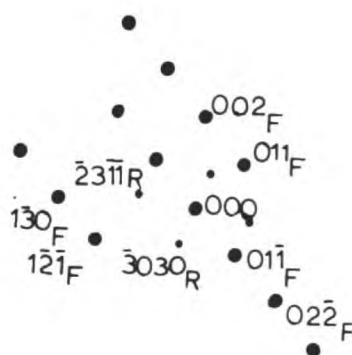


FIG 39 Schematic representation
of Fig 38.

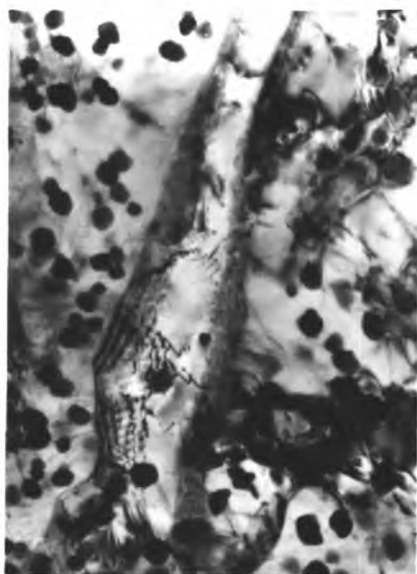


FIG 40 Solution treated aged
60 mins 700°C
(x45,000)

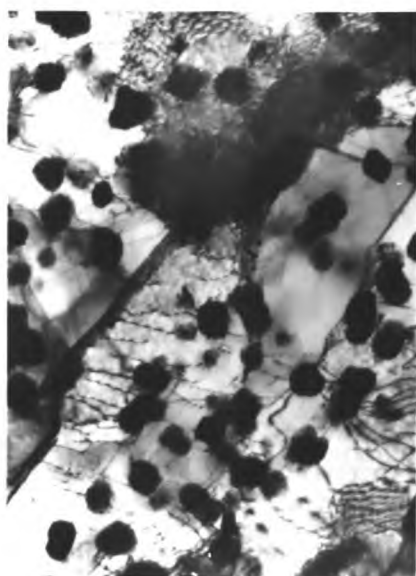


FIG 41 Solution treated, aged
1200 mins 700°C
(x45,000)

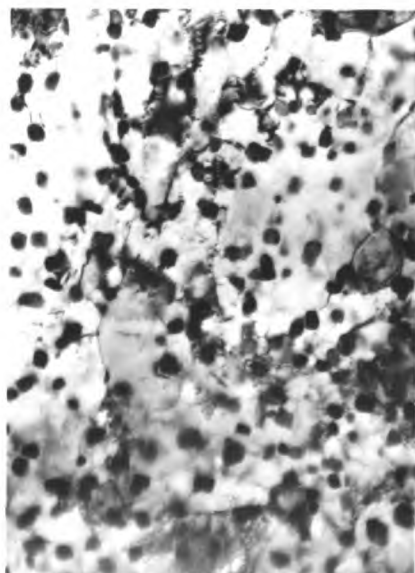


FIG 42 Solution treated aged
1200 mins 700°C
($\times 45,000$)



FIG 43 Selected area
diffraction pattern
of FIG 42

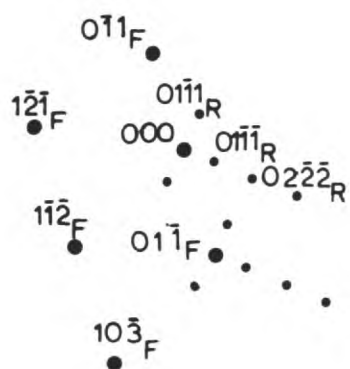


FIG 44 Schematic
representation of
FIG 43.

as Chi phase; the particle size was approximately $6500\text{\AA}$ by $2500\text{\AA}$.

Figs 46 and 47 show how the Chi phase particles grow while the R phase precipitates dissolve. Therefore in one specimen there will be chi phase particles surrounded by a small region of recovered matrix which itself is surrounded by areas of high dislocation density containing R phase precipitates.

After ageing for 60,000 minutes, Fig 48, all the R phase had dissolved leaving Chi phase precipitates on the boundaries; the particles were still irregular in shape and varied in size from $5000 - 10,000\text{\AA}$. The matrix had recovered, consisting of extensive dislocation networks and also some movement of sub-grain boundaries had occurred.

Figs 49, 50, 51 and 52 show two of the diffraction patterns from which the matrix-precipitate orientation was obtained. The orientation relationship was found to be

$$[111]\text{ferrite} \parallel [111]\text{chi}$$

$$(10\bar{1})\text{ferrite} \parallel (1\bar{1}0)\text{chi}$$

$$(\bar{1}\bar{1}0)\text{ferrite} \parallel (0\bar{1}1)\text{chi}$$

4.6. M_s AND A_s VALUES

The length changes on heating a specimen up to 900°C and cooling to 100°C were recorded in the dilatometer. With a heating rate of $2^\circ\text{C}/\text{min}$ there was a continuous increase in length up to $777^\circ\text{C} \pm 1^\circ\text{C}$ at which point a rapid decrease in length, corresponding to the transformation to austenite, occurred. This was completed at approximately 800°C and from this temperature up to 900°C an increase in length was noted. The



FIG 45 Solution treated,
aged 1200 mins.
700°C (x45,000)

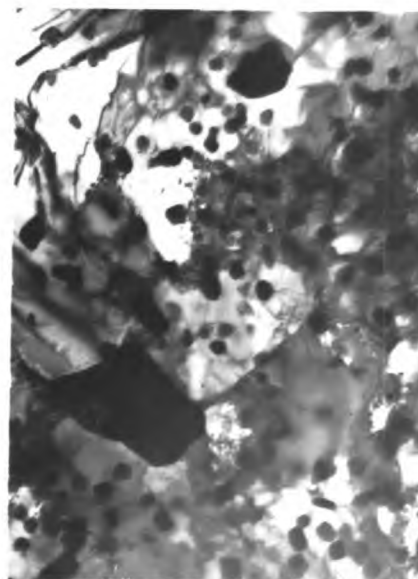


FIG 46 Solution treated,
aged 3000 mins 700°C
(x24,000)



FIG 47 Solution treated
aged 60,000 mins
700°C (x24,000)



FIG 48 Solution treated,
aged 60,000 mins
700°C (x24,000)



FIG 49 Solution treated aged 50,000 mins 700°C . Selective area diffraction pattern.

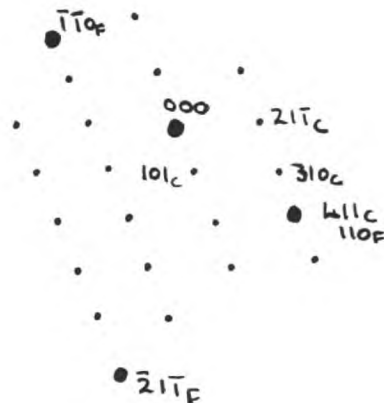


FIG 50 Schematic representation of Fig. 49



FIG 51 Solution treated aged 50,000 mins 700°C . Selective area diffraction pattern.

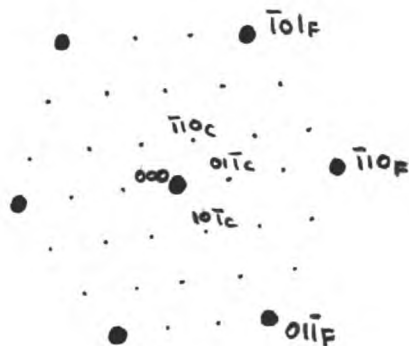


FIG 52 Schematic representation of Fig 51.

value of A_s was taken as $777^\circ \pm 1^\circ\text{C}$.

On cooling at $15^\circ\text{C}/\text{min}$ a steady fall in the length, due to thermal contraction, was recorded. However, at $400^\circ \pm 1^\circ\text{C}$ there was a rapid increase in the length which corresponds to the martensitic transformation. This increase in length finished at approximately 265°C ; however, magnetic balance results showed that there was approximately 10% non-magnetic phase present which was reduced to below 5% after a refrigeration treatment of 15 hours at -196°C . The M_s temperature was taken as $400^\circ \pm 1^\circ\text{C}$.

B. KINETIC RESULTS.

4.7 ISOTHERMAL HARDNESS RESULTS

Isothermal hardness curves for temperatures in the range $500^\circ\text{--}665^\circ\text{C}$ are shown in Fig. 53. They are plotted as hardness v's log time and show, as expected, curves displaced to longer times as the temperature is decreased. At 500°C and 540°C definite incubation periods are observed whereas with higher temperatures even for the shortest treatments, 4 minutes, an increase in hardness was obtained.

The solution treatment hardness was 330 V.P.N. and the approximate hardness increments to peak value were 75 V.P.N. at 665°C , 145 V.P.N. at 600°C , 155 V.P.N. at 565°C , 165 V.P.N. at 550°C , 160 V.P.N. at 540°C and 195 V.P.N. at 500°C . It is clear that there is a steady rise in the peak values with decrease in ageing temperature from $600^\circ\text{--}500^\circ\text{C}$. However, above 600°C the hardness increment falls off markedly.

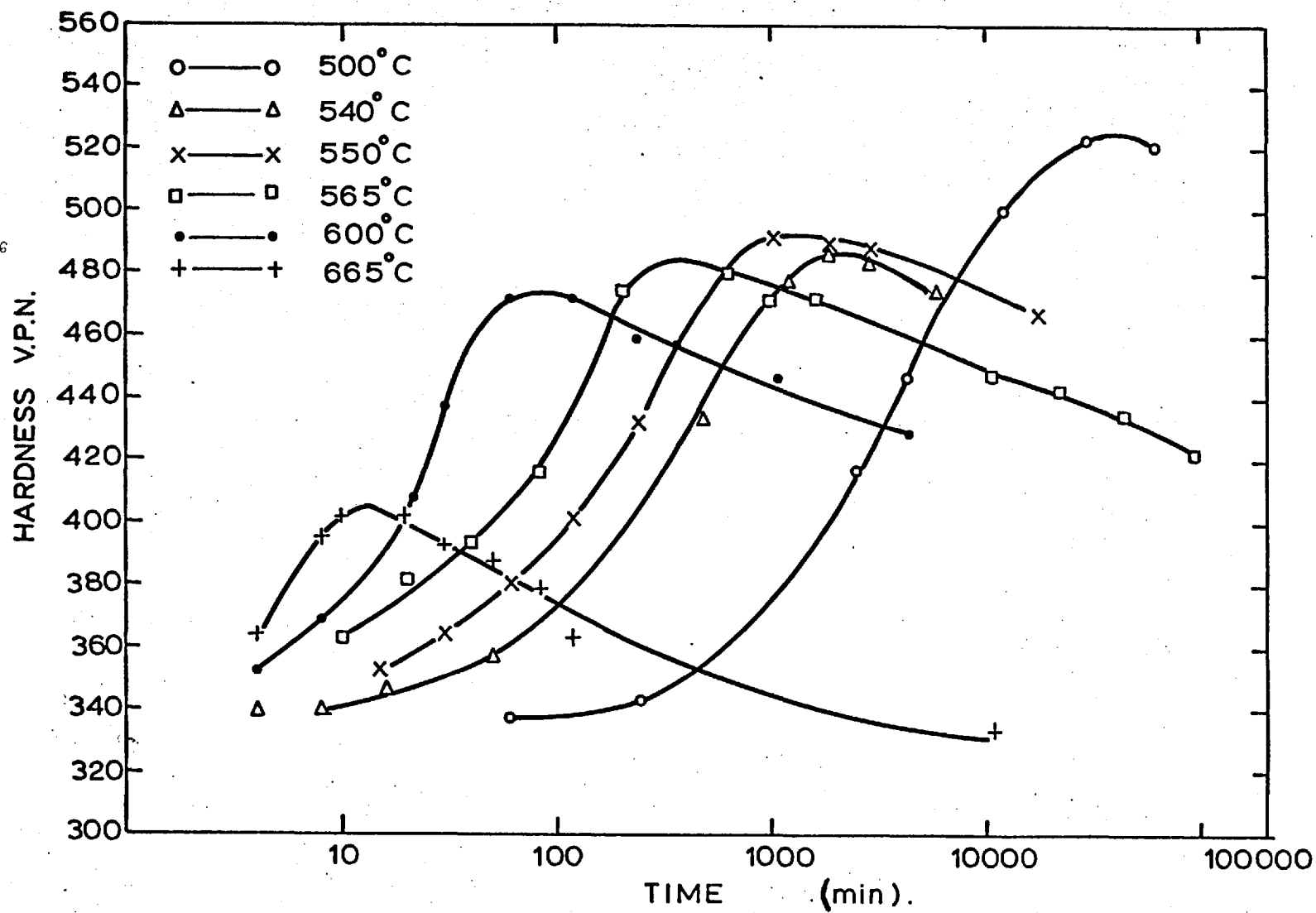


FIG. 53. Hardness curves.

Overaging at 665°C takes place quite rapidly and the hardness reaches a value of 250 V.P.N. after 50,000 minutes. No such low values are obtained at any other temperature even though overaging was taking place e.g. a value of 420 V.P.N. was obtained after ageing for 100,000 minutes at 565°C .

4.8. ISOTHERMAL DILATOMETRY RESULTS

The length change to be expected on precipitation of R phase can be calculated knowing the lattice parameters of the R phase and the matrix before and after precipitation. The following calculation assumes that 1 wt% of Mo is left in solution after ageing

Consider 100 atoms of solid solution.

a) Volume before precipitation.

Lattice parameter of solid solution = 2.8795°Å .

A unit cell of bcc ferrite contains 2 atoms
therefore

$$\begin{aligned}\text{Volume of 100 atoms of matrix} &= (2.8795)^3 \times \frac{100}{2} \\ &= \underline{\underline{1193.772^{\circ}\text{Å}^3}}\end{aligned}$$

b) Volume after precipitation = volume of matrix + volume of precipitate.

1) Volume of precipitate assuming it to be R phase.

Lattice parameter of R phase $a = 11.00^{\circ}\text{Å}$ $c = 19.36^{\circ}\text{Å}$

A unit cell of R phase contains 159 atoms.

therefore

$$\begin{aligned}\text{Volume of 1 atom of R phase} &= \frac{\text{Volume of unit cell}}{159} \\ &= \frac{\frac{1}{2} a^2 \sin 60^{\circ} \times 2c}{159} \\ &= \frac{(11.00)^2 \times \frac{3}{2} \times 19.36 \times \frac{1}{159}}{159} \\ &= \underline{\underline{12.772^{\circ}\text{Å}^3}}\end{aligned}$$

If 1 wt% of Mo is assumed to remain in solution then, taking 4.5 wt% Mo in the original solid solution, $3\frac{1}{2}$ wt % forms R phase. Taking the composition of the R phase to be that obtained by electron probe analysis on precipitates extracted after ageing at 500°C i.e. 34.9 at % Fe, 27.5 at % Cr 6.0 at % Co and 31.6 at % Mo.

Then 2.077 atoms of Mo (3.5 wt%) produce 6.583 atoms of R phase i.e. there are 2.077 atoms of Mo

2.294 atoms of Fe

0.393 atoms of Co

1.819 atoms of Cr

$$\begin{aligned}\text{therefore Volume of R phase} &= 6.583 \times 12.772 \\ &= \underline{\underline{84.078 \text{ \AA}^3}}\end{aligned}$$

2) Volume of matrix after precipitation

There are $100 - 6.583 = 93.417$ atoms of matrix remaining

$$\begin{aligned}\text{Lattice parameter of matrix (overaged at } 550^{\circ}\text{C)} \\ &= \underline{\underline{2.8731 \text{ \AA}}}\end{aligned}$$

therefore

$$\begin{aligned}\text{Volume of matrix} &= \frac{(2.8731)^3}{2} \times 93.417 \\ &= \underline{\underline{1107.766 \text{ \AA}^3}}\end{aligned}$$

$$\begin{aligned}\text{Total volume after precipitation} &= 1107.766 + 84.078 \\ &= \underline{\underline{1191.844 \text{ \AA}^3}}\end{aligned}$$

Difference in volume before and after precipitation

= Volume before - Volume after

$$= 1193.772 - 1191.844$$

$$= \underline{\underline{1.928 \text{ \AA}^3}}$$

i.e. This is a decrease in volume.

Expressed as a fractional change = $\underline{\underline{1.928}}$

$$1193.772$$

$$= \underline{\underline{0.001615}}$$

However, if ΔV is very small

$$\Delta V \approx \delta \Delta l$$

where ΔV = change in volume

Δl = change in length.

Therefore the fractional change in length = 0.000538.

Considering a specimen 45,000 microns long, the resulting change in length on precipitation would be a decrease of 24.20 microns.

Experimental length changes were in the range 19-22 microns and are decreases in length. Magnetic balance measurements and electron microscopy showed that no austenite formed in the temperature range studied so that all the length change was due to the precipitation reaction.

Any retained austenite present initially would give an increase in length on transforming to ferrite. A run was carried out at 420°C and an increase in length did occur which was found to be equivalent to approximately 3% austenite transforming to ferrite. On ageing at 500°C this reaction was completed in less than 10 minutes and so for ageing temperatures above 500°C it was assumed that the retained austenite had transformed by the time the specimen reached the ageing temperature.

Above 665°C the majority of the precipitation reaction had taken place by the time the specimen reached temperature so that no accurate information could be obtained. The lower limit on the temperature range studied, i.e. 530°C was determined by the long times needed for the transformation to take place.

It was found that the precipitation of the Chi phase, along with the dissolution of the R phase, could not be recorded since the times involved, even at 700°C, were of the order of weeks. Therefore all the kinetic

data will deal with the precipitation of the R phase only.

Isothermal curves of % transformation vs log time are plotted in Figs 54 and 55.

Those curves in the range 530° - 580° C are typical sigmoidal curves displaced to the right as the temperature falls. In all cases there is a definite incubation period ranging from approximately 2 minutes at 580° C to approximately 65 minutes at 530° C. Also marked on the appropriate curves are the times corresponding to peak hardness which in all cases occurs in the range 80-85% transformation.

The curves for the temperature range 595° - 665° C (Fig 55) show no detectable incubation periods and at higher temperatures some precipitation must take place during the heating of the specimen to the ageing temperature.

Values of fraction transformed and times were substituted in various rate equations but none were found to correspond over the full transformation. However, nearly all the theoretical rate equations can be reduced to the empirical Johnson-Mehl equation so that it was this equation which was used for the kinetic analysis. It was found to give quite a good fit up to values of 50% transformation, which is reasonable since the Johnson-Mehl equation is never accepted to hold for values approaching 100% transformation.

The equation can be written

$$y = 1 - \exp^{-(kt)^n}$$

$$\text{rearranging } \log \left(\frac{1}{1-y} \right) = \frac{1}{2.3} (kt)^n$$

$$\text{taking logs } \log \left(\log \frac{1}{1-y} \right) = n \log K + n \log t - \log 2.3$$

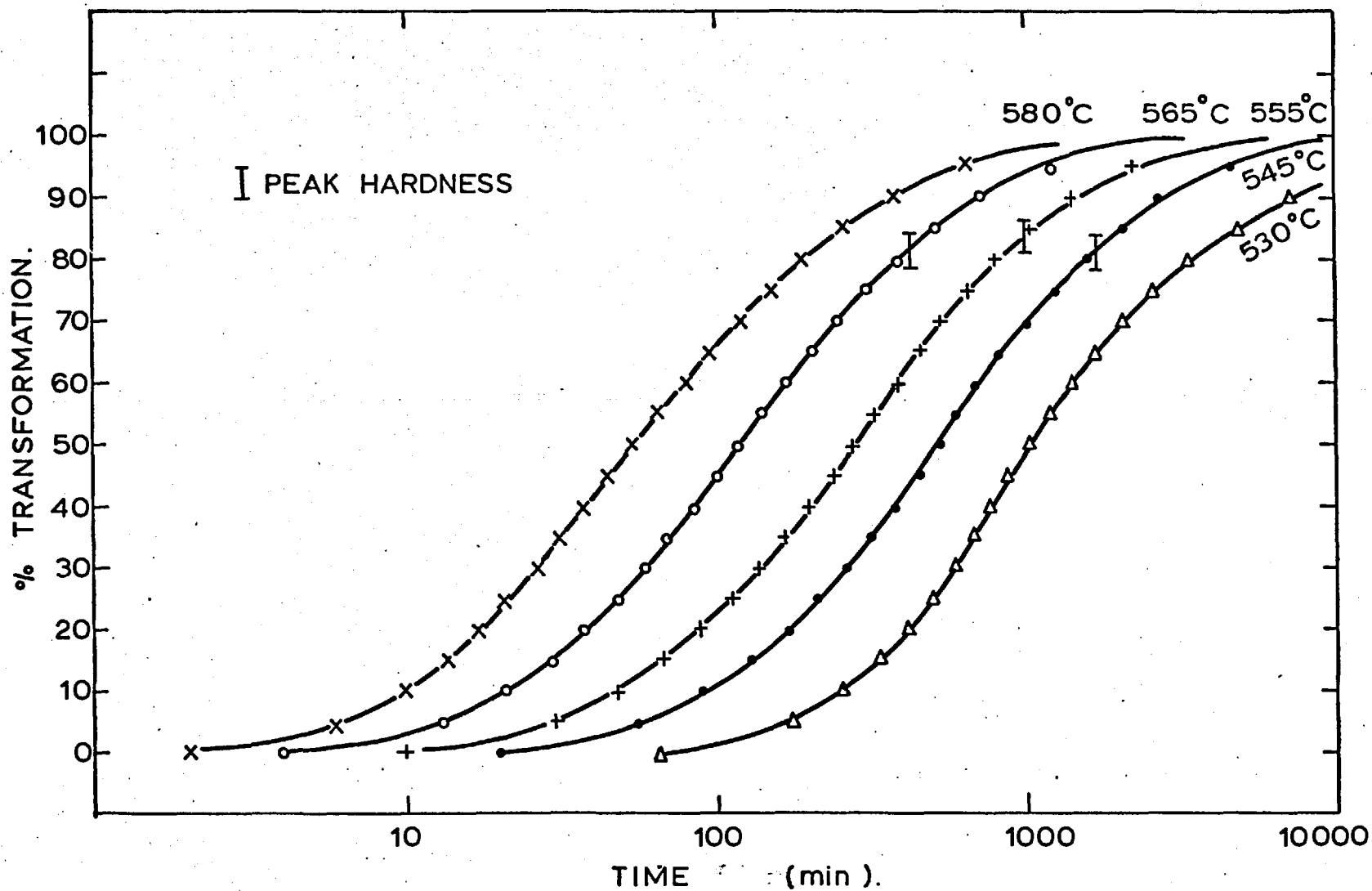


FIG. 54. Ageing curves for temperatures up to 580°C

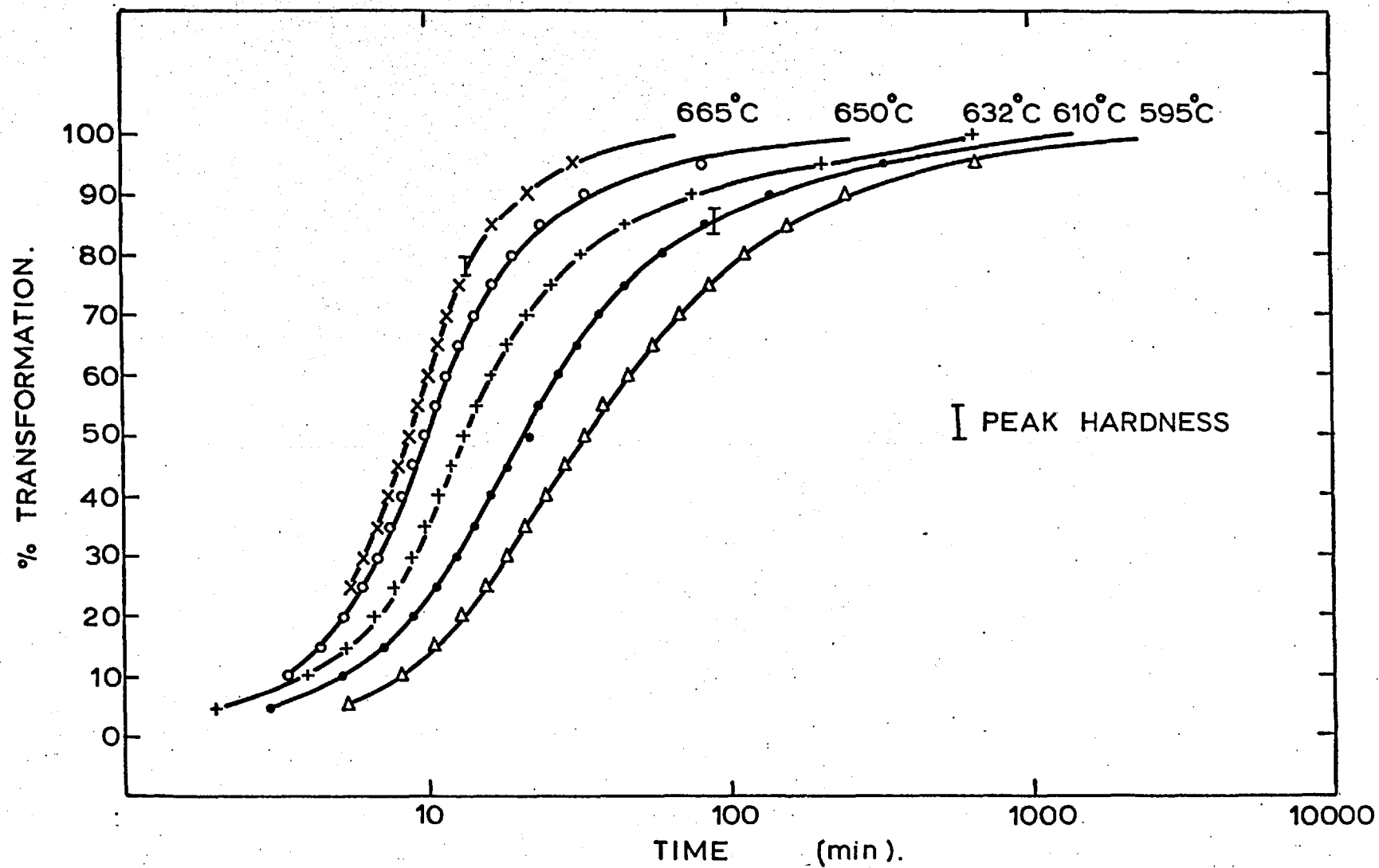


FIG.55. Ageing curves for temperatures between 595 - 665°C

On plotting a graph of $\log \left(\log \frac{1}{1-y} \right)$ vs $\log t$ the slope gives the value of "n". The value of "t" in this equation is taken from the start of transformation so that the incubation period, where appropriate, must be subtracted from the time values obtained from the % transformation vs log time plots. It is from the value of "n" that a guide to the precipitation process can be obtained.

Such plots are shown in Figs 56 and 57, from the isothermal data given in Figs 54 and 55. In all cases the plots show a linear portion from below 10% up to between 35-65% transformation. During the remainder of the transformation the slope gradually decreases to values less than 0.5. The "n" values for the initial period of transformation are given in Table 8.

It can be seen that in the temperature range 545°-580°C the "n" values are all approximately equal to 1.00 for the period up to, at the most, 45% transformation. The data at 530°C gives a higher initial slope which could be due to the uncertainty with which the beginning of transformation was determined.

The plots at higher temperatures (Fig 57) show "n" values, for the initial period, which increase with temperature from 1.19 to 2.00. The range over which "n" is constant is also greater than that for the lower temperature range, being at least 55%.

4.9. ISOTHERMAL DILATOMETRY RESULTS ON PREAGED SPECIMENS.

In order to see whether nucleation plays an important role in the kinetics of the early stages of precipitation three dilatometry runs were performed using samples in which a constant number of stable

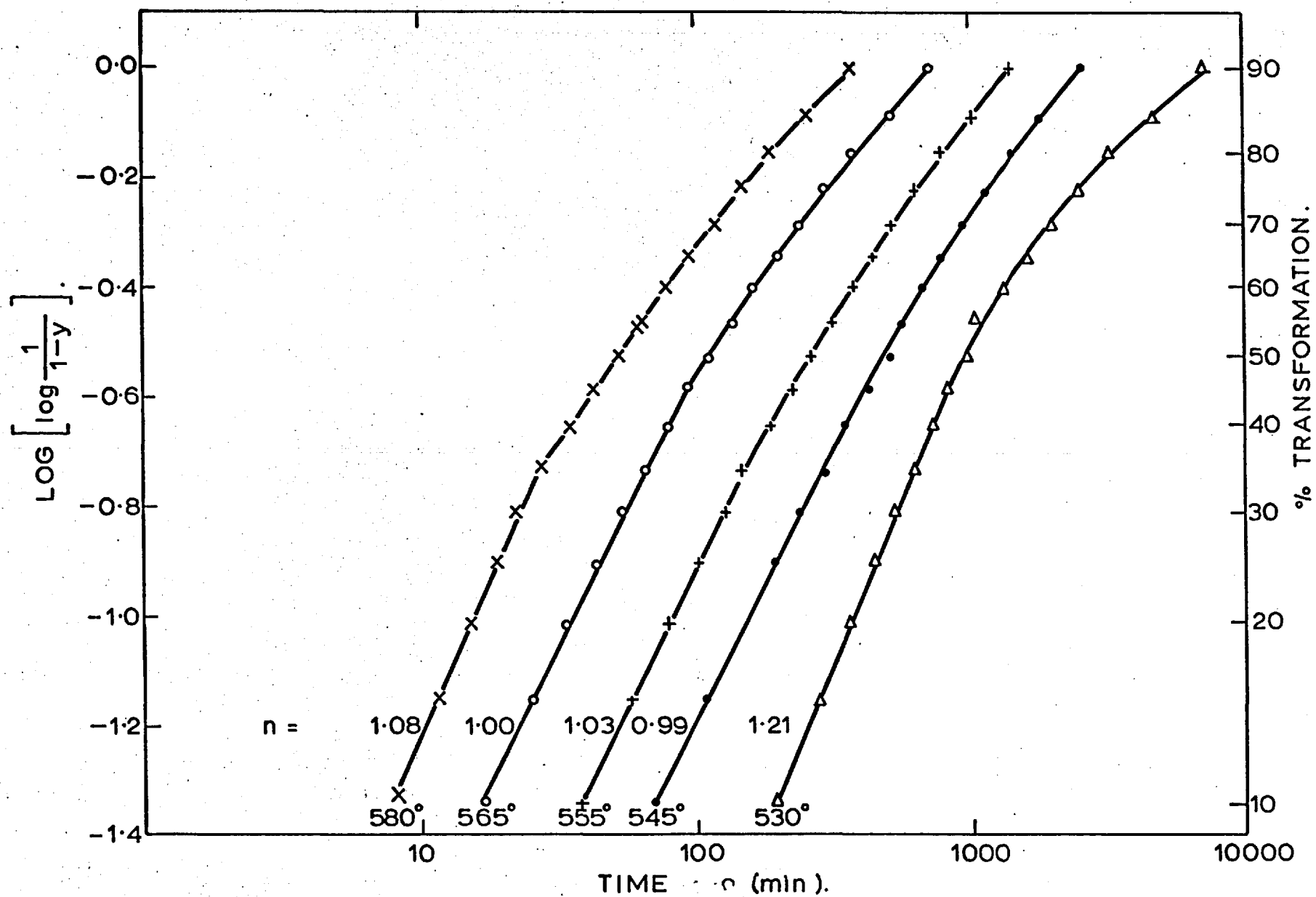


FIG.56. Derived log plots for ageing temperatures up to 580°C

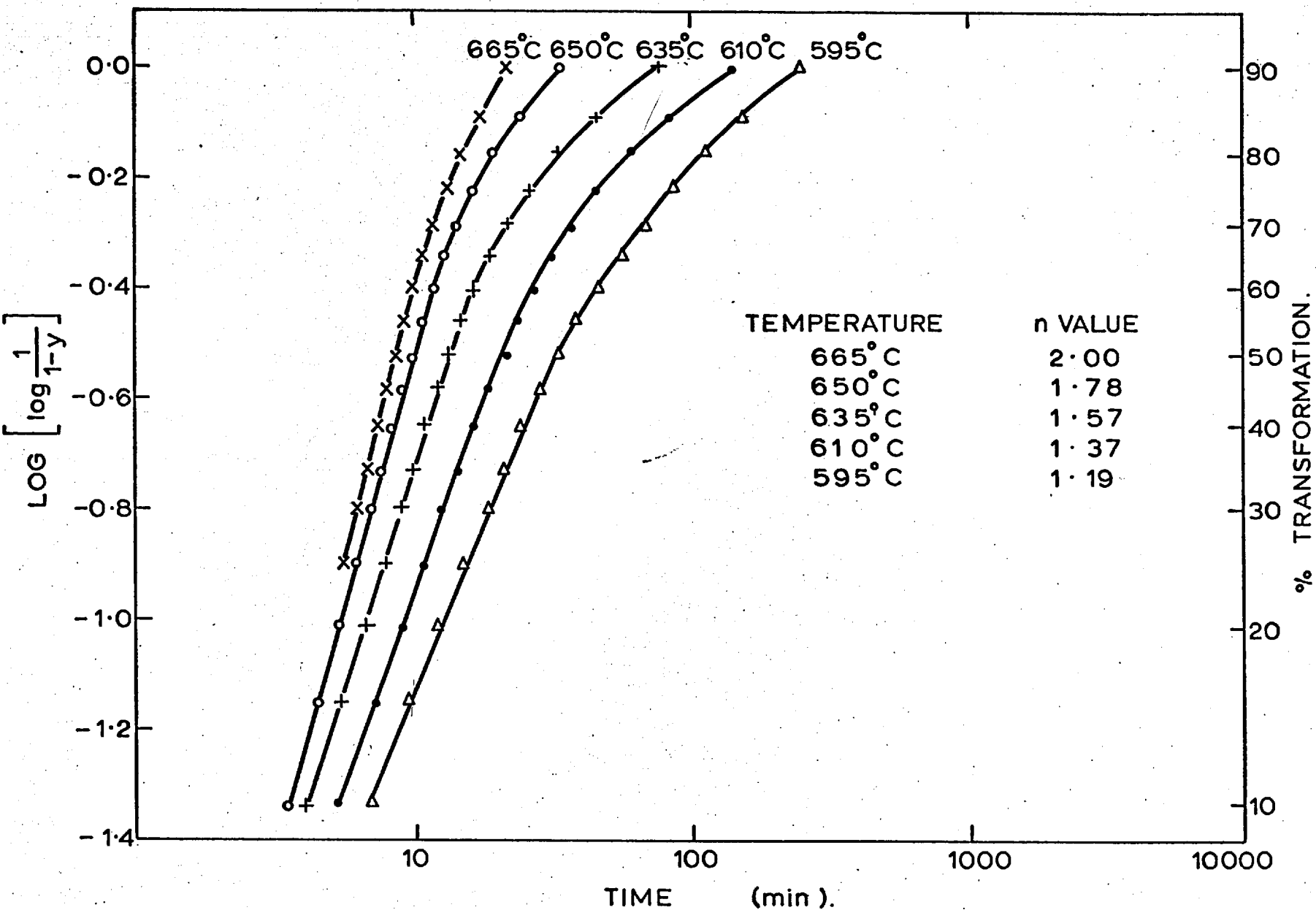


FIG.57. Derived log plots for ageing temperatures between 580 - 665°C

TABLE 8"n" VALUES FROM FIG 56 AND 57

TEMPERATURE ($^{\circ}\text{C}$)	"n" Values	LIMIT OF "n" VALUE (% TRANSFORMATION)
665	2.00	60
650	1.78	65
635	1.57	60
610	1.37	55
595	1.19	55
580	1.08	35
565	1.00	40
555	1.03	40
~~545~~	0.99	45
530	1.21	45

nuclei had been formed. These were produced by ageing the specimens at 540°C for 200 mins which corresponds to 20% transformation. It is after this amount of transformation the precipitate particles can be clearly seen in the electron microscope and there does not appear to be any significant increase in their numbers as ageing proceeds. These samples were tested in the dilatometer and 100% transformation was taken as the length change occurring at the temperature used.

The isothermal ageing curves are given in Fig 58 and as expected there are no incubation periods. The $\log \left(\log \frac{1}{1-x} \right)$ vs $\log t$. plots are given in Fig. 59 and the corresponding "n" values in Table 9. Once again there is an initial constant slope with an "n" value in the range 1.00-1.50. The constant slope exists up to approximately 70% transformation, when the characteristic decrease in slope occurs.

4.10 ISOTHERMAL DILATOMETRY RESULTS ON DEFORMED SPECIMENS

Another series of runs was performed on specimens which had been subjected to severe cold work. These experiments were carried out in order to study the effect of increasing the dislocation density on the nucleation of precipitates. The density of dislocations in the lath martensite is already very high so that deformation of the order of 90% was required to produce a measurable change.

The most noticeable difference was that the decrease in length had altered from the normal value of 19-22 microns to 50 microns. Also the reactions were completed in much shorter times so that results at temperatures as low as 500°C could be obtained.

The isothermal ageing curves are given in Fig.60 and once more at the low temperatures there is an

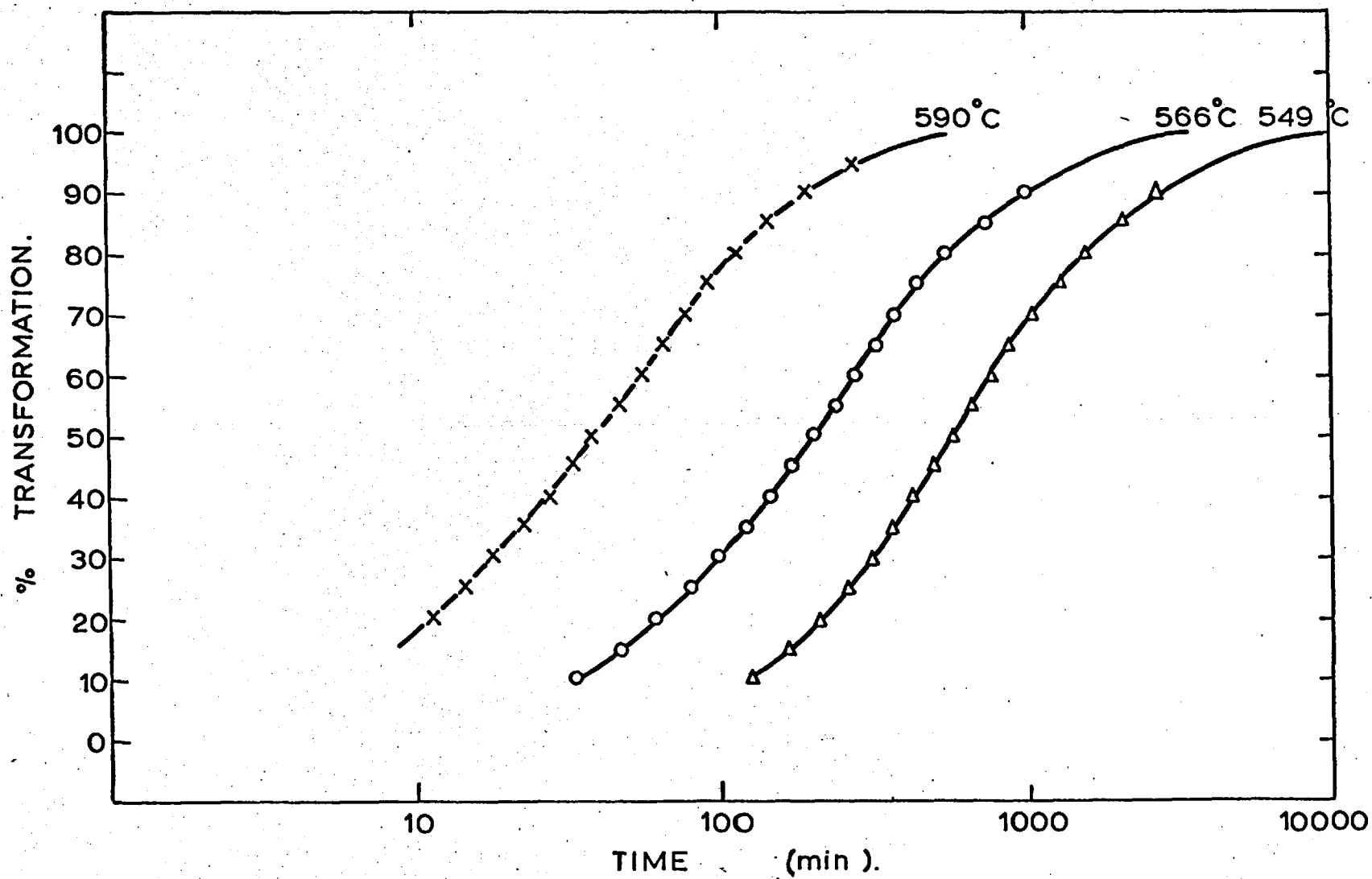


FIG.58. Ageing curves for alloys preaged 20% at 540°C

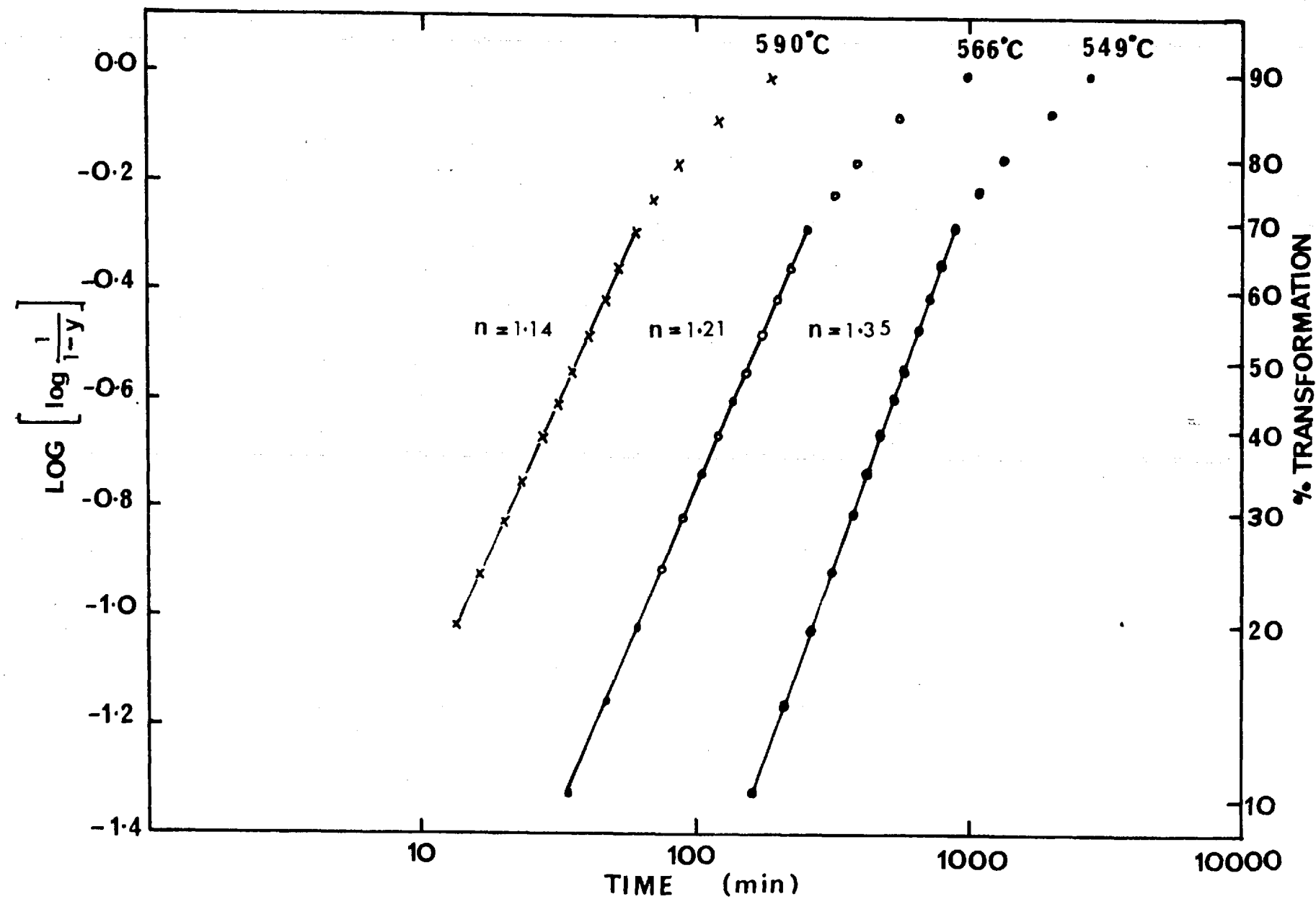


FIG. 59. Derived log plots for specimens preaged 20% at 540°C

TABLE 9 "n" VALUES FROM FIG 59, PREAGED SPECIMENS

TEMPERATURE (°C)	"n" VALUES	LIMIT OF "n" VALUE (% TRANSFORMATION)
590	1.14	70
566	1.21	70
549	1.35	70

TABLE 10 "n" VALUES FROM FIG 61, DEFORMED SPECIMENS

TEMPERATURE (°C)	"n" VALUES	LIMIT OF "n" VALUE (% TRANSFORMATION)
620	1.41	75
545	0.72	60
528	0.87	70
505	1.02	70

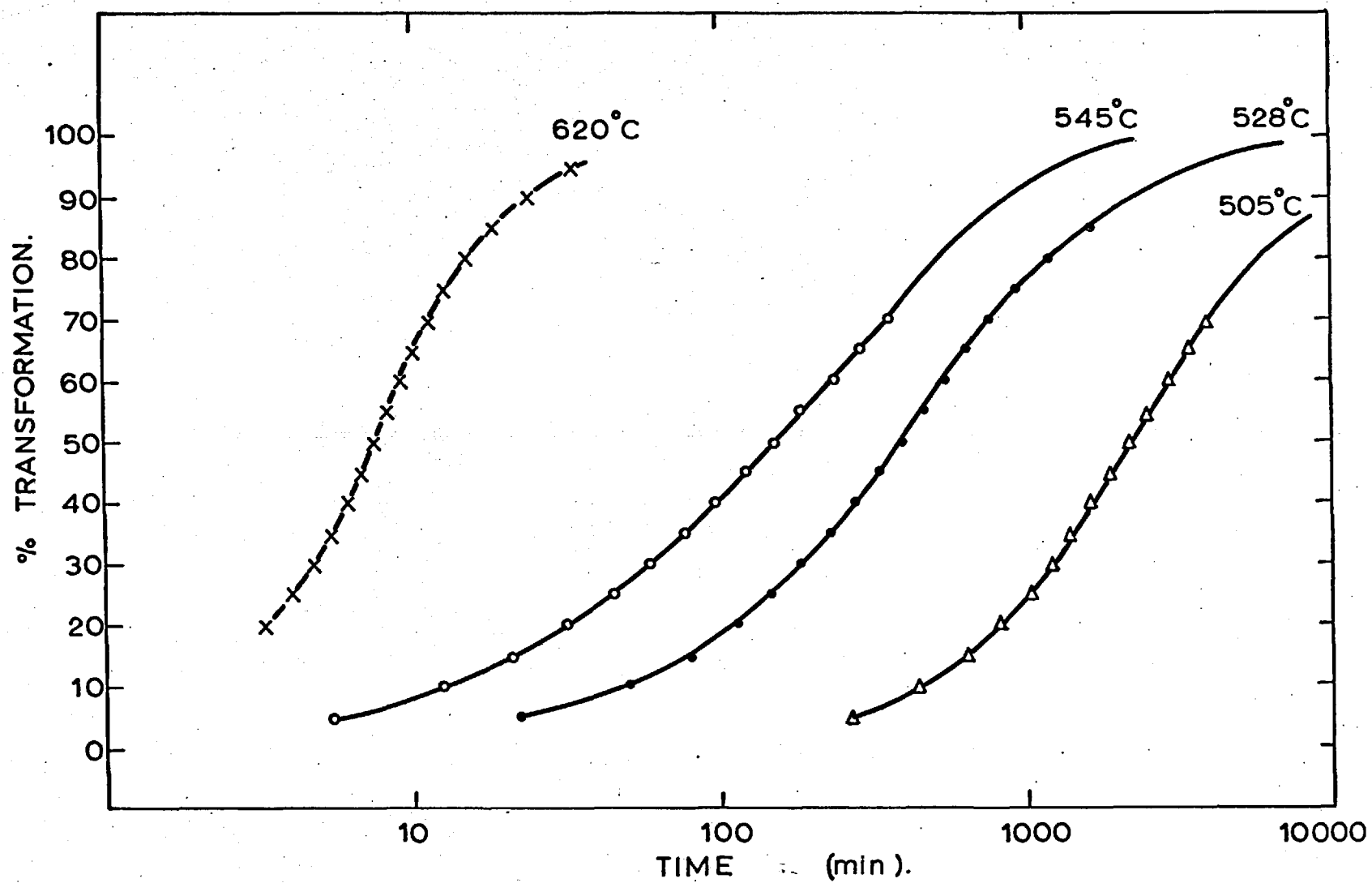


FIG.60. Ageing curves for 90% deformed specimens

incubation period. The $\log \left(\log \frac{1}{1-y} \right)$ vs $\log t$ curves in Fig. 61 show the initial constant slope then a decreasing slope. The "n" values are given in Table 10 and it can be seen that for the temperature range 345° - 505° C they are in the range 1.02-0.72 up to 70% transformation. However at 620° C the "n" value is much greater, being 1.41 up to 75% transformation.

4.11. ACTIVATION ENERGY ANALYSIS FROM ISOTHERMAL DILATOMETRY DATA

The rate constant in the empirical equation used, can be fitted to an Arrhenius type equation,

$$k = A_A e^{-\frac{E_A}{KT}}$$

If the reaction is controlled by a single process then A_A and E_A can represent meaningful values.

The most useful form of the above equation is that which relates the time to a given fraction of transformation to the right hand side of the equation.

$$\text{If } \frac{dy}{dt} = kf(y)$$

$$\text{then } dt = k^{-1} f^{-1}(y) dy.$$

$$t_y = k^{-1} \int_{y=0}^{y=y} f^{-1}(y) dy.$$

$$\text{i.e. } t_y \propto k^{-1}$$

$$t_y \propto A_A^{-1} e^{\frac{E_A}{KT}}$$

taking logs.

$$\log t_y = \text{const} - \log A_A + \frac{E_A}{2.3 KT}$$

A graph of $\log t_y$ vs $\frac{1}{T}$ should then give a straight line whose slope is $\frac{E_A}{2.3K}$ from which the apparent activation energy $\frac{E_A}{2.3K}$ of the process can be obtained. However, the value of activation energy is the average value up to that amount of transformation.

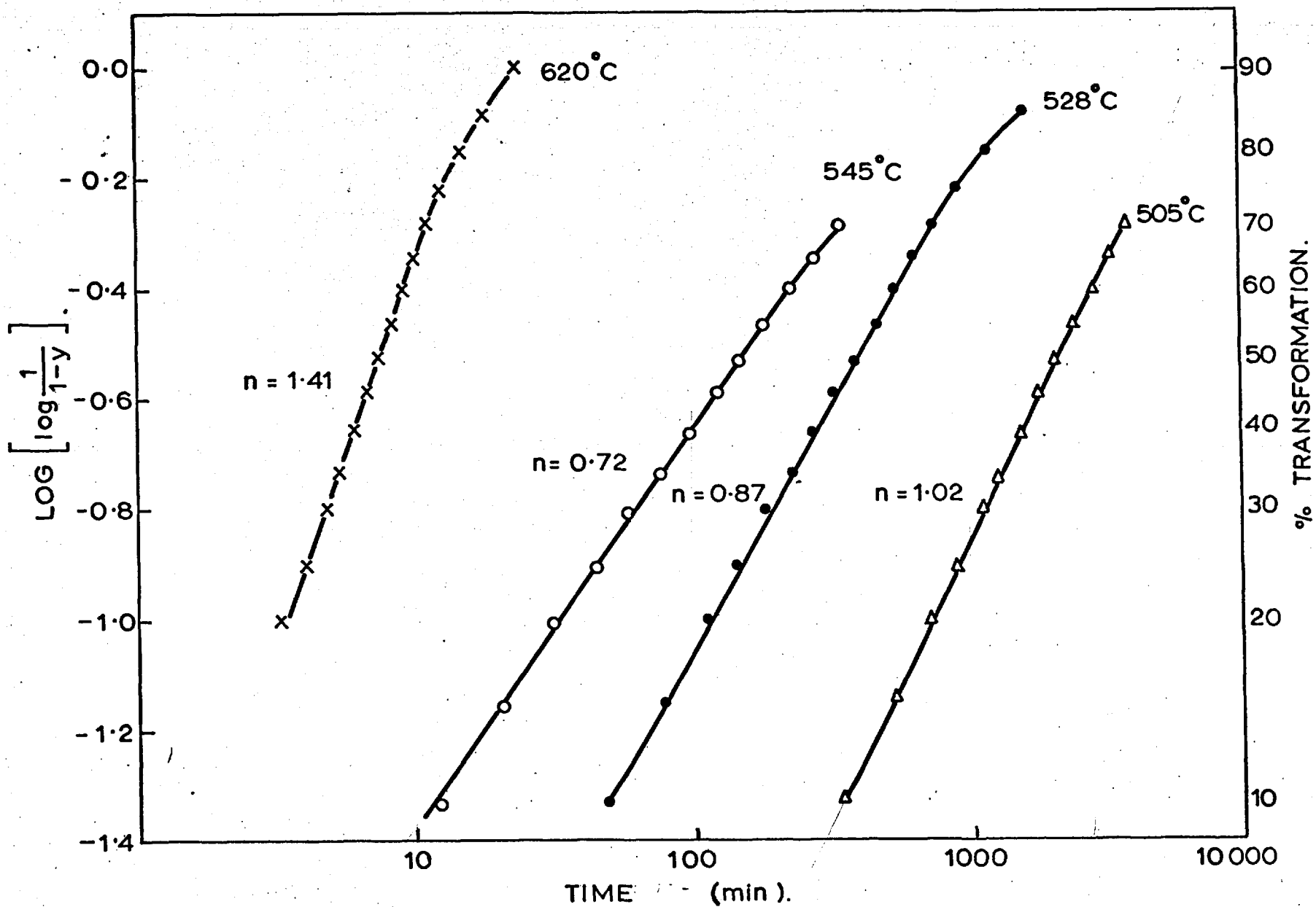


FIG.61. Derived log plots for specimens deformed 90%

Plots for the data of Figs 54 and 55 are shown in Fig. 62, the curves correspond to different amounts of transformation from 20% up to 90%. It can be seen that there are two distinct parts for any value of % transformation, a steep slope at low temperatures and a shallow one at high temperatures. The values of the apparent activation energies are given in Table 11 and range from 97 Kcal/mole at 20% transformation to 83.

Kcal/mole at 90% transformation in the low temperature range and 24 Kcal/mole at 20% to 52 Kcal/mole after 90% in the high temperature range. The transition takes place at a temperature of approximately 570°C and appears to be a distinct change rather than a gradual one.

Plotting the values for the preageing experiments, Fig. 63, gives activation energies which vary from 100 Kcal/mole at 20% transformation to 88 Kcal/mole at 80% transformation. This only covers the low temperature range.

Fig. 64 shows the results obtained from the deformed specimens. Once more the low temperature range gives a relatively high slope resulting in activation energies of 95 Kcal/mole at 20% transformation decreasing to 75 Kcal/mole at 70% transformation. The values for the 620°C plot do not lie on the above slopes and it would appear that much lower activation energies, corresponding to the undeformed values, govern this temperature range.

4.12 ACTIVATION ENERGY ANALYSIS FROM HARDNESS DATA.

Activation energy values can be obtained from the hardness results if it is assumed that in each case the peak hardness value corresponds to the same percentage transformation. The dilatometry curves do show that this assumption is approximately correct,

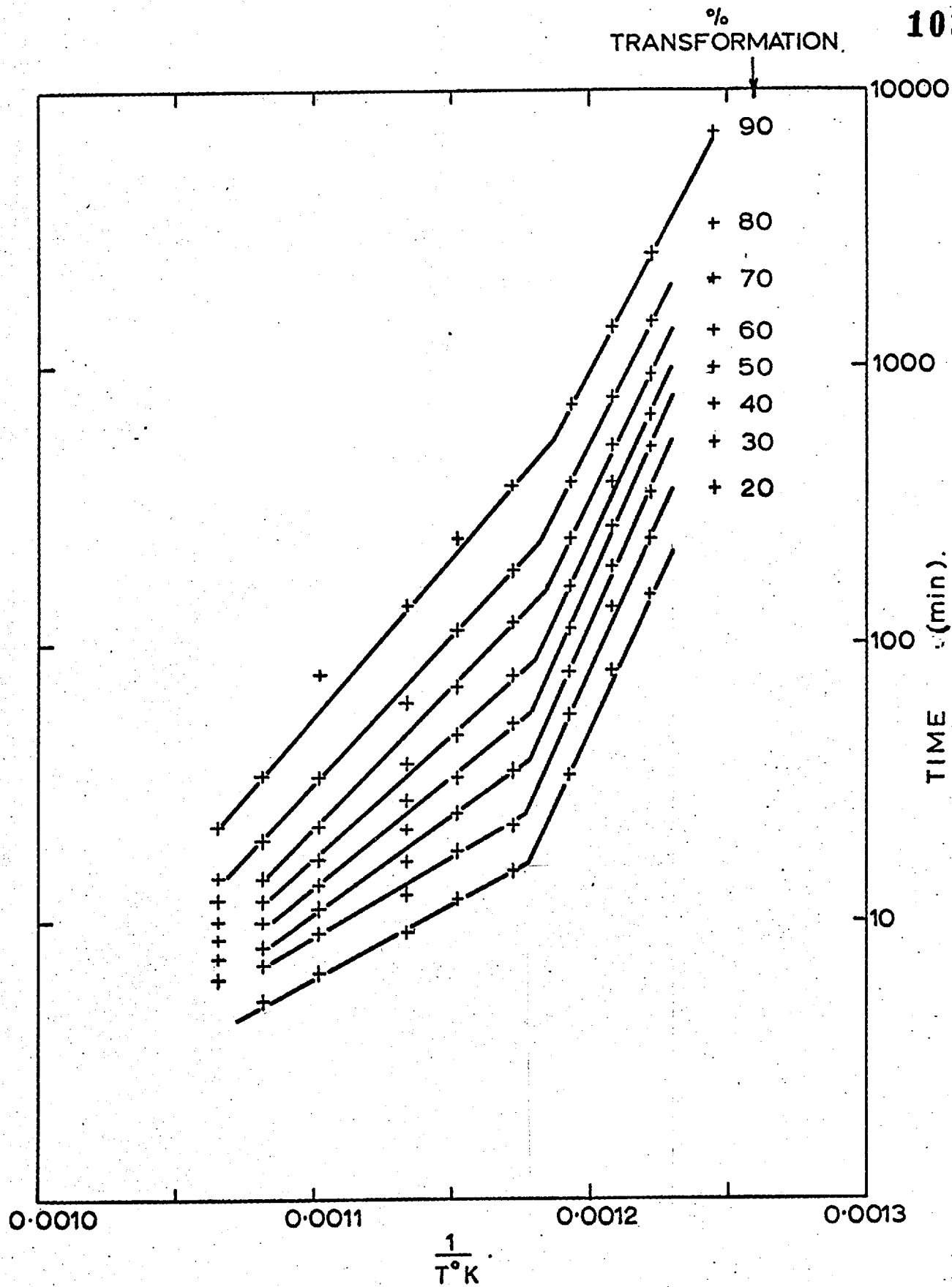


FIG. 62. Activation energy plots, values given in Table II

TABLE 11ACTIVATION ENERGIES FROM FIG.62

% TRANSFORMATION	ACTIVATION ENERGY (Kcal/mole)	
	TEMPERATURE RANGE 530-575°C	TEMPERATURE RANGE 575-665°C
20	97	24
30	98	26
40	100.	32
50	98	36
60	95	40
70	92	45
80	85.	48
90	83	52

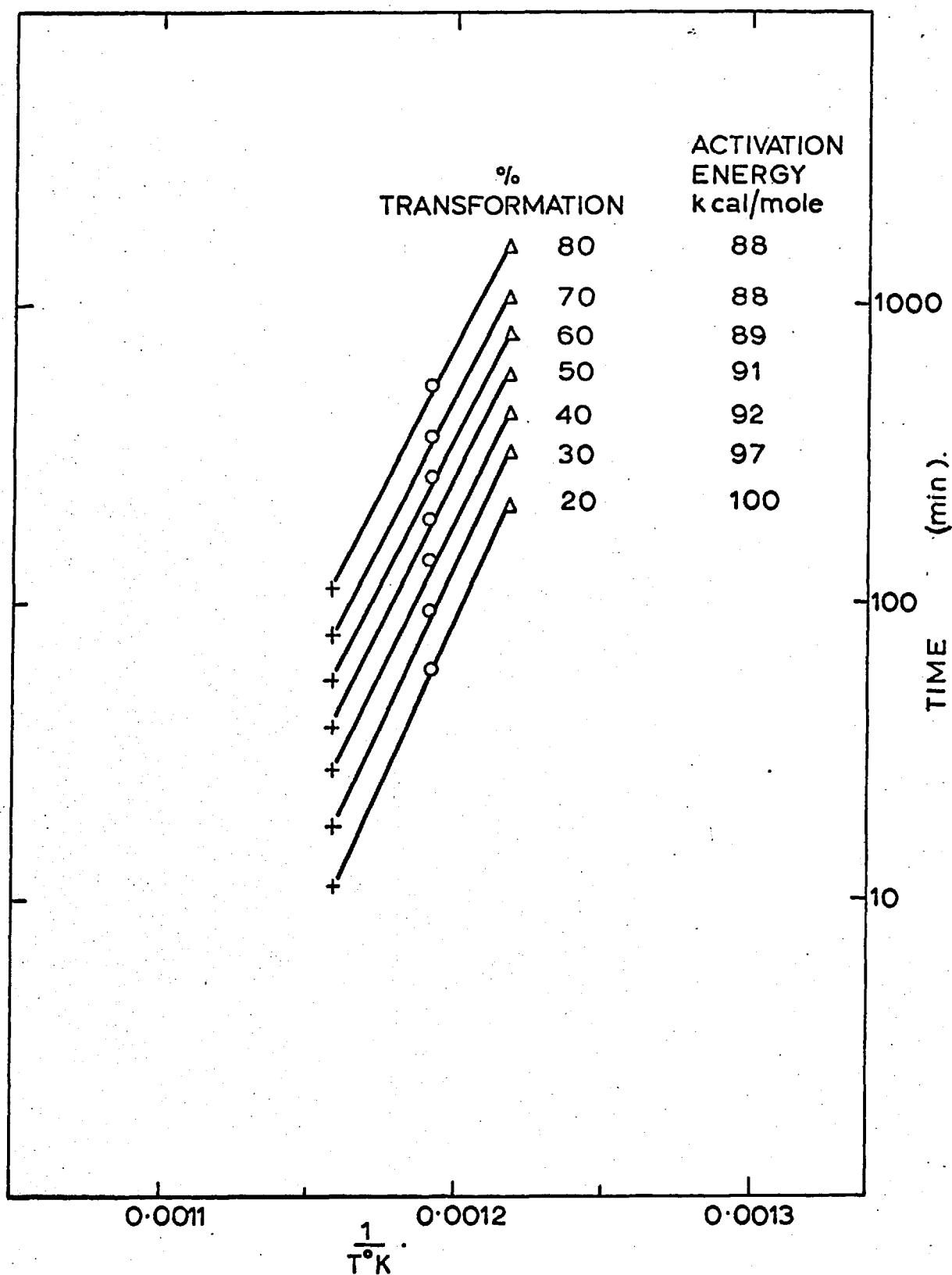


FIG.63. Activation energy plots for the preaged specimens

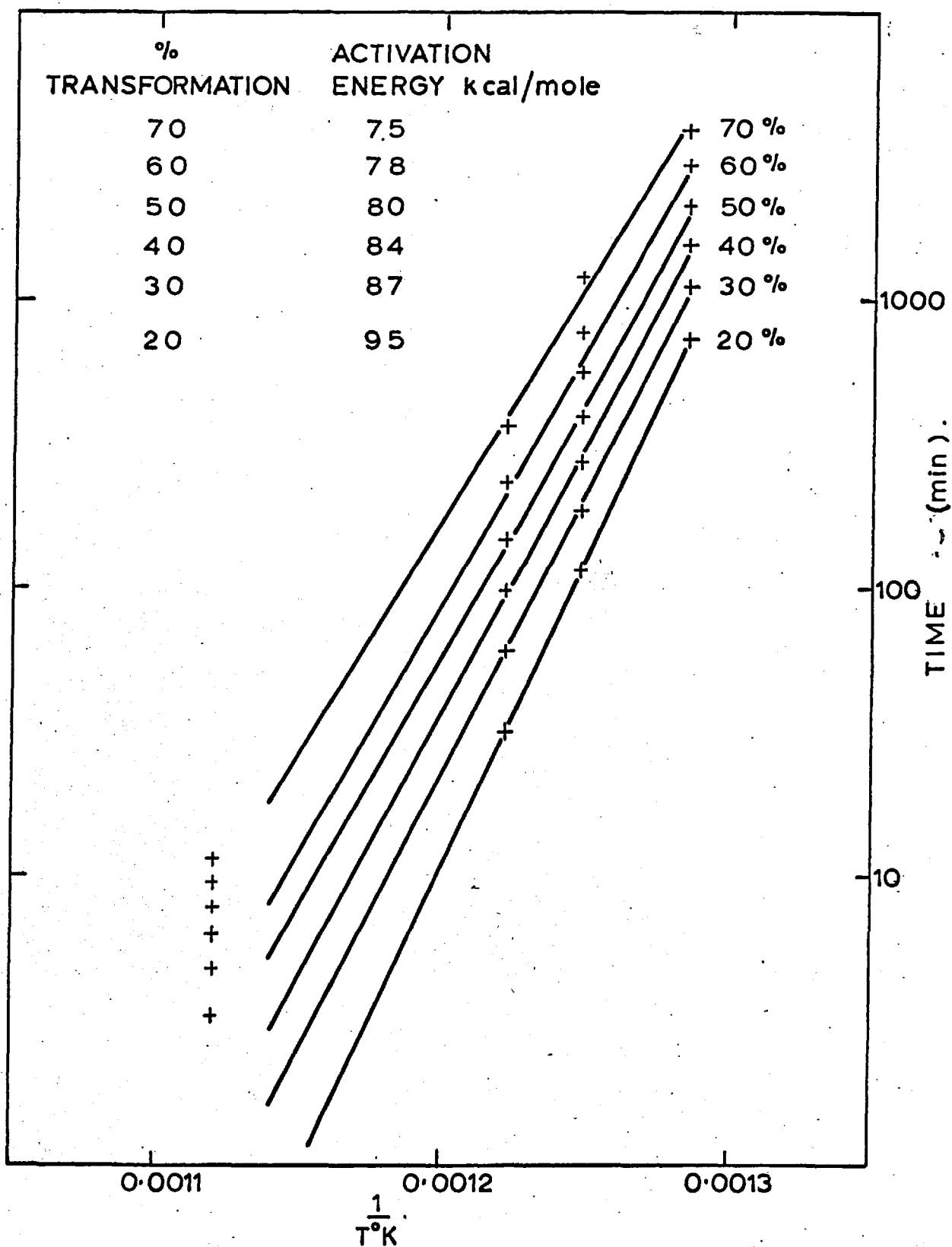


FIG. 64. Activation energy plots for 90% deformed specimens

with peak hardness occurring after 80-85% transformation. The resulting graph from plotting the time to peak hardness against $\frac{1}{T}$ is shown in Fig 65 and once again two distinct slopes are obtained which appear to intersect at approximately 575°C. The lower temperature slope corresponds to an activation energy of 91 Kcal/mole while the higher temperature value is 40 Kcal/mole.

4.13 ACTIVATION ENERGY ANALYSIS FROM CHANGE OF TEMPERATURE DILATOMETRY DATA

As previously stated the activation energies obtained by the above method are average values up to the % transformation, but actual values at a given % transformation can be obtained by another method. Here the rates of transformation at a constant % transformation at two different temperatures are used, i.e. $\left(\frac{dy}{dt}\right)_{T_1 Y}$ and $\left(\frac{dy}{dt}\right)_{T_2 Y}$

Since both are some function of "y" it must be assumed that the function does not alter over the range studied.

$$\left(\frac{dy}{dt}\right)_{T_1 Y} = K_{T_1} = A_A e^{-\frac{E_A}{KT_1}}$$

$$\left(\frac{dy}{dt}\right)_{T_2 Y} = K_{T_2} = A_A e^{-\frac{E_A}{KT_2}}$$

take logs and subtract the two equations.

$$\log \left(\frac{dy}{dt}\right)_{T_1 Y} - \log \left(\frac{dy}{dt}\right)_{T_2 Y} = \frac{E_A}{2.3K} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

By substituting values in the above equation, E_A , may be obtained at a known percentage transformation.

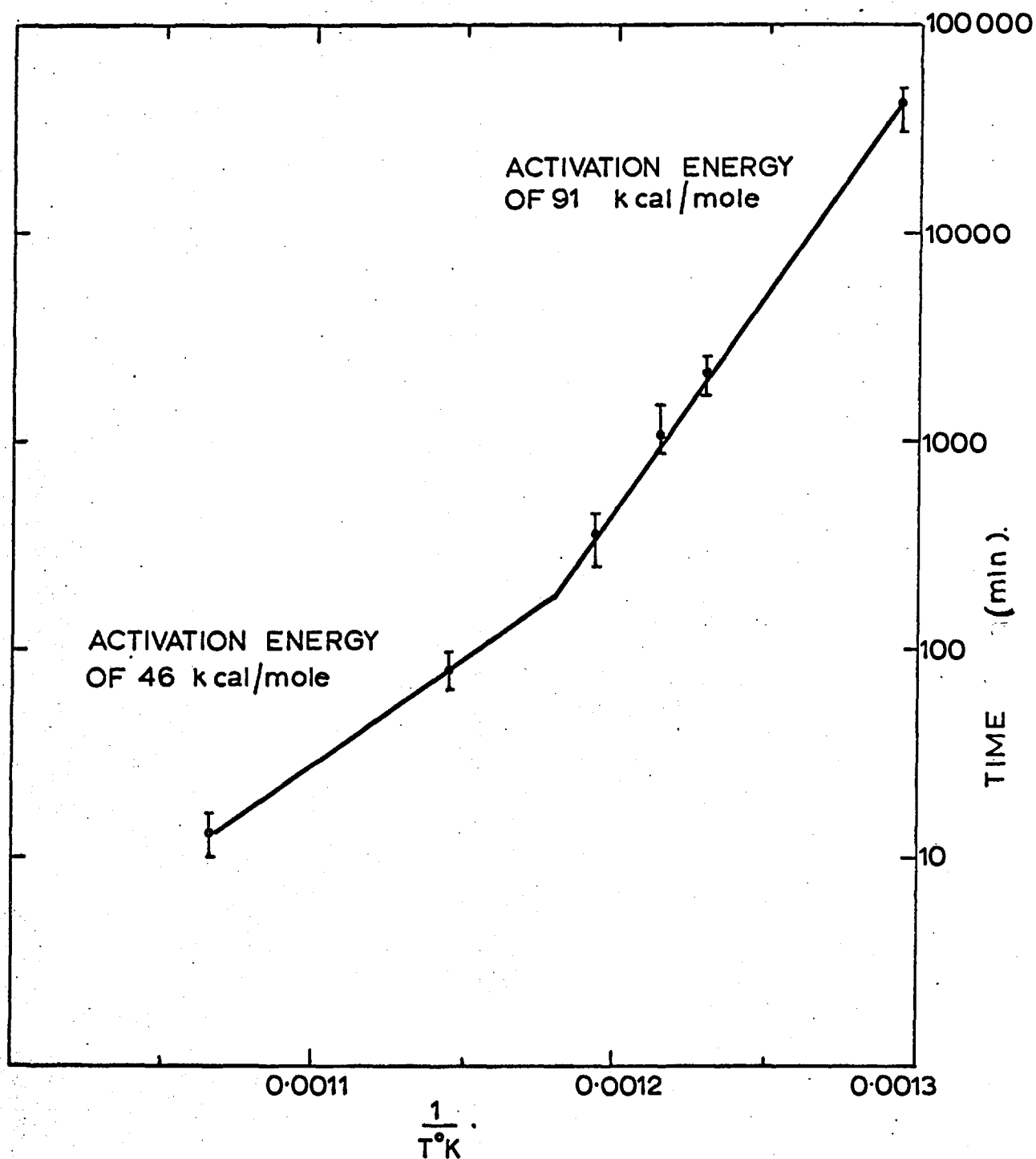


FIG.65. Activation energy plots for time to peak hardness

Results of this type of analysis are given in Table 12. Once more the values obtained at the lower temperature, below 575°C , are in the range 80-100 Kcal/mole. The values over 100 K cal/mole obtained from the lowest temperature plots can be explained by the errors involved in determining the slopes of the transformation vs time plots, which are very shallow at the low temperatures. At temperature above 575°C the values once more fall in the range 40-55 Kcal/mole.

4,14, DIRECT QUENCHING RESULTS.

A number of specimens were directly quenched from the solution treatment temperature of 1100°C to ageing temperatures of 600 and 700°C . It was hoped that the study of the resulting precipitation would help in identifying the precipitates obtained in the aged martensitic structure. The M_s temperature of the alloy had been determined as 400°C so that the direct quenching produced an austenitic matrix.

The electron micrograph, FIG 66, shows a typical structure after ageing for 72,000 minutes at 600°C , (similar structures are obtained after ageing at 700°C). The austenite has decomposed to a structure of ferrite and plate shaped precipitates, which has been initiated at the austenite grain boundaries. On quenching to room temperature the remaining austenite transforms to martensite.

Prolonged ageing, for 42,000 minutes at 700°C , produced a structure in which a different precipitate occurred, having been nucleated at the prior austenite grain boundaries; however, there were still areas in which the original plate shaped precipitates were present. X-ray analysis of the particles extracted

TABLE 12

ACTIVATION ENERGIES DERIVED FROM CHANGE
OF TEMPERATURE DILATOMETRY RESULTS.

% TRANSFORMATION	ACTIVATION ENERGY (Kcal/mole)	TEMPERATURE RANGE (°C)
5.0	93.0	560-573
7.0	95.4	550-562
15.0	93.4	547-562
15.0	96.1	571-558
17.0	92.8	570-545
20.0	98.0	560-548
22.0	98.7	561-549
22.0	109.0	545-530
25.0	104.0	530-545
27.5	99.0	548-560
31.2	104.0	532-553
40.4	93.0	530-560
54.6	109.0	553-545
59.8	84.9	545-567
66.8	82.0	567-544
17.4	43.0	562-572
28.0	43.0	569-583
50.0	47.8	568-582
60.0	49.6	569-583
63.4	52.0	560-590

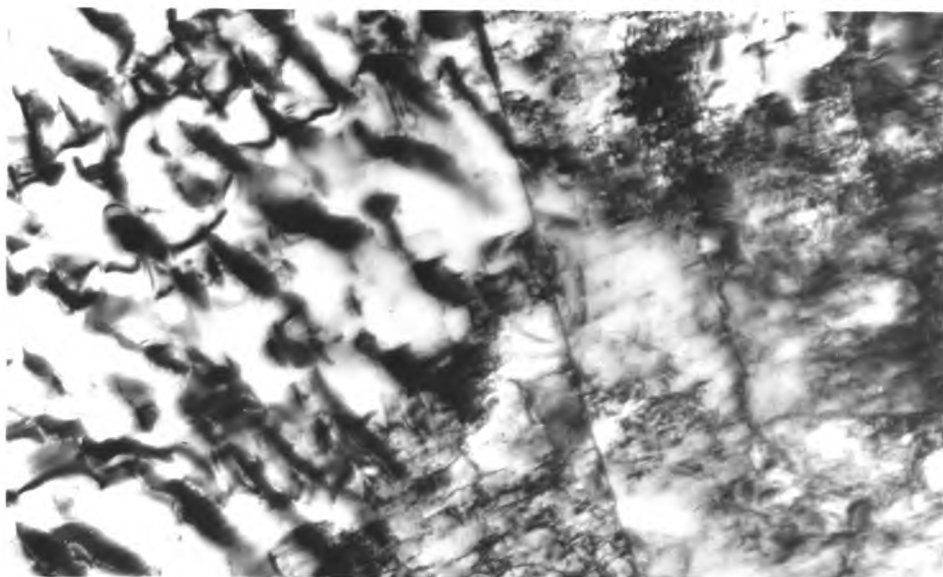


FIG 66. Solution treated, directly quenched to 500°C and aged for 6,000 mins (x45,000)

from samples given this heat treatment are shown in Table 13. It can be seen that the majority of the lines can be accounted for by a sigma phase. The remaining lines fit a hexagonal structure corresponding to an Fe_2Mo type laves phase with a lattice parameter $a = 4.72\text{\AA}$ $c = 7.69\text{\AA}$ and $\frac{c}{a} = 1.63$.

TABLE 13 PRECIPITATES EXTRACTED FROM A SPECIMEN
DIRECTLY QUENCHED TO 700°C AND AGED FOR
700 HOURS.

EXTRACTED PRECIPITATES dÅ INTENSITY		SIGMA PHASE ⁸¹ (Cr Co) dÅ INTENSITY		CALCULATED VALUES OF dÅ FOR Fe ₂ Mo a = 4.72Å c = 7.69Å
2.738	W			2.745
2.643	VW	2.62	5	
2.367	W	2.36	20	2.366
2.243	M	2.26	20	
2.163	W	2.155	5	
2.117	S	2.128	100	
2.077	S	2.066	50	2.079
2.038	MS	2.014	50	2.041
1.945	MS	1.962	50	1.945
		1.962	100	
1.882	W	1.882	50	
1.831	W	1.831	20	
1.802	W			1.805
1.793	W			1.795
1.769	VW	1.756	20	1.769
1.663	VW	1.658	5	1.663
1.603	W	1.610	5	
1.520	W	1.532	20	
1.437	W			1.439
1.349	W	1.373	5	1.351
1.332	VW	1.326	20	
1.303	S	1.302	5	1.303
1.292	VW	1.290	5	
1.280	MW	1.281	5	
1.277	MS			1.277
1.256	S	1.257	50	
1.231	M	1.231	20	
1.226	W	1.222	50	
1.209	S	1.207	50	
1.184	W			1.186
1.179	W			1.180
1.172	W	1.175	50	1.172

CHAPTER 5

DISCUSSION.

5.1. INTRODUCTION

The chapter will be divided into sections which will discuss in detail the findings of this project. The principle observations were

- a) The alloy underwent a transformation to a lath type martensite on quenching from the solution treatment temperature of 1100°C .
- b) On ageing at temperatures between 500° and 700°C a precipitate, identified as R phase, nucleated and grew on dislocations. The kinetics of the transformation showed a discontinuity at a temperature between 570 - 580°C .
- c) On prolonged ageing at temperatures above 650°C a second precipitate, identified as Chi phase, forms on boundaries, and at the same time R phase particles dissolve.
- d) Directly quenching specimens to ageing temperatures of 600 and 700°C (i.e. in the metastable austenite range) produces a discontinuous precipitation process with the formation of ferrite and an Fe_2Mo type precipitate. After prolonged ageing at 700°C this precipitate is partially replaced by sigma phase which nucleates and grows on the prior austenite grain boundaries.

5.2. SOLUTION TREATED CONDITION.

The solution treated material had a hardness of 330 V.P.N and the microstructure was typical of the structure described by Marder and Marder³⁹ for an Fe-Ni based material. The structure observed by

electron microscopy showed no sign of twinning inside the martensite laths, nor was there any evidence of retained austenite being present.

The martensite could be cold worked relatively easily; the specimens used in certain dilatometry runs were 90% deformed and had a hardness of 418 V.P.N.

Dilatometry results showed that the M_s temperature of the material was $400^{\circ}\text{C} \pm 1^{\circ}\text{C}$ with an apparent M_f temperature of $265^{\circ}\text{C} \pm 5^{\circ}\text{C}$. However, magnetic balance measurements showed that a further 5% martensite was formed on giving the alloy a refrigeration treatment. On heating a specimen at a rate of $2^{\circ}\text{C}/\text{minute}$ no austenite was found to form below $777^{\circ}\text{C} \pm 1^{\circ}\text{C}$. With such a slow heating rate precipitation occurred by the time the temperature reached 777°C so that austenite formed from a structure containing intermetallic compound. When a much faster rate was employed austenite was still formed at approximately 775°C , thus showing that the precipitate present had little effect on the A_s temperature.

5.3. PRECIPITATION OF R PHASE.

5.3.1. STRUCTURE.

On ageing at all temperatures between 500 and 700°C a very fine dispersion of precipitate, nucleated on dislocations, was obtained. Using particles extracted from overaged specimens the X-ray diffraction results indicated that the precipitate was R phase, which agreed with the results of selected area diffraction work on single crystal particles in thin foils. No similar proof could be obtained for the early stages of precipitation, but it was found that the diffraction

patterns could be indexed assuming the precipitates to be R phase.

In all cases the precipitate was nucleated on dislocations inside the laths but it was not found to nucleate preferentially on any of the boundaries present. Dyson and Keown⁶⁹ have shown that the precipitation of R phase requires only small lattice strains and the dislocations help to counteract these strains and so provide sites for nucleation. This was considered by Cahn³ who showed that if the supersaturation was sufficient there would be no energy barrier to nucleation. In the case of the alloy studied, i.e. FeCoCrMo, at all temperatures precipitates nucleate on dislocations. At temperatures below 580°C an incubation period is detected due to the decrease in the diffusion rate with fall in temperature. From 580°C up to 700°C there was no detectable incubation period which suggests that the supersaturation is sufficiently high at all temperatures to enable precipitates to nucleate on dislocations.

The electron micrographs also show that precipitates are formed on relatively few of the dislocations present in the structure, which would suggest that the nature of the dislocation itself plays a part in the nucleation of R phase. Cahn shows that edge dislocations are more important sites than are screw dislocations so that it would be expected that precipitates would nucleate on predominantly edge dislocations in a mixed structure. It was shown by Patterson and Wayman⁴¹ that the dislocation structure of a lath martensite consisted primarily of screw dislocations so that nucleation

would only be expected to occur on the relatively few edge type dislocations present.

At no temperature was there any indication that R phase nucleated either in the matrix or on the boundaries present. The lath boundaries themselves would appear to be of very low energy as they remain stable throughout the transformation even at temperatures as high as 700°C. High angle boundaries are normally assumed to be more preferred sites for nucleation than dislocations as they contribute to the surface energy term of the nucleation process as well as, although to a lesser extent, to the strain energy term. The surface energy of the non-coherent R phase particles must be fairly high as they undergo coarsening at all temperatures. However, the contribution of high angle boundaries to the surface energy as well as the strain energy term must not be as favourable as that made by the dislocations to the strain energy term. Dyson and Keown⁶⁹ show that very little lattice strain is needed for R phase precipitation in ferrite and it would seem that the dislocations can accommodate all of it.

Calculations (Section 4.8) show that the density of the R phase is less than that of the matrix so that for particles to grow either vacancies must migrate to the particles or else dislocations must form at, or move to, the precipitate-matrix interface. To determine with certainty which occurs, is difficult due to the structure of the alloy, but in the overaged condition there is a noticeable reduction in the dislocation density and at high magnification a number of dislocations are seen to be associated with the precipitate. Dyson and Keown⁶⁹ also noticed

a similar decrease in dislocation density and suggests that the misfit between precipitate and matrix was large enough for dislocations to be accommodated at the interface.

If it is taken that the R phase precipitates harden the alloy by an Orowan type mechanism, then the peak hardness value should correspond to the smallest interparticle spacing. Precipitate coarsening produces an increase in the interparticle spacing so that a decrease in hardness can be expected. With this alloy the minimum spacing should correspond to 100% transformation, but in fact peak hardness occurs after approximately 80% so that some coarsening must be occurring in the last 20% of transformation. The gradual rise in peak hardness with decrease in temperature can be explained in terms of the greater volume fraction of solute being available due to the increased supersaturation. This would give rise to larger precipitates and so a smaller interparticle spacing; it would not mean an increase in the number of precipitates as this is controlled by the number of edge type dislocations present in the structure which does not alter significantly with temperature .

5.3.2. KINETICS.

The dilatometry results showed that approximately 20% transformation took place before precipitates were first observed in the microscope. This is not surprising as the martensite structure gives rise to a great deal of contrast from the dislocations which very easily hides any fine precipitate particles.

The kinetics in the range up to 20%

transformation do not differ from those found immediately above this value, so that it can be assumed that the process occurring both above and below 20% transformation is the same. This would indicate that, as far as dilatometry can tell, no clustering or intermediate precipitate formation is taking place. Coutsouradis et al⁶⁴, working on similar alloys, suggests that the halos around matrix reflections in diffraction patterns of specimens given short ageing treatments, indicated that clusters were forming. No such effect has been observed with the diffraction patterns of the present alloy which would once more suggest that clustering was not taking place.

The dilatometry results were fitted to the Johnson-Mehl equation and at all temperatures very good agreement up to, at the very least 35% transformation, was found. For greater percentages of transformation a continuously decreasing rate was found.

The results could be split into three groups depending on the values of "n" obtained from plots of $\log \left(\frac{1}{1-y} \right)$ vs log time,

a) "n" approximately equal to 1.0.

This value was obtained for ageing up to 35-45% transformation in the temperature range 530-580°C, and above this amount of transformation the "n" values started to decrease.

An "n" value of 1.0 can correspond to a number of different growth conditions, all of which are diffusion controlled:-

1) Rods of constant diameter with solute capture and growth at the ends only.¹³

- 2) Growth of rods or spheres on dislocations¹⁷.
- 3) Growth of needles and plates of finite long dimension small in comparison with their separation²².
- 4) Radial growth of rods after end impingement²².

Electron microscopy shows that up to approximately 50% transformation the precipitates are in the form of rods nucleated on dislocations. However, they are observed to grow radially as well as increase slowly in length so that the first alternative cannot be used.

In the theory of Bullough and Newman¹⁷ the strain fields of dislocations attract solute atoms which can then migrate along the dislocations to the precipitates. In the present alloy the solute atoms are substitutional ones so that only edge dislocations will attract them; however, it has been shown that the edge dislocations present in the structure provided the nucleation sites for the R-phase. The strain fields of the dislocations are utilised by the precipitates in nucleation so that once a precipitate has formed on a dislocation there is no longer a strain field to attract solute atoms. It might be expected that in the early stages of ageing the dislocations are important but they cannot be expected to make a contribution up to 50% transformation, so that the second alternative can be ruled out.

The third alternative can also be eliminated as the assumption that the particles are widely spaced is not correct for the R phase precipitates.

However, the radial growth of rods after end impingement can be taken as the case for R phase precipitation. Electron microscopy shows that rods of R phase nucleate on certain lengths of dislocation,

probably the pure edge sections and once these have been used up, growth in the long direction appears to slow down and only radial growth occurs. The difference in growth rates is probably due to the precipitate having a relatively high surface energy so that further growth must try and minimise the surface area, which results in radial growth being more favourable. This is now equivalent to the radial growth of rods after end impingement.

It may be concluded that the observed "n" values of approximately 1.0 result from the diffusion controlled radial growth of rod shaped particles.

b) "n" in the range 1.0 - 1.5

At temperatures above 580°C there was no measurable incubation period by dilatometry or hardness measurements; a similar zero incubation ^{47,51} period is common in the Fe-Ni based maraging alloys. The n values were found to be constant for any one temperature up to approximately 60% transformation, but the values altered from 1.19 at 595°C to 2.00 at 665°C.

As in the case of the lower temperature range, electron microscopy shows that rod shaped R phase particles nucleate on dislocations. It is evident that some transformation must occur when heating the dilatometry specimens up to the ageing temperature, which takes approximately ten minutes, as precipitates are clearly seen at most temperatures after only 4 minutes.

Ham¹² considered the growth of particles, of any shape, from appreciable initial volumes. He calculated the equivalent n value to lie in the range 1.0-1.5 so that it can be concluded that it is this situation that occurs at temperatures above

580°C.

The values of n above 1.5 can occur by nucleation taking place at the same time as growth of the particles. This seems unlikely in the present case as at all other temperatures nucleation has been completed in the early stages. However, these values can also result from inaccuracies in determining the beginning of transformation. At the very high temperatures i.e. above 635°C, the amount of transformation taking place while the specimen is reaching temperature is quite substantial so that an error here would alter the initial slope by a large amount. In view of this error, the higher values cannot be closely correlated with a particular growth situation, but growth is probably occurring from particles of appreciable initial volume.

c) "n" decreasing to approximately 0.5.

At all temperatures from 530-665°C the value of n starts to decrease as the transformation proceeds above approximately 50%, the lowest values being approximately 0.5 after 90-95% transformation.

Electron microscopy on specimens in this range reveal that the rod shaped particles are less numerous than spherical precipitates. Selected area diffraction shows that both the rod and spherical precipitate are R phase. As mentioned in a) (" n " values approximately equal to 1.0) the growth of rods is greater in the radial direction than along the length, so that eventually a spherical precipitate would tend to form. From the surface energy point of view this is the most stable

precipitate shape and it would continue to grow as such.

The possible reasons as to why there should be a deviation from a constant "n" value can be listed as:-

(i) The Johnson-Mehl equation is an over-simplification of the kinetics involved, and Ham¹² pointed out that it is only really a good approximation to the theoretical equations for values up to 50% transformation. The empirical impingement factor used is probably contributing to the deviation from the experimental results at high %transformations. Using the Austin-Rickett⁸⁴ equation, marginally better agreement is obtained but a much more complex impingement factor would be needed to give any substantial improvement.

(ii) Stress assisted growth by dislocations. Harper¹⁵ and Meisel²⁰ have given a value of $n = \frac{2}{3}$ for this condition; however, this would not account for the much lower values of 0.5.

(iii) Growth of plates in one dimension only,²² would give an "n" value of 0.5. Electron microscopy shows that the precipitates are growing in at least two dimensions so that this condition cannot be the cause of the low "n" values.

(iv) The dissolution of a precipitate while another is forming. In work by Peters and Cupp⁴⁷ on the ageing of an Fe-18% Ni alloy a very low "n" value of 0.33 was obtained. Structural observations showed that there were two types of precipitate present and one of them was going back into solution as the other formed. Peters and Cupp associated the low "n" value with this situation, but in the present alloy only one type of precipitate was observed.

(v) Two transformations overlapping. If two separate transformations were occurring but with different "n" and "k" values, then the overall "n" value could be very low. Once again, in the present alloy there is no evidence for more than one type of precipitate.

In the majority of the kinetic studies on the Fe-Ni maraging alloys, "n" values of 0.25-0.5 have been obtained, and these have been explained in terms of the dense dislocation structure affecting the transformation; however, there is no theoretical verification for this. Peters and Cupp⁴⁷ showed that austenite was forming at the same time as precipitation was occurring but they assumed that the volume was small enough to be neglected.

Some very recent work by Thomas, Cheng and Mihalsin⁸⁵ working on an Fe-Ni-Co alloy indicates that this assumption of Peters and Cupp was incorrect. No intermetallic compound is expected to form in the Fe-Ni-Co alloys but on ageing, very similar structures to those of the maraging alloys are obtained. Perhaps more significant was that the diffraction patterns were just as complex. The authors show that the second phase was austenite and the diffraction patterns can be analysed by assuming double diffraction to take place between the b.c.c. and f.c.c. reflections. On adding a small amount of titanium, they were able to show that the intermetallic compound formed within the austenite particles.

If these results are applied to other maraging alloys, they would probably assist in solving the problem of the identification of the precipitates present. They could also be used to help solve the

kinetic results as they indicate two different transformations occurring which are not separated in the kinetic studies. Thus, the combined effect of the processes would give the low "n" values recorded.

The work by Peters and Floreen⁵⁵ on an Fe-Ni-Mo alloy shows that higher "n" values, in the range 2.0 decreasing to 0.5, can be obtained in maraging alloys. It is probable that austenite formation, if it does occur, is not taking place until after the inter-metallic compound precipitation is complete so that these results of Peters and Floreen are for the precipitation of intermetallic compound only.

In the present FeCoCr Mo alloy there was no evidence of austenite formation even after prolonged ageing at the highest temperature so that only the precipitation of the intermetallic compound is being studied. Therefore it can be concluded that the decreasing value of "n" is due to the fact that the empirical equation cannot be expected to approximate to the actual situation above about 50% transformation.

The results of the preageing experiments were as expected, with an "n" value between 1.0 and 1.5 at all temperatures corresponding to the growth of particles of appreciable initial size.

The situation with the deformed specimens was a little more complicated as the cold working introduced many more dislocations into the structure, as well as giving rise to a preferred orientation of the precipitate structure on ageing. The cold worked structure should now contain a greater number of edge dislocations segments to act as nuclei, which is in agreement with the observed increased number of precipitate particles in the structure. The increased number of edge dislocations can also lead

to a contribution to the precipitate growth by attracting solute atoms; this is shown by the values of "n" being in the range 0.66-1.0 for temperatures between 505^o-545^oC i.e. that expected for dislocation aided growth by Harper¹⁵ and Meisel²⁰. Due to the greater ease with which precipitate can nucleate and grow, the incubation times are reduced and the transformation rates increased which allows the transformation to be followed at lower temperatures. It was also found that the length change was more than twice that recorded with the undeformed specimens i.e. approximates 50 microns in the deformed specimens and approximately 20 microns in the undeformed specimens.

Electron microscopy showed that the rod shaped precipitates were present in the deformed samples even after 100% transformation. This could result from the increase in the number of precipitate particles leading to a reduction in the amount of solute available for each particle to grow; so that they could not grow into spheres before the transformation was complete. The preferred orientation due to the rolling gave rise to an alignment of the rods so that the dilatometry results were for the length change corresponding to one dimension of the particle only, and not to the average growth in all three dimensions as in the undeformed specimens.

At 620^oC, with deformed specimens, an "n" value of 1.41 was obtained, which once again can be interpreted as the growth of particles of appreciable initial volume.

5.3.3. ACTIVATION ENERGY ANALYSIS.

Arrhenius plots from dilatometry and hardness

data all show similar results in that there are two distinct parts to the curves. At temperatures below 575-580°C an activation energy of the order of 85-100 kcal/mole is obtained whereas above this temperature values of 24-52 Kcal/mole are obtained.

If any meaningful information is to be obtained from the activation energies it must be decided what process or processes are taking place. A study of the "n" values shows that the transformation is diffusion-controlled so that the activation energies should correspond to those of diffusion of solute atoms. In the investigation of the precipitation of R-phase the chemical analysis results show that Mo and Cr atoms must diffuse to the precipitate while Fe and Co atoms must diffuse away from it. From the data available the activation energies for the diffusion of all these atoms in b.c.c. iron are in the range 50-62 Kcal/mole, which makes it virtually impossible to distinguish which is the rate - controlling species.

a) Activation energies for the temperature range above 580°C.

The values are given in TABLE 11, derived from log time vs $1/T$ plots, and in Table 12 for the results obtained by the change in temperature method. In both cases the values are well below those reported for ordinary diffusion. The values also increase as the transformation proceeds, indicating a change in the rate-controlling diffusion process (log time vs $1/T$ plots give values of 24 and 52.0 Kcal/mole after 20 and 90% transformation respectively, while the change in temperature plots, 43.0 and 52.0 Kcal/mole after 17.4 and 63.4% transformation). As the results from the log time

vs $1/T$ plots give average values over a range of transformation, the change in temperature method will give the more accurate results in this case. However, in the earlier stages of transformation the two methods would be expected to give the same results, but it was found that the log time vs $1/T$ method gave much lower results. This can be explained in terms of the unknown amount of transformation occurring while the specimen is being heated to temperature, so giving an erroneous time for a given % transformation. In the determination of the activation energy by the change in temperature method this source of error is eliminated.

Therefore the activation energy for this temperature range must be taken as altering from 43 Kcal/mole after 17.3% to 52.0 Kcal/mole after 63% transformation. This suggests that for greater % transformations the activation energies will continue to rise, approaching the values reported for solute diffusion in a ferrite matrix. These low values can be explained in terms of enhanced diffusion occurring along the boundaries and dislocations, since Christian²⁷ suggests that these defects approximately halve the activation energy values. Experimental evidence of activation energies for grain boundary diffusion, (Table 2) also shows that the values are much lower than those of bulk diffusion. The increases in value of activation energy as the transformation proceeds is probably due to the enhanced diffusion being replaced by volume diffusion as the particles start to increase in size.

b) Activation energies for the temperature range below 580°C. It has been shown that this process is

also diffusion controlled even though the activation energies are higher than those for the normal solute diffusion. The value obtained remains constant at approximately 95 Kcal/mole throughout the transformation as shown by the similar results obtained for both the log time vs $1/T$ and change in temperature methods. The high values are also obtained for the preaged and deformed specimens so that the same process is controlling in all cases.

The high activation energy values could result from

1) A different mode of solute diffusion. As mentioned in section 2.3.5. vacancy diffusion is not the only means by which an atom can move in a lattice; interstitial movement and some type of ring mechanism can also occur. In b.c.c. metals Burke²⁵ suggests that the activation energies for the different methods will be much closer than those in f.c.c. metals. Therefore if the vacancies were somehow prevented from taking part in the diffusion process then one of the other methods would occur which would lead to a higher activation energy.

2) In certain Al-based alloys⁸⁵ a decrease in the activation energy for diffusion can be shown to be due to a binding between solute atoms and vacancies. It might therefore be possible for the reverse to occur, in that an increase in activation energy for diffusion can be brought about by a solute-solute binding.

The results on the deformed alloy specimens show the same high activation energy at low temperatures, and although it is difficult to determine exactly where the change-over occurs, it is very near to

580°C. Therefore the added defect structure does not appear to affect the diffusion mechanism, which would suggest that the high activation energies arise from solute-solute interactions rather than from interstitial or ring movement.

At temperatures above 580°C the solute-solute pairs or clusters become unstable and the solute atoms are then able to diffuse as individual atoms, so that the activation energy is reduced.

5.4 PRECIPITATION OF CHI-PHASE.

Optical microscopy showed that on prolonged ageing at temperatures above 650°C another phase was formed which nucleated on prior austenite boundaries and at certain places inside the grains. X-ray diffraction on these precipitates gave a positive identification of Chi-phase.

A detailed study was carried out on samples aged at 700°C and it was found that the R phase nucleated and grew, eventually coarsening to particles approximately 1200Å in diameter. On continued ageing, the dislocation structure in certain areas adjacent to prior austenite grain boundaries and high angle block and packet boundaries, started to recover. As ageing proceeded, Chi-phase precipitates were observed to have nucleated on the boundaries in these partially recovered areas. As the Chi-phase grew the R phase particles decreased in size and eventually dissolved, which allowed more recovery to occur.

There are two possibilities as to the sequence of events. In the first, the Chi-phase precipitates are nucleated on the high angle boundaries and the R phase particles in the neighbourhood start to dissolve to provide solute atoms. This enables the

structure to recover as the dislocations pinned by the R-phase particles are released. In the second possibility the recovery and R phase dissolution occur together and these enable the Chi-phase precipitates to nucleate.

Although electron microscopy reveals recovered areas long before Chi-phase is seen the fact that recovery only occurs at certain specific areas in the matrix would suggest that it is the nucleation of the Chi-phase which is the controlling factor. Therefore the first alternative is probably correct and Chi-phase precipitates are present in the structure but are initially so small that they cannot be identified in the electron microscope.

It was observed that Chi-phase did not nucleate on the lath boundaries but only on the prior austenite boundaries and on the high angle packet and block boundaries. This would once more suggest that the lath boundaries are of very low energy.

The final structure at 700°C consisted of irregular shaped particles of Chi phase set in a recovered and partially recrystallised ferritic matrix which was completely free from R phase particles. Therefore the R phase must be metastable at 700°C and after an incubation period a further decrease in the free energy of the system is brought about by the precipitation of Chi-phase.

The orientation relationship between Chi phase and the matrix was found to be

$$\begin{aligned} [111] \text{ferrite} & \parallel [111] \text{chi} \\ (10\bar{1}) \text{ferrite} & \parallel (1\bar{1}0) \text{chi} \\ (1\bar{1}0) \text{ferrite} & \parallel (0\bar{1}1) \text{chi} \end{aligned}$$

The hardness curve for ageing at 650°C shows a sudden drop in value to 250 V.P.N. after 12,000 minutes. The explanation as to why this occurs is that Chi-phase has been nucleated and the R phase has started to dissolve, so leaving a very coarse dispersion of particles in ferrite.

5.5. DIRECT QUENCHING EXPERIMENTS.

Two different types of precipitate were formed when the alloy was aged in the austenitic condition. Ageing for periods at 600° and 700°C produced a discontinuous mode of precipitation which involved areas of two phase structure growing from the austenite boundaries with the precipitate forming as plates perpendicular to the growing interface (the precipitate was identified as $(\text{FeCr})_2\text{Mo}$ type).

The transformation began by the $(\text{FeCr})_2\text{Mo}$ precipitate plates nucleating on the austenite grain boundary; this depleted the immediate area of solute atoms allowing ferrite to form. As the ferrite grew it rejected solute until there was a sufficient concentration to form other precipitate particles on the ferrite-austenite boundary. Prolonged ageing at 700° produced a more massive precipitate which nucleated on the grain boundaries and grew at the expense of the $(\text{FeCr})_2\text{Mo}$ precipitates. However, even for the longest ageing times used there was always some $(\text{FeCr})_2\text{Mo}$ precipitate present in the structure.

The X-ray results show that one type of precipitate could be identified as sigma phase while the other was either Fe_7Mo_6 or Fe_2Mo type precipitates. Electron microscopy revealed very streaked diffraction patterns as a result of faulting in the initial precipitate. Similar results were obtained by

Yagisawa, Okamoto and Yashilda⁸⁶ and Yagisawa and Fujita⁸⁷ working on Fe-Mo alloys. They were able to show that above 1000°C the Fe_7Mo_6 precipitate formed while below 900°C it was Fe_2Mo . It may therefore be concluded that the initial precipitate in this complex alloy, formed in the range 600°-700°C, is an $(\text{Fe Cr})_2\text{Mo}$ type precipitate. The grain boundary nucleated precipitate must then be the sigma phase.

5.6 PRECIPITATES IN FeCoCrMo ALLOYS.

In the Fe-rich corner of the FeCoCrMo quaternary diagram it would seem that only relatively small changes in composition are needed to produce various precipitating phases. In the present alloy R, Chi $(\text{FeCr})_2\text{Mo}$ and Sigma phases have been identified, while in similar alloys Cr-rich clusters⁶⁴ and Mo-rich zones⁷³ have been found. The presence of carbides in some of the FeCoCrMo alloys also complicates the situation by depriving the matrix of solute atoms, especially Mo.

The situation is therefore very complex and virtually no help can be obtained from the phase diagram since the phase fields have not been determined with any accuracy.

R phase appears to be a part of the equilibrium structure at temperatures up to 650°C since prolonged ageing does not reveal any further change in the structure. The relative ease with which the precipitates are nucleated in the martensite makes it unnecessary for clustering or an intermediate precipitate to form.

At temperatures above 650°C Chi-phase also forms, resulting in an equilibrium structure of

ferrite and Chi phase at 700°C. However on heating to the ageing temperature R phase precipitates are nucleated and once formed it seems energetically more favourable for them to continue growing, than for the Chi-phase to nucleate. After 100% R phase transformation there is still an incubation period before the Chi-phase nucleates on the grain boundaries.

In the direct quenching experiments the $(\text{FeCr})_2\text{Mo}$ type precipitate nucleates in preference to the R phase for a number of reasons:-

- 1) The matrix is f.c.c. so that the atomic movements needed for R phase formation are different from those in the ferrite.

- 2) The $(\text{FeCr})_2\text{Mo}$ precipitate probably finds the ferrite-austenite interface a favourable site on which to form.

- 3) The discontinuous transformation process provides a region at the interface which is rich in solute atoms and as the $(\text{FeCr})_2\text{Mo}$ precipitate contains a larger fraction of solute atoms it is able to form with little long range diffusion being necessary.

- 4) The R phase nucleates on the dislocations in ferrite where the strain field helps to counteract that of the precipitate. However, in the f.c.c. matrix there are relatively few dislocations so that, even if the atomic movement necessary was small, there would be few favourable nucleation sites available.

After the first type of precipitate has formed in each of the two conditions, the structures are both ferrite plus an intermetallic compound; it might be expected that if on ageing at the higher temperature a more stable phase forms this would be

the same in both the direct quenching and normal quenched and aged structures. However, it was found that a different type of precipitate nucleated in each case, even though both types nucleated on grain boundaries at the same ageing temperature of 700°C . It must therefore be the difference in matrix composition and/or the stability of the original precipitate which determines the new phase to form.

It is difficult to determine which is the equilibrium structure at 700°C as prolonged ageing did not show whether one of the phases, Chi or sigma, was more stable than the other. Coutsouradis et al.⁶⁴ found sigma phase after prolonged ageing Fe,13Cr,20Co,5Mo at 600°C , which might suggest that it is the more stable phase. However no definite conclusion can be drawn from the alloy studied in this investigation.

In the work on the Fe-Ni^{44,49} maraging alloys, and in that of Dyson and Keown⁶⁹, very little cobalt was found in the precipitates. This is especially unusual in the case of R phase which has been identified in the CoCrMo⁶⁸ system but not in the FeCrMo⁸² and FeCoMo^{60,88} systems. The present work shows a much larger amount of cobalt in the R phase but it is still less than that of the matrix. The extracted R phase precipitates did not appear to have any of the matrix associated with them so that the cobalt must be part of the precipitate and not present from contamination with matrix. There must still be an increase in the solid solution hardening produced by the cobalt in the matrix as the transformation proceeds. This is offset by the decrease in solid solution hardening due to the

removal of chromium and molybdenum from the matrix. The overall effect will be a slight decrease in the matrix hardness.

In the FeCoCrMo alloy studied, of all the structures formed, ferrite plus R phase, ferrite plus Chi-phase, ferrite plus $(\text{FeCr})_2\text{Mo}$ and ferrite plus sigma phase plus $(\text{FeCr})_2\text{Mo}$, the one which gives rise to the highest strengths is that of ferrite plus R phase. It would therefore seem to be this precipitate which gives rise to the strengthening in stainless maraging alloys, as the particles are only 400 Å in diameter with an interparticle spacing of approximately 1500 Å at peak hardness. However, the strength is drastically reduced at temperatures above 650°C by the appearance of brittle Chi-phase, nucleated at grain boundaries.

CHAPTER 6

CONCLUSIONS

(1) In an Fe 9.9 Cr, 12.8 Co, 4.8 Mo alloy approximately 95% lath martensite was produced on quenching from a solution treatment temperature of 1100°C . The M_s temperature was determined dilatometrically as $400^{\circ} \pm 1^{\circ}\text{C}$.

(2) Ageing the quenched alloy at temperatures between $500 - 700^{\circ}\text{C}$ resulted in the precipitation of an intermetallic compound identified as R phase.

(3) At all temperatures within the range studied, dislocations were the preferred nucleation sites for the R phase precipitates; no evidence was found of nucleation on sub-grain boundaries, grain boundaries or in the matrix.

(4) Relatively few of the dislocations in the lath martensite had precipitates nucleated upon them and it was concluded that these dislocations were predominantly edge in nature.

(5) Neither electron microscopy nor dilatometry revealed any evidence of clustering or zone formation.

(6) At all ageing temperatures studied the dilatometry data up to approximately 50% transformation could be fitted to a Johnson-Mehl equation for diffusion-controlled growth. Between $530^{\circ} - 580^{\circ}\text{C}$ the kinetics corresponded to the radial growth of rods, which was confirmed by electron microscopy. Above 580°C the kinetics corresponded to the growth of particles of appreciable initial volume as a result of precipitate nucleation and growth taking place as the specimen was heated to temperature. In all cases beyond approximately 50% transformation, the morphology of the R phase precipitates tended to change from rods to spheres and

the kinetic data deviated from the simple Johnson-Mehl equation.

7) Arrhenius plots based on both hardness and dilatometry data representing various degrees of transformation, showed a discontinuity at a temperature of approximately 580°C . Above this temperature the value of activation energy was 43 Kcal/mole after 17% transformation, which corresponds to the enhanced diffusion along dislocations and boundaries; after 63% transformation the value had risen to 52 Kcal/mole which is close to those expected for diffusion of solutes in ferrite.

At temperatures below 580°C , for quenched alloys aged with or without prior deformation, a very high activation energy of 95 Kcal/mole was obtained. It was concluded that this high value results from some form of solute-solute interaction which inhibits the diffusion process.

8) Ageing cold worked specimens gave rise to a greater number of precipitates because of the presence of additional edge dislocations introduced into the structure by the deformation.

9) On prolonged ageing at and above 650°C an additional phase, identified as Chi-phase, was nucleated at high angle boundaries while the R phase redissolved. The Chi-phase grew at certain areas along the boundaries and thus allowed the dislocation structure to recover as the R phase went back into solution to provide the solute atoms for Chi-phase formation. The final structure at 700°C was found to be ferrite plus Chi-phase, indicating that R phase was metastable at this temperature.

10) Ageing the alloy in the austenitic region after directly quenching to the ageing temperature produced two types of precipitates not observed on

ageing the martensite. The metastable austenite decomposed initially in a discontinuous manner producing ferrite and an $(\text{Fe Cr})_2 \text{Mo}$ type precipitate. Prolonged ageing led to the formation of a more stable precipitate identified as sigma-phase. However, even for the longest ageing times studied there was always some $(\text{Fe Cr})_2 \text{Mo}$ present.

(11) Precipitation strengthening in this type of stainless maraging steel results from the nucleation and growth of R phase on the dislocation sub-structure produced by the martensitic transformation. However at temperatures above 650°C the precipitation of Chi-phase and the resolution of R phase would greatly effect the mechanical properties of the alloy.

SUGGESTIONS FOR FUTURE WORK.

1) Further work is needed to determine exactly the cause of the very high activation energies obtained at temperatures below 575°C . This aspect can be studied by carrying out dilatometry experiments on alloys of various compositions.

2) Prolonged ageing experiments should be carried out at various temperatures on both directly quenched and water-quenched and aged specimens in order to determine the phases present and their location in the phase diagram.

3) A programme of mechanical tests should be carried out to study the effect of R phase precipitates on the mechanical properties, this may also give some clue as to the proposed solute-solute binding.

4) Further study is required of the complex crystallographic relationship between the ferrite and $(\text{FeCr})_2\text{Mo}$ type precipitates obtained by directly quenching.

5) It would be of commercial interest to study the effect of carbon additions to the alloy. Particularly the way in which it might affect the initial precipitate nucleation.

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APPENDIX

The dilatometric method for following phase transformations was chosen for the reasons stated in 3.7.1, the apparatus constructed being similar to that of J. Barford.⁴¹

The dilatometry assembly is shown in fig. A1 in which the Philips PR 9310 transducer is suspended in such a way that it is only free to move in the vertical direction. The two specimens of the differential system are mounted on silica rods which extend through the water-cooled base into the furnace. One specimen activates the transducer pin while the other, the control specimen, moves the transducer bodily which results in only length differences between the two being recorded. The whole dilatometry assembly and specimens are kept under a vacuum of 0.001 mm of Hg by means of an oil diffusion and rotary pump.

The furnace, which moves vertically so as to enable the specimens to be changed, was constructed with three sets of windings, which could be independently altered. The control unit consisted of an A.E.I. controller with a Power Regulator using a platinum resistance thermometer. The hot zone of the furnace was adjusted to be approximately 8 cm long with a variation of no more than 0.1°C along the full length. The specimen temperature was recorded by means of a Pt/PtRd thermocouple which was mounted between the two specimens.

The transducer output was fed into an S.E. Laboratories transducer meter which was calibrated to give readings in the range 0-1000 μ . The output from the meter, along with that from the specimen thermocouple, was fed into a high

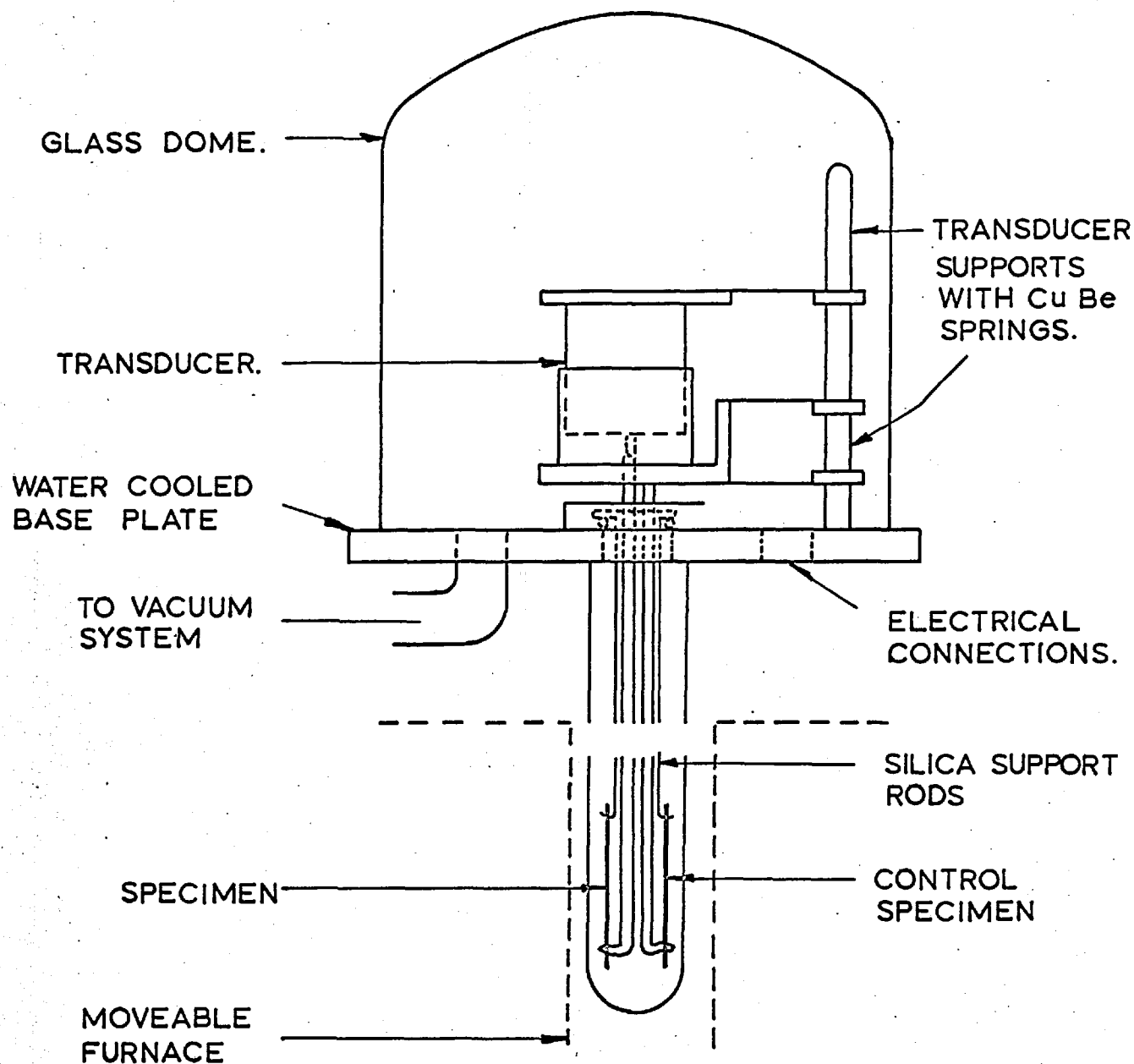


FIG.A1. Dilatometer assembly

speed potentiometric recorder which provided a record of the readings for the whole of the run.

The specimens were in the form of 0.5 m.m. sheet 5 cm long by 1 cm wide. The location holes for the silica rods were accurately positioned by means of a jig. The control specimen was always in the fully aged condition so that it would not give rise to any length change due to transformation.

CALIBRATION

(1) The transducer and transducer meter were calibrated, with the aid of a micrometer, to give ranges from 0-20 microns up to 1000 microns with an accuracy of $\pm 0.5\%$.

(2) The recorder chart could be read to within 0.1 divisions which on the 0-40 micron scale represents 0.04 microns. On a typical run a deflection of 20 microns is recorded so that a possible error is 0.2%.

(3) The initial difference in length between the control and test specimens was no more than 200 microns which would give rise to a thermal expansion of 3 microns on heating from 0-800°C. The measured length change due to thermal expansion effects, with two nickel specimens, was found to be approximately 6 microns. The calculated thermal expansion of the overall specimen length is 615 microns so that the error due to the difference in length of the specimens and support silica rods is only 1%. This indicates that a variation of 1°C at the test temperature will give rise to a recorded length change of 0.0075 microns.

(4) The majority of the dilatometer runs were carried out at constant temperature; for these the furnace was maintained at the test temperature and then quickly drawn up around the specimens. It was found that the temperature took between 5 and 10 minutes to fully stabilise but due to the differential system length changes could be recorded immediately. In most cases the incubation period was of such a length that there was no length change until the temperature had stabilised; however care had to be taken in interpreting the length changes when the incubation period was less than 10 mins.

(5) Reproduceability was tested by repeating runs on different specimens at exactly the same temperatures. It was found that the difference in results did not exceed the errors involved in taking the measurements. In the change of temperature plots for calculations of activation energies the temperature would stabilize in one minute after a change of 10°C .

(6) The errors involving in making calculations from the resulting graphs were A) "n" values

were accurate to $\pm 5\%$

B) Activation energies were accurate to $\pm 5\%$

C) Activation energies from
the change of temperatures

plots were accurate to $\pm 0.5\%$.