THE EFFECT OF MAGNETIC FIELDS ON

PHASE TRANSFORMATIONS IN METALS

by

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ABSTRACT

This thesis investigates and explains the effect of strong magnetic fields on two types of phase transformation. The first of these is a diffusionless, martensitic transformation, occurring isothermally in a Fe - 26% Ni - 2% Mn alloy. The experimental results have been used to deduce information about the nature of martensite embryos, and tend to support the Kaufman - Cohen model, rather than the more recent Ragharan - Cohen proposals.

The second transformation studied was the bcc - fcc transformation in Fe - Co alloys containing 30 - 50 wt. % Co. This is the first time that systematic information has been established for magnetic field effects on diffusion - controlled, high temperature transformations. The experimental results have been used to check the accuracy of empirical phase - stability data, and to assess the general validity of current models describing nucleation kinetics.

Generally, similar explanations of the magnetic effect apply to both transformations, but certain of the nucleation parameters can be differentiated. The size of critical embryos, deduced from the experimental data, is much larger \( r_c \sim 200 \text{ Å} \) for martensite nucleation than for diffusion - controlled nucleation at high temperatures \( r_c \sim 70 \text{ Å} \). Also, the calculated nucleus / matrix interfacial energy for martensite embryos is about 110 erg / cm\(^2\) (i.e. appreciable incoherency) whereas for diffusion - controlled nucleation this parameter has the much lower value of \( \sim 25 - 30 \text{ erg / cm}^2 \), indicating that nuclei are fully coherent.
Introduction

Previous work has clearly demonstrated that phase transformations in metals can be affected by the presence of magnetic fields, both in terms of the temperature at which a transformation occurs, and also with respect to the transformation kinetics. In general, magnetic fields have a significant effect only on transformations in which the parent and product phases differ considerably in their magnetic properties; the effect is largest when one phase is ferromagnetic whilst the other is paramagnetic. In a magnetic field, the free-energy of ferromagnetic phases is lowered significantly relative to non-ferromagnetic phases; hence the stability of the ferromagnetic phase is increased.

The magnetic effect has previously been extensively investigated during the athermal martensitic transformation in various steels. The purpose of the research reported in this Thesis was to extend the investigation of the magnetic effect to other phase transformations, starting with isothermal martensitic transformations. In these, exhibited by, for example, certain Fe-Ni, Fe-Ni-Hn and Fe-Ni-Cr alloys, the amount of martensite formed at a given temperature T below M_s is dependent on time, and not merely on the temperature difference (T - M_s). Various models have been proposed for the nucleation of isothermal martensite; it was hoped that experimental data for the magnetic effect on such transformations could be used to assess the relative merits of competing hypotheses.

All the work described so far has been confined to investigation of the magnetic effect on low-temperature, diffusionless transformations. Theoretically, the magnetic effect should be generally exhibited by any phase change, given that the competing phases differ markedly in their magnetisation. In order to verify this, the diffusion controlled bcc \rightarrow fcc and fcc \rightarrow bcc transformations in three Fe-Co alloys were investigated.
It was hoped to demonstrate that magnetic fields affect transformation temperatures and transformation kinetics, and also to verify whether the observed changes were compatible with the same model used for the magnetic effect on martensitic transformations. In addition, the magnetic effect on transformation kinetics provides an opportunity of testing competing models for solid state nucleation many of which remain largely unchecked experimentally.

The experimental work in the Thesis is divided into two parts; the first deals with magnetic effects on isothermal martensitic transformations, whilst the second part is concerned with the diffusional transformation in Fe - Co alloys. This is an arbitrary division since the magnetic effect has, in both cases, the same origin and explanation; however the experimental techniques used to investigate the two modes are widely different, as are the quantitative treatments of their kinetics, and it was therefore considered desirable to consider each transformation separately in detail. Information derived from both sources has been combined to form the general conclusions made in the final Chapter of the Thesis.
Main Symbols Used in the Text

$\alpha$  Denotes bcc phase in Fe - Co system

$\alpha'$  Denotes ferrous martensite phase

A  Martensite strain-energy factor  \( (2 \times 10^{10} \text{ erg/cm}^3) \)

$A_o$  Frequency factor for diffusional nucleation

$A_s$  Temperature at which martensite transforms to austenite on heating

$\beta_T$  Magnetisation at temperature $T$

b  Burgers vector of dislocation loop

c  Martensite embryo semi-thickness

d  Grain diameter

E  Euler's constant (0.577....)

$E_H$  Hall voltage

F  Chemical free-energy per unit volume

$F_M$  Excess free-energy of mixing

f  Volume fraction of transformed phase

G  Gibbs free-energy per unit volumes

G  Diffusional growth rate of product phase

Y  Denotes fcc phase in Fe - Co system

H  Magnetic field strength

$I_s$  Saturation magnetisation per unit volume

k  Boltzmann's constant \( (1.38 \times 10^{-16} \text{ erg/°K}) \)

$M_B$  Martensite burst temperature

$M_s$  Temperature at which austenite transforms to martensite on cooling

m  Denotes thickness:length ratio of martensite plates

$\mu$  Shear modulus
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N)</td>
<td>Nucleation rate of product phase</td>
</tr>
<tr>
<td>(n_i)</td>
<td>Initial concentration of martensite embryos</td>
</tr>
<tr>
<td>(v)</td>
<td>Lattice vibration frequency (10^{13}) sec(^{-1})</td>
</tr>
<tr>
<td>(Q)</td>
<td>Activation energy for diffusion</td>
</tr>
<tr>
<td>(R)</td>
<td>Universal gas constant (1.987 \text{ cal/mole/°K})</td>
</tr>
<tr>
<td>(r)</td>
<td>Embryo or nucleus radius</td>
</tr>
<tr>
<td>(S)</td>
<td>Entropy per unit volume</td>
</tr>
<tr>
<td>(\sigma)</td>
<td>Interfacial energy per unit area</td>
</tr>
<tr>
<td>(T_c)</td>
<td>Curie temperature °K</td>
</tr>
<tr>
<td>(T_o)</td>
<td>Temperature at which competing phases (specified) have equal free energy</td>
</tr>
<tr>
<td>(\theta)</td>
<td>Contact angle of nuclei</td>
</tr>
<tr>
<td>(\bar{v})</td>
<td>Average martensite plate volume</td>
</tr>
<tr>
<td>(\Delta W)</td>
<td>Activation energy for nucleation</td>
</tr>
</tbody>
</table>
Part I  THE EFFECT OF MAGNETIC FIELDS ON ISOTHERMAL MARTENSITE FORMATION

CHAPTER I  THE FORMATION OF MARTENSITE IN STEELS

1.1 Introduction

The martensitic transformation in steels has long been one of the least-understood solid-state phase transformations. This arises mainly from the complex variety of possible crystallographic relationships between parent and product phases, the wide spectrum of observed transformation kinetics and the failure of classical transformation theory to predict or explain these kinetics.

In presenting a review of the progress which has been made in the understanding of the mechanisms of martensitic reactions, it is proposed to treat the subject in two stages, namely:

a) Observed kinetics of martensite formation.
b) Theories of martensite nucleation and growth.

In this way, whilst recognising that these two aspects of the problem are fundamentally inseparable, the major areas of controversy may be more easily identified.

1.2 Kinetics of the Austenite $\rightarrow$ Martensite Transformation

Because of the wide variety of transformation kinetics exhibited by different ferrous alloys, it is intended to describe separately the four major transformation modes which have been distinguished, namely:

(i) The 'athermal' mode
(ii) The 'burst' transformation
(iii) The 'thermoelastic' mode
(iv) The 'isothermal' mode
Although it will be shown later that from the viewpoint of operational nucleation, these four subdivisions are purely arbitrary, their use will serve to clarify the rather confusing variations in reaction kinetics.

1.2.1 The 'Athermal' Transformation

This kinetic behaviour is commonly observed in plain carbon steels and low-alloy steels. Transformation from austenite to martensite begins at a well defined temperature (denoted $M_S$) on cooling. The $M_S$ temperature has been found to be virtually independent of the cooling rate (Bibby and Parr, 1964). However, a critical minimum cooling rate is required in order to suppress equilibrium phase changes such as the formation of bcc ferrite or other austenite decomposition products. The critical cooling rate varies markedly with composition. Below $M_S$ the extent of transformation depends only on the amount of undercooling ($\Delta T$) below $M_S$. Transformation takes place extremely rapidly during quenching to the reaction temperature, and no transformation to martensite occurs during further isothermal holding. (Howard and Cohen, 1948).

The relationship between the extent of transformation and the amount of undercooling ($\Delta T$) below $M_S$ has been extensively investigated (e.g. Harris and Cohen, 1949; Koistinen and Marburger, 1959; Brook et al 1960). Harris and Cohen (1949) derived the following empirical expression for the relationship between the volume fraction of martensite formed ($f$), and the undercooling below $M_S$:

$$f = 1 - 6.956 \times 10^{-15} \left[ 455 - \Delta T \right]^{5.32} \quad \text{Equation (1)}$$

whilst Koistinen and Marburger (1959) proposed the simpler relationship:
Both these relationships give reasonable agreement with experimental data for the early stages of transformation, although equation (2) has a wider range of accuracy.

Entwisle (1971) pointed out that during the first 50 pct of transformation, it was not possible from experimental data to distinguish the foregoing empirical relationships from a linear dependence of \( f \) on \( \Delta T \), (Figure 1) in agreement with the findings of Brook et al (1960).

With the exception of Cobalt, all elements which dissolve in austenite lower the \( M_S \). Interstitial alloying elements are approximately one order of magnitude more effective in lowering \( M_S \) than substitutionals. Various attempts have been made to derive empirical relations allowing calculation of \( M_S \) knowing the alloy composition. The formula of Stevens and Haynes (1956) is fairly accurate for describing the \( M_S \) of low alloy steels:

\[
M_S \text{ (°C)} = 561 - 474 \, C\% - 33 \, Mn\% - 17 \, Ni\% - 17 \, Cr\% - 21 \, Mo\% \quad \text{(wt. pct.)}
\]

Many attempts have been made to correlate the driving force for the martensitic reaction \( \Delta G^{\gamma \rightarrow \alpha} \), where \( \Delta G^{\gamma \rightarrow \alpha} = G^{\gamma} - G^{\alpha} \) is the difference in volume free energy between austenite and martensite, with the extent of transformation. Magee (1970) has derived the following relationship between these two parameters, assuming that the number of new martensite plates formed due to an increase in driving force is directly proportional to the change in the driving force.

\[
1 - f = \exp \left[ K \left( \frac{\Delta G^{\gamma \rightarrow \alpha}}{\Delta T} \right) \Delta T \right] \quad \text{Equation (3)}
\]
Fig. 1 Volume fraction of martensite formed at different temperatures below $M_s$, in Fe-10%Ni-0.6%C.
(This assumption is supported by the work of Magee and Paxton (1968) who demonstrated that the amount of martensite formed under an applied stress is linearly proportional to the stress level, equivalent to a driving force).

Equation (3) is similar to the empirical equation previously suggested by Koistinen and Marburger (Equation 2).

For small undercoolings, Equation (3) reduces to:

\[ f = -K \frac{\Delta G^{\gamma \rightarrow \alpha}}{dT} \Delta T \quad \text{Equation (3b)} \]

As already noted, experimental results indicate a linear relationship between \( f \) and \( \Delta T \) over a range of \( f \) values; the general form of equation (3b) hence appears correct. Moreover, if this relationship is correct, the slope of the line (i.e. \( \frac{df}{dT} \)) should be directly proportional to \( \frac{d(\Delta G^{\gamma \rightarrow \alpha})}{dT} \) i.e. \(-\Delta S^{\gamma \rightarrow \alpha}\).

Brook et al (1960) have demonstrated that \( \frac{df}{dT} \) can in some cases be correlated directly with \( \Delta S^{\gamma \rightarrow \alpha} \), but were hampered by lack of available thermodynamic data. However Satyanarayana et al (1968) were able to obtain the value of \( \Delta S^{\gamma \rightarrow \alpha} \) directly by superimposing a strong magnetic field during transformation. The magnetic field changes the driving force for the martensitic reaction, hence causing a shift in the \( M_S \). Knowing the change in driving force, and the corresponding \( M_S \) shift, the value of \( \Delta S^{\gamma \rightarrow \alpha} \) may be obtained. It was shown that the rate of martensite formation below \( M_S \) \( \left( \frac{df}{dT} \right) \) is directly proportional
to $\Delta S^{\gamma \rightarrow \alpha}$, as shown in Figure (2) giving additional support to equation (3b).

Cooling rate variations have little or no effect on the $M_s$ temperature, but influence the progress of transformation below $M_s$, owing to the phenomenon of stabilisation. Stabilisation occurs as a result of slowing down, or interruption of cooling before complete transformation has occurred, resulting in a retardation of transformation. If a partially transformed specimen is held isothermally, before the temperature is again lowered, renewed transformation only occurs after a considerable temperature hysteresis. (Harris and Cohen, 1949; Kinsman and Shyne, 1967).

The latter have proposed a stabilisation mechanism involving carbon segregation to dislocations in the martensite/austenite interface: this pins the interface and hinders further transformation. This model is supported by the work of Philibert (1956) who showed that the stabilisation phenomenon disappeared from nickel steels when all carbon was removed from the specimens.

1.2.2 The 'Burst' Transformation

This transformation mode is strongly evident in some Fe - Ni and Fe - Ni - C alloys, and its kinetics differ markedly from those of athermal transformations.

Transformation commences abruptly during cooling at temperature $M_b$, and a volume of martensite is formed in a single event, called a 'burst'. The burst is accompanied by the evolution of a considerable amount of energy (often an audible 'click' may be heard) which may cause a large rise in local temperature.

In some cases, up to 70 pct martensite can form in a single burst,
accompanied by a temperature rise in excess of 30 deg. C. Entwistle and Feeney (1969) showed that burst transformations were influenced by prior heat treatment; raising the austenitising temperature from 800 °C to 1200 °C raised \( N_B \) by 40 °C. This effect was assigned to a change in the potency of the martensite embryos. It was also shown that the magnitude of the burst was a function both of the burst temperature (\( N_B \)) and of the prior austenitic grain size. (See Figure 3)

1.2.3 **Thermoelastic and Stress-Induced Transformation**

The initial formation of thermoelastic martensite may obey athermal or burst kinetics or a mixture of these. The difference between thermoelastic martensite and normal martensite lies in the reversibility of the austenite \( \rightarrow \) martensite transformation. Thermoelastic martensites often have a temperature hysteresis of only 20 degrees between \( M_S \) and \( A_S \) (austenite start temperature). Moreover, the martensite transforms back to austenite in exactly the reverse order of its formation.

Reversible thermoelastic martensite may also be formed by the application of stress above \( M_S \). The formation of stress-induced martensite gives rise to large strains. On removal of the stress, the martensite reverts completely to austenite (though showing a stress-strain hysteresis between loading and unloading) together with complete strain recovery. These phenomena are intimately linked with pseudoelasticity and the shape-memory effect.

Although this type of transformation is most common in non-ferrous systems (e.g. Au - Cd, Ni - Ti, Cu - Zn etc.) it also occurs in some stainless steels and other iron base alloys.

Further discussion of thermoelastic martensites will not be attempted in this thesis. Comprehensive reviews e.g. Tas, Delaey and
Fig. 3  Variation of burst size with temperature and grain size. (Entwisle & Peeney 1969).
Deruyttere (1974) are available in the literature.

1.2.4 The Isothermal Transformation

In most martensitic transformations, an isothermal component is either not operative, or is obscured by a predominant athermal reaction. Kurdjumov and Maksimova (1948, 1951), pioneered the investigation of isothermal transformations, having discovered this reaction mode in an Fe - Ni - Mn alloy. This system has formed the basis of the majority of subsequent investigations.

In the absence of prior athermal martensite, isothermal transformation kinetics are as shown in Figure (4). In a typical reaction, transformation commences slowly, accelerates rapidly to a maximum rate (which may remain constant for a time) then dies away slowly. As the reaction temperature is lowered, the overall transformation rate increases, together with the total amount of martensite formed. Below a certain temperature level however, the rate of reaction begins to decrease, leading to C - shaped time - temperature - transformation curves, (Figure 5) similar to those found for diffusional isothermal transformations. The C - curve behaviour has been amply demonstrated by the work of Cech and Hollomon, (1953); Shih et al, (1955), and Pati and Cohen, (1969). The existence of C - curve kinetics has been explained in the following manner by Pati and Cohen (1969).

At temperatures near $M_S$, thermal fluctuations are large, but the driving force for the transformation is low, which means that a very large martensite nucleus is necessary. Thus the transformation (or nucleation) rate is slow. As the temperature is lowered below $M_S$, the required nucleus size decreases giving easier and more rapid nucleation. Below a certain temperature, however, thermal energy drops to a level where it
Fig. 4 Kinetics of isothermal martensite formation (schematic).
Fig. 5  T-T-T diagram for isothermal martensitic transformation in Fe-23.2Ni-3.62Mn alloy.
is difficult for embryo growth, although the driving force is large. Therefore the nucleation rate again decreases.

The isothermal kinetics in Fe-Ni-Mn alloys have been found to be very sensitive to changes in grain size (Raghavan and Entwisle, 1965). It was found that the 'incubation time' (defined as the time to form 0.2% martensite) varied inversely as the cube of the grain diameter (Figure 6), indicating that the nucleation sites are uniformly distributed in the austenite, and do not depend on the amount of grain boundary area in the sample; that is to say that grain boundaries do not supply effective nucleation sites for martensite formation.

The shape of experimental isothermal transformation curves has been quantitatively explained using two concepts, namely:

(1) Autocatalysis

(2) Austenite partitioning

Autocatalysis may be defined for present purposes as the creation of new nucleation sites in the vicinity of a newly-formed volume of martensite. Autocatalysis greatly increases the concentration of available nucleation sites, leading to an increasing nucleation rate, as the transformation proceeds.

As more and more martensite forms, the remaining austenite becomes severely 'networked' (partitioned) by martensite plates. The existing plates hamper the growth of newly-formed ones, reducing the volume of martensite formed as a result of each nucleation event. Hence, although the nucleation rate is increasing, the actual volume of transformation taking place gradually decreases, as the partitioning effect slowly becomes more influential.

Raghavan and Entwisle (1965) have proposed a quantitative kinetic
Fig. 6 Variation of incubation time with grain diameter.
theory, based on autocatalysis, and including the partitioning theory of
Fisher et al (1949). They assumed that the number of autocatalytic nuclei
at any time was proportional to the volume of transformation, and that
these nuclei have the same effectiveness (or 'potency') as the original
natural nuclei. They obtained the following expression for the trans­
formation rate:

\[
\frac{df}{dt} = (n_i + Cf - N) \nu q (1 - f)^{1 + \frac{1}{m}} \exp\left(\frac{-\Delta W}{RT}\right)
\]

Equation (4)

where
- \( f \) is the volume fraction of martensite formed
- \( n_i \) is the initial nuclei concentration (per cm\(^3\))
- \( C \) is the number of autocatalytic embryos produced during
  the formation of 1 cm\(^3\) of martensite
- \( N \) is the number of martensite plates in volume \( f \)
- \( m \) is the thickness - to - length ratio of plates
- \( q \) is the mean austenite grain volume
- \( \Delta W \) is the energy of activation of martensite nuclei
- \( \nu \) is an attempt frequency

Using this relationship, satisfactory agreement between computed and
experimental transformation curves could be obtained (up to approximately
10% transformation) as shown by Figure (7).

Raghavan (1969) and Pati and Cohen (1971) were able to improve
the correlation between computed and experimental transformation curves
realising that the simple partitioning theory of Fisher et al (1949)
and Fisher (1953) did not adequately describe the actual sequence of
plate formation. Pati and Cohen (1971) measured the actual mean volume
per martensite plate (by metallography) at various stages during trans­
formation. Using these values, satisfactory agreement between computed
Fig. 7 Comparison between observed and computed (equation 4) transformation curves.
and experimental transformation curves was obtained up to at least 25% transformation, as shown in Figure (8).

The basic features of martensitic transformation kinetics have now been described, but the main problem preventing a more complete understanding of the reaction has been the lack of a viable model for martensite nucleation. The development of martensite nucleation theories will therefore be described in the next section.

1.3 The Nucleation of Martensite

1.3.1 Introduction

Application of classical nucleation theory to martensitic transformations produced a dilemma. Classical homogeneous nucleation theory predicted an activation energy for the formation of martensite from defect-free austenite which was about four orders of magnitude greater than that experimentally observed (Kaufman and Cohen, 1953). This disparity rules out any possibility of classical homogeneous nucleation. This situation was aggravated by later experimental work on the kinetics of isothermal martensite formation which established a direct proportionality between the activation energy of martensite nucleation and the chemical driving force for the reaction (Entwisle, 1966; Pati and Cohen, 1969), as shown in Figure (9). This finding is at variance with classical heterogeneous nucleation theory which predicts that the activation energy for nucleation is inversely proportional to the fourth power of the driving force. Thus, one is forced to reject the possibility of either classical homogeneous or classical heterogeneous nucleation of martensite.

Investigation of the formation of martensite in small particles of austenite (Cech and Turnbull, 1956; Cech and Holloman, 1953; Magee, 1971) has shown that, in some particles, no transformation to martensite occurs,
Fig. 8 Improved correlation between observed and computed transformation curves. (Fati & Cohen 1971).
Fig. 9  Variation of activation energy for martensite nucleation with the transformational driving force, for Fe-Ni-Mn.
even after a severe quench. This is a clear indication of the heterogeneous nature of the martensitic transformation; the problems remaining are to define firstly the nature and properties of the nucleation site, and secondly the nucleation mechanism.

1.3.2 Karee's Hypothesis

Karee (1970) proposed that the classical nucleation barrier may be circumvented by considering the energy interaction between a martensite nucleus and its nucleation site. It was suggested that as the nucleus grows its strain field interacts with that of the nucleating site, thereby reducing the elastic free-energy of the site. In this manner, the nucleus can grow from any size with an attendant reduction of overall free-energy, as shown schematically in Figure (10). The controlling factor in the growth of the nucleus is postulated to be the motion, or propagation through the surrounding austenite, of dislocations in the nucleus/austenite interface, which suggests that the factors controlling the nucleation process should be very similar to those controlling plastic deformation processes. Both of these depend on the resistance to dislocation motion through the lattice. This hypothesis is supported by the results of deformation experiments on iron (Wynblatt and Dorn, 1966) which demonstrated a linear dependence of the activation energy for plastic flow ($Q_D$) on the stress level $\sigma_D$ (driving force). This is formally identical to the variation of the activation energy for martensite nucleation ($\Delta W$) with the chemical driving force, $\Delta G^{\gamma\alpha}$ (Entwisle, 1968; Pati and Cohen, 1969). Additionally, the value of $\frac{d(Q_D)}{d(\sigma_D)}$ is in close agreement with that found for $\frac{d(\Delta W)}{d(\Delta G^{\gamma\alpha})}$. The model has not, as yet, been developed sufficiently to define the origin, structure or size
Figure 10: Schematic plot of the free energy of a bcc particle in austenite and the free energy of the nucleation site as a function of the volume of the particle.
of the nucleation site, neither does it yield quantitative predictions concerning nucleation kinetics.

1.3.3 The 'Pre-existent Embryo' Approach

The classical nucleation barrier may be circumvented by postulating that pre-formed martensite embryos are present in austenite. Kaufman and Cohen (K-C) (1958) have developed a quantitative model of martensite nucleation based on this premise. The martensite embryos are assumed to be of the type envisaged by Knapp and Dehlinger (1956), namely a thin oblate spheroid of bcc material, possessing a semi-coherent interface composed of dislocation loops, as shown in Figure (11). The driving force for the martensitic transformation is regarded as a stress, acting on the interface dislocations, tending to move them out into the surrounding austenite, thereby generating the martensitic structure behind them. As the temperature is lowered, and the driving force thereby increased, suitably large embryos can lower their overall free-energy by growth in this manner. Referring to Figure (11) it may be seen that growth in the thickening direction involves the expansion of existing screw dislocations whereas growth in the radial direction involves both edge-component dislocation expansion in the [1 1 0]_γ direction, together with the creation of new dislocation loops at the tips of the embryo to obtain growth in the [5 5 4]_γ direction.

The above model (Knapp and Dehlinger, 1956) was simplified by K-C (1958), who proposed that the complex interfacial screw dislocation array could be replaced by a single, equivalent 'giant' dislocation loop, in the manner suggested by Frank and Stroh (1952). The growth of the embryo was described in terms of unit growth steps of the 'giant' loop under the 'stress' supplied by the chemical driving force. When the
Dislocation loops

Knapp and Dehlinger's model of the martensite embryo\textsuperscript{(56)}

Fig. 11
embryo reaches a critical size, further growth leads to a rapid reduction in the free-energy of the giant loop. Thus, beyond this critical size growth accelerates rapidly, becoming cataclysmic and leading to the formation of a full-size martensite plate within a few microseconds of the critical event. The critical steps in the nucleation process at some temperature $T$ may be defined with reference to Figure (12). At temperature $T$, embryos smaller than $r_*$ cannot be activated, since their further growth entails an increase in their free-energy. Embryos of size $r_*$ may lower their overall free-energy by growth. As they grow the energy required for further growth steps decreases, leading to accelerated growth. At size $r_c$, the giant dislocation loop may also lower its free energy by further growth. Hence from size $r_c$, growth becomes cataclysmic as the activation energy falls to zero, resulting in the almost instantaneous formation of a macroscopic martensite plate.

Using this model, K - C (1958) showed that the activation energy for a unit growth step of the giant dislocation loop was given by:

$$
\Delta W = 4 \times 10^{-2} \left( \frac{\sigma}{A} \right)^{\frac{1}{2}} \left[ 3\sigma r^{3/2} + \Delta G_{\gamma^c\alpha} \left( \frac{\sigma}{A} \right)^{\frac{1}{2}} r^2 \right] \tag{5}
$$

where $\sigma$ is the specific embryo/matrix interfacial energy

$A$ is a strain energy parameter

$r$ is the initial embryo radius

$\Delta G_{\gamma^c\alpha}$ is the chemical driving force

This model may be tested using experimental kinetic data. Equation (5) governs initial stages of observed transformation kinetics when the embryo radius ($r$) corresponds to that of the most-potent embryos present at the isothermal reaction temperature.

Entwistle (1968) determined the activation energy of initial
Fig. 12  Critical steps in martensite nucleation.
nucleation $\Delta W$, at various temperatures, for the isothermal martensitic transformation in three Fe - Ni - Mn alloys of similar composition (22 - 23% Ni 3 - 4% Mn). The method of calculation of $\Delta W$ using experimental kinetic data will be described in Section 4.4.1. Entwisle's values were plotted against corresponding values of the chemical driving force $\Delta G^{\text{re}}$ derived from the formula due to Imai and Izumiya (1963). A linear relationship was found, see Figure (9), supporting the general form of Equation (5). The slope and intercepts of this line were used to evaluate the parameters $\sigma$ and $r$ in Equation (5). These are given in Table I, and are reasonable values for both parameters on the basis of the employed nucleation model. Further work by Pati and Cohen (1969) on a similar alloy yielded comparable $\Delta W$ values, which were plotted (together with those of Entwisle, 1968 and Shih et al, 1955) against the corresponding chemical driving force. The derived embryo parameters are given in Table I. The embryo size indicated by these results is large ($\sim 200 \text{Å}$); it would hence appear that embryos should be directly observable, using electron microscopy. An electron micrograph claiming to show martensite embryos above $M_S$ in Fe - 29.3 at pct Ni has been published by Richman, Cohen and Wilsdorf (1959). Later attempts at direct observation of embryos have proved fruitless; in the absence of further concrete evidence, their existence remains speculative; it was demonstrated by Pati and Cohen (1969) that because of the small initial density of embryos (estimated at $\sim 10^7$ per cm$^3$), the chances of actually observing one are exceedingly rare. In addition, the stresses involved in thinning samples for transmission electron microscopy may well be sufficient either to 'trigger-off' embryos into martensite plates, or to change their structure or morphology. The K - C nucleation model has been extended successfully to the case of isothermal martensite formation.
in Fe - Ni alloys (Raghavan and Cohen, 1971) and Fe - Ni - Cr alloys (Jones and Entwisle, 1971). When experimental kinetic data for these transformations was analysed (in a similar manner to that outlined above) values of embryo radius were obtained; these are given in Table I.

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<tr>
<th>Composition</th>
<th>Interfacial Energy (( \sigma )) erg/cm(^2)</th>
<th>Embryo Radius (( r )) cm</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>Fe - 22% Ni 3% Mn</td>
<td>132</td>
<td>2.03 \times 10^{-6}</td>
<td>Entwisle (1968)</td>
</tr>
<tr>
<td>Fe - 23% Ni 4% Mn</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As above, plus</td>
<td>120 - 130</td>
<td>1.8 - 2.0 \times 10^{-6}</td>
<td>Pati &amp; Cohen (1969)</td>
</tr>
<tr>
<td>Fe - 23.4% Ni 3.5% Mn</td>
<td></td>
<td></td>
<td>Raghavan &amp; Cohen (1971)</td>
</tr>
<tr>
<td>Fe - 30% Ni</td>
<td>-</td>
<td>4.2 \times 10^{-6}</td>
<td></td>
</tr>
<tr>
<td>Fe - 24% Ni 3% Cr</td>
<td>-</td>
<td>1.78 \times 10^{-6}</td>
<td>Jones &amp; Entwisle (1971)</td>
</tr>
</tbody>
</table>

Table I Martensitic Embryo Parameters Derived for Various Alloys

The marked difference in calculated embryo size between the binary and ternary alloys has been explained in terms of stabilisation of the embryo by the addition element, possibly by pinning of dislocations in the embryo interface (Raghavan and Cohen, 1971). Interfacial pinning hence produces a less-potent (i.e. apparently smaller) embryo.

The basic K - C model has recently been modified by Raghavan and Cohen (1972a, 1972b). In this new approach (K - C - R), the simplified picture of the embryo interface (equivalent giant dislocation loop) is
discarded, and the more realistic model of Frank (1953) adopted. The 'stresses' acting on the interface dislocations in the thickening and radial-growth directions are obtained by resolving the free-energy change accompanying embryo growth into two components acting in the thickening and radial directions respectively. It is shown that radial growth occurs before thickening, and that radial growth (and hence the nucleation kinetics) is controlled by the formation of new dislocation loops at the tips of the embryo. The activation energy for loop formation decreases rapidly as the embryo grows; eventually growth becomes cataclysmic, and a macroscopic martensite plate is formed. During the radial-growth stage, the stress acting in the thickening direction gradually increases, eventually exceeding the yield-stress of the austenite. Thickening then occurs in addition to radial growth. The actual kinetics of the radial growth and thickening processes have been calculated, using Gilman's (1960) dislocation velocity relationships. The results show that most of the radial growth occurs within a few microseconds. When the martensite particle meets an obstacle (e.g. a grain boundary or an adjacent martensite plate), radial growth is arrested, but thickening can continue over a long period, at a gradually diminishing rate, until the thickening stress drops below the yield stress of the surrounding austenite.

The mathematical relationships defining initial (i.e. radial growth) nucleation kinetics predicted by the K - C - R model are as follows:

\[
\frac{d(\Delta G)}{dr} = \frac{-5}{4} \mu b^2 \frac{rc^*}{\rho \delta r} \left[ \ln \left( \frac{\rho^*}{b} \right) + 0.4 + z \right] \quad \text{Equation (5a)}
\]

\[
\Delta U^* = \frac{5}{16} \mu b^2 \rho^* \left[ \ln \left( \frac{\rho^*}{b} \right) - 1.6 + z \right] \quad \text{Equation (5b)}
\]
where $\Delta G$ = free energy change attending the formation of a martensite particle, radius $r$ and semi-thickness $c$

$\mu$ = shear modulus (austenite)

$b$ = Burgers vector of dislocation loop

$\delta r$ = unit radial growth distance

$c'$ = embryo semi-thickness after unit growth

$p^*$ = critical dislocation loop radius

$z$ = dislocation core energy parameter ($\approx 1$)

Initially $p^*$ is determined from equation 5 (b), to give satisfactory agreement with an experimental $\Delta W (= \Delta U^*)$ value. Then the embryo radius $r$ is calculated from equation 5 (a). Keeping $r$ constant, $p^*$ at various temperatures may be calculated, and the $\Delta U^*$ values so obtained may be compared with those obtained experimentally. Much larger embryo sizes than those predicted by the K-C model are necessary to yield good agreement with experimental data. Raghavan and Cohen (1972) showed good correlation with experimental $\Delta W$ values for a 29.5% Ni 0.25% Mn alloy, assuming an embryo radius of $6 \times 10^{-5}$ cm.

We are now in a position to interpret the transformation kinetics described in Section 1.2 on the basis of pre-existing embryos. This will show that certain subdivisions of martensite kinetics are mechanistically unnecessary.

1.4 Interpretation of Transformation Kinetics on K-C-R Model

(a) Isothermal Martensite Formation

This follows directly from the pre-existing embryo model, and has already been discussed.

(b) Athermal Martensite Formation

This occurs in alloys where the martensite embryos are extremely
potent. The largest embryos are the first to be activated; the temperature at which this occurs is the athermal $M_s$. However, with sufficiently slow cooling, martensite will form isothermally above the athermal $M_s$, due to the slow activation of the largest embryos in the same manner as described previously. Therefore athermal martensite formation may be regarded merely as a very rapid isothermal reaction, as demonstrated for the Fe–Ni system by Raghavan and Cohen (1971). If specimens are held isothermally after quenching below $M_s$, sufficiently sensitive equipment can detect a small isothermal increment of transformation after the main athermal component. This 'tail' is due to the slow thermal activation of those embryos which are just too small for cataclysmic 'triggering', but which can grow isothermally to the critical size.

(c) Burst Martensite

This has been explained (Entwisle and Feeney, 1969) on the basis of extremely potent autocatalysis, where the first embryo to be isothermally activated creates very many nucleation sites of high energy which may be sufficiently potent to be immediately available for cataclysmic growth at the temperature considered. Thus, the first plate (or first few plates) formed triggers off a chain reaction of nucleation events leading to a large 'burst' of martensite formation.

The three most commonly observed modes of martensite formation may therefore be interpreted satisfactorily (in a qualitative manner) with recourse to only one model of martensite nucleation. A suggested reclassification of nomenclature for martensitic kinetics is tabulated below:
<table>
<thead>
<tr>
<th>Old Nomenclature</th>
<th>Suggested Nomenclature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Athermal</td>
<td>Rapid Isothermal</td>
</tr>
<tr>
<td>Burst</td>
<td>Autocatalytic</td>
</tr>
<tr>
<td>Isothermal</td>
<td>Slow Isothermal</td>
</tr>
<tr>
<td>Thermoelastic</td>
<td>Reversible Rapid Isothermal</td>
</tr>
</tbody>
</table>
CHAPTER 2  EFFECT OF MAGNETIC FIELDS ON MARTENSITE FORMATION

2.1 Introduction

The ability to influence the martensitic transformation in certain alloys by means of strong magnetic fields has become well established over the past decade. The experimental work leading to a successful model for the magnetic effect will now be described.

2.2 The Effect of Pulsating Magnetic Fields

Sadovskiy et al (1961) were the first to seriously investigate reports that a magnetic field could influence the martensitic transformation. They observed that only 1 - 3 pct martensite was formed in a 0.5\% C, 1.5\% Cr, 23\% Ni steel on quenching from 900\°C to -196\°C, whereas when the specimen was subjected to a pulsating magnetic field of 350 K0e, at the latter temperature, a large (unspecified) amount of martensite was formed. This phenomenon was further investigated by Fokina and Zavadskiy (1963) using a similar steel (0.5\% C, 2\% Cr, 22\% Ni). They discovered the existence of a threshold field strength below which no effect could be observed. Martensite was induced only if the threshold field was exceeded, the amount of martensite formed increasing rapidly as the field strength was increased, as shown in Figure (13). It was also found that practically all of the induced martensite was formed during the first two field pulses; the third and subsequent pulses had negligible effect. Using the same steel, Fokina et al (1965a) showed that the major effect of the magnetic field was to shift the austenite → martensite transition temperature (M_S) to higher values, with a corresponding increase in the amount of martensite formed at a given temperature below M_S. The M_S shifts observed for different field strengths are given in Table (II).
Fig. 13 Amount of Martensite formed in pulsating magnetic fields of various strengths.
Table II  
Variation of $M_S$ Temperature with Applied Field Strength in a 0.5% C - 2% Cr - 22% Ni Steel

<table>
<thead>
<tr>
<th>Field Strength (KOe)</th>
<th>Shift in $M_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>15 Deg. C</td>
</tr>
<tr>
<td>170</td>
<td>55</td>
</tr>
<tr>
<td>300</td>
<td>85</td>
</tr>
<tr>
<td>350</td>
<td>115</td>
</tr>
</tbody>
</table>

2.3 The Effect of Steady Magnetic Fields

Fokina et al (1965b) showed that similar results to those given above could be achieved using steady magnetic fields, although the field strengths available were necessarily much lower than those obtainable with pulsed electromagnets. Specimens of a 0.5% C - 2% Cr - 22% Ni steel were austenitised, and then cooled to liquid helium temperature, resulting in the formation of about 8% martensite. A constant magnetic field of 40 KOe increased the amount of martensite to about 21%. The increments of extra martensite formed in this steel under the influence of steady magnetic fields of various strengths are given in Table III below:

<table>
<thead>
<tr>
<th>Field Strength (KOe)</th>
<th>Field Induced Martensite (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>30</td>
<td>9</td>
</tr>
<tr>
<td>40</td>
<td>13</td>
</tr>
</tbody>
</table>

Table III  
Amount of Martensite Formed in Steady Magnetic Fields
Bernshteyn et al (1965) studied the effects of steady magnetic fields on martensite formation in a series of nickel steels (0.03 - 1.1% C, 5 - 16% Ni). They were unable to detect a measurable shift in $M_S$ due to a field of about 4.2 KOe but observed that much more martensite formed at a given temperature when the magnetic field was applied. It was also noticed for the first time that the 'disintegration' of martensite on heating (i.e. tempering) in the same alloy was noticeably retarded by a magnetic field. Estrin (1965) observed that a steady field of 18.6 KOe raised the $M_S$ of a 0.5% C, 19% Ni steel by 5° C. A similar result was obtained by Malinen and Sadovskiy (1966) who reported a shift in $M_S$ of 5° C for a 0.5% C, 2% Cr, 16% Ni steel, subjected to a field of 24 KOe. Malinen and Sadovskiy also investigated the reverse (martensite → austenite) transformation in Fe - Ni - C alloys. It was found that magnetic fields significantly reduced the extent of transformation in all the alloys which were investigated. This effect was ascribed to a shift in the transformation temperature, similar to that found for the martensitic transformation. Satyanarayana (1968) found a marked $M_S$ shift due to magnetic fields up to 16 KOe in both a 1% C - 1.5% Cr steel and a 0.3% C - 0.6% Cr - 3% Ni steel. This work will be discussed more fully in the next section.

Thus far, discussion has been confined to the effect of magnetic fields on athermal martensitic transformations. However, there are a few references (Estrin, 1964, 1965; Malinen et al, 1967; Korenko 1973) to magnetic effects in Fe - Ni - Mn alloys, which transform isothermally.

Estrin (1965) investigated a Fe - 22.7% Ni, 3.3% Mn alloy which undergoes isothermal transformation. He noticed that the application of a magnetic field during transformation produced not an increased amount of martensite but an increase in the rate of transformation. When
the field was removed, the transformation rate was reduced to its original value. Korenko (1973) has studied the effect of fields up to 140 KOe on a range of Fe – Ni alloys exhibiting isothermal and burst transformation kinetics, and a Fe – Ni – Mn alloy which transforms isothermally.

In a Fe 28.7% Ni alloy which exhibits isothermal kinetics, a field of 40 KOe raised the $M_s$ temperature from 12°C to 24°C. Above the zero-field $M_s$, the isothermal transformation rate increased with increasing field strength up to 95 KOe as shown in Figure 14.

In a Fe – 29.6 Ni alloy, isothermal transformation was first observed at -9°C. As the temperature was lowered the transformation rate increased until at -20°C the transformation became of the burst type with a measurable incubation period. Application of magnetic fields of increasing strength at -2°C and +9°C (i.e. 7°C and 18°C above $M_s$) had effects similar to lowering the temperature below $M_s$ as shown in Figure 15. The transition from isothermal to burst kinetics was reproduced at both temperatures by field strengths of 60 KOe and 90 KOe respectively. The martensite morphology in this alloy underwent a transition near -20°C; above this temperature lath-type martensite predominated, but below this point definite plate structures appeared. As the temperature of transformation was lowered below -20°C, more and more plate martensite was produced. This structural transition could also be reproduced at higher temperatures by application of magnetic fields. This demonstrates that the morphological transition is not merely a function of temperature, but depends intrinsically on the total driving force for transformation.

Experimentation on a composition exhibiting bursting at all temperatures (Fe 30.8 Ni) showed that magnetic fields raised the $M_s$ temperature. A field of 90 KOe raised $M_s$ from -45°C to -20°C, and gave rise to a large incubation period prior to bursting.
Fig. 14 Increased isothermal transformation rate due to magnetic fields.
Fig. 15  Effect of magnetic fields on transformation kinetics in a Fe-29.6%Ni alloy.
The Fe - Ni - Mn alloy investigated (Fe 22.5 Ni 4 Mn) did not detectably transform at any holding temperature down to -196° C. However, transformation could be induced by a magnetic field of 80 KOe at -80° C. Application of a field of 140 KOe at this temperature produced 40% isothermal transformation in 3 hours.

2.4 Theory of the Magnetic Effect

Sadovskiy et al (1961) suggested that stresses, (termed 'ponderomotive forces'), arising from magnetostriction of the ferromagnetic phase in a magnetic field, were mainly responsible for the activation of the martensitic transformation by a field. This view was supported by Fokina and Zavadskiy (1963) but order-of-magnitude calculations by Bernshteyn et al (1965) and some experimental observations by Sadovskiy et al (1967) showed that this could not be the case.

Later theories were based on a thermodynamic approach, the main postulate being that magnetic fields influence phase stability via their effect on the relative free-energies of competing phases. The Clausius-Clapeyron equation was modified to predict the effect of a magnetic field on the martensite transformation temperature . The shift in temperature is given by:

\[
\Delta T = \frac{\Delta I_s H T_0}{q} \quad \text{Equation (6)}
\]

where \( \Delta I_s \) is the difference in saturation magnetisation between unit volumes of austenite and martensite

\( q \) is the latent heat of transformation per unit volume

\( T_0 \) is the temperature at which austenite and ferrite have equal free energy

\( H \) is the magnetic field strength
This expression was used by Estrin (1965) and subsequent workers to explain observed $M_S$ shifts. Satyanarayana et al (1968) utilised experimental $M_S$ shifts in a magnetic field to derive thermodynamic data. The entropy of transformation $\Delta S^{\gamma \rightarrow \alpha}$ was determined as follows:

Consider a homogeneous steady magnetic field of strength $H$ interacting with an alloy containing a mixture of austenite ($\gamma$) and martensite ($\alpha$):

The free energy of unit volume of each phase will be lowered by an amount $I_s H$ where $I_s$ is the saturation magnetisation of the phase concerned. Hence the free energy of austenite will be lowered by an amount $I_s \gamma H$ and that of martensite by an amount $I_s \alpha^1 H$.

The relative free-energy change ($\Delta G_{mag}$) between austenite and martensite is given by:

$$\Delta G_{mag} = H \left( I_s \alpha^1 - I_s \gamma \right)$$  

Equation (7)

In iron, and low alloy steels $I_s \gamma \ll I_s \alpha^1$ hence in this case we may rewrite equation (7) as:

$$\Delta G_{mag} = I_s \alpha^1 H$$  

Equation (8)

Knowing the $M_S$ shift ($\Delta T$) produced by a magnetic field $H$, the entropy of transformation may now be obtained since

$$|\Delta S^{\gamma \rightarrow \alpha}| = \frac{d \Delta G^{\gamma \rightarrow \alpha}}{dT} = \frac{\Delta G_{mag}}{\Delta T}$$  

Equation (9)

Hence $\Delta S^{\gamma \rightarrow \alpha} = \frac{-I_s \alpha^1 H}{\Delta T}$  

Equation (10)
Values of $\Delta S^{\gamma \rightarrow \alpha}$ calculated in this manner have been utilised to test the suggestion that the rate of athermal martensite formation below $M_S$ can be linearly correlated with the entropy of transformation (see Section 1.2.1). The predicted linear relationship was confirmed (Figure 2).

The general validity of thermodynamic models for the magnetic effect has been further demonstrated by the work of Malinen and Sadovskiy (1969) on 14 - 16% Mn - Fe alloys. It was found that the $\gamma \rightarrow \epsilon$ transformation (both phases paramagnetic, hence $\Delta E_{\text{mag}} \approx 0$) was practically unaffected by magnetic fields, but that the $\epsilon \rightarrow \alpha$ transformation (paramagnetic $\rightarrow$ ferromagnetic) was strongly affected. This underlines the previous conclusion that magnetic fields only exert an effect when parent and product phases differ widely in saturation magnetisation.

On the basis of his experimental results, Korenko (1973) concluded that the magnetic effect could not be ascribed solely to the additional magnetic free energy component. This conclusion, however, depends to some extent on the accuracy of models used to calculate the free-energy of component phases as functions of temperature and composition.

2.5 **Effect of Magnetic Fields on some other Metallurgical Processes**

2.5.1 **Tempering of Martensite**

Bernshteyn et al (1965) found that martensite tempering at 175°C in a 1.1% C 8% Ni steel was considerably retarded by a steady magnetic field of 20 kOe. It was also observed that tempering was similarly retarded if the material was quenched in a magnetic field prior to normal tempering without a field. It was suggested by Granik et al (1967) that the latter effect could be attributed to spontaneous tempering of the martensite on quenching in a field, as evidenced by a reduction in the width of the $(211)_\alpha$ (martensite) X-ray diffraction line after magnetic
quenching. Satyanarayana (1968) observed similar retardations of tempering in a 1% C, 1.5% Cr steel and a plain carbon steel. He suggested that the driving force for \(\varepsilon\)-carbide nucleation was reduced by quenching in a magnetic field, owing to the lower saturation magnetisation of \(\varepsilon\)-carbide compared with the parent martensite. Values of the activation energy of tempering both with and without a magnetic field were found to be virtually identical, indicating that magnetic fields have little or no effect on the basic tempering mechanism.

2.5.2 Recrystallisation and Growth

The major effect observed due to recrystallisation in a magnetic field is preferred orientation of the recrystallisation products. This has been demonstrated by Smoluchowski and Turner (1949; 1950) who investigated the recrystallisation behaviour of Fe - 30% Co, in a magnetic field. It was found that a magnetic field increased the amount of recrystallised products having their \(<100>\) direction parallel with the field, and decreased the fraction having their \(<110>\) direction parallel with the field. This was attributed to the high magneto-crystalline anisotropy energy in the alloy. Roberts (1955) and Boothby et al (1958) showed that Mn - Bi alloys recrystallised in a magnetic field exhibited a fibre texture, the recrystallisation products having their direction of easy magnetisation oriented parallel with the field. A proposed reason for the marked influence of a magnetic field, despite the low anisotropy energies involved, is that the driving force for recrystallisation is itself sufficiently small to be affected by very small contributions to the overall thermodynamics of the system (Satyanarayana, 1968).

Later work by Berenbaum (1959) showed that similar orientation could be obtained in Mn - Bi in the absence of a magnetic field, thereby casting some uncertainty on Boothby's results.
2.5.3 Solid/Gas Reactions

It has been reported (Skorski, 1972) that the rate of reduction of haematite powder to metallic iron by hydrogen is significantly increased by the application of magnetic fields. Skorski (1972) suggested that the accelerated reduction (by about 10% in a field of 1500 Oe) was due to the magnetic properties of hydrogen. The proposed model did not satisfactorily account for the observed changes in reduction kinetics as a function of applied field strength. Peters (1973) pointed out that a thermodynamic model (similar to that used to explain the magnetic effect on martensitic transformations) was able to predict qualitatively the experimentally observed effects of magnetic reduction.
3.1 Introduction

The effect of magnetic fields on the athermal martensitic reaction has already been described in Chapter 2. It is expected that magnetic fields will also have an effect on isothermal martensite formation, given that the parent and product phases differ widely in saturation magnetisation values. Very little information is available on this topic.

Estrin (1965) noticed that a magnetic field increased the isothermal transformation rate in a Fe - Ni - Mn alloy. Malinen et al. (1967) attempted to explain the effect quantitatively using a thermodynamic model, but were unable to do so. It was concluded that the increase in the transformation rate due to a magnetic field could not be described solely in terms of a reduction in the activation energy of martensite nucleation. The implications of the recent work by Korenko (1973) will be discussed later.

The purpose of the present experimental work is to investigate more thoroughly the effect of magnetic fields on isothermal martensite formation, and to derive a better understanding of the specific action of the magnetic field on the transformation processes.

3.2 Alloy and Specimen Preparation

The alloy used in this investigation was supplied, in the form of 0.25 in diameter rod, by the British Steel Corporation Laboratories. Chemical analysis showed the composition to be:

\[
25.9 \text{ wt. } \% \text{ Ni - } 27 \% \text{ Mn - 0.023 } \% \text{ C - balance Fe}
\]

Impurities totalled less than 0.01\%.

The material was given a thermomechanical treatment as follows:
Suitable lengths of rod were homogenised at 1050° C for 24 hours in pure argon. This avoids loss of manganese which would occur at high temperatures in vacuum. After homogenisation, the material was quenched in water at room temperature. After removal of surface scale by machining, the rods were cold-swaged through successively smaller dies to a final diameter of 0.26 cm. The swaged rod was annealed at 1000° C for 30 minutes in argon, followed by water quenching to room temperature. The rod was then cut into specimens 1 cm long suitable for dilatometric measurements.

The material was austenitic at room temperature, with no sign that any transformation to martensite had occurred during quenching. The austenitic grain size was found to be 0.09mm (average grain diameter) and did not vary significantly in different regions of the specimens.

In order to minimise any room temperature ageing effects during storage, the specimens were given a final anneal at 100° C for 30 minutes.

3.3 Apparatus

3.3.1 Cryostat Assembly

The experimental alloy commences isothermal transformation to martensite at about -50° C. In order to investigate the transformation kinetics, a low temperature reaction bath was required, having a useable temperature range of -40° C to -100° C. Liquid nitrogen was chosen as the refrigerant since this was fairly cheap, easy to use, inert and readily obtainable. The cryostat design is shown schematically in Figure (16). Liquid nitrogen was pumped into the refrigerant dewar, until the level reached the 'Hi - level' sensing probe when the pump stopped automatically. If the refrigerant level subsequently fell below the 'Lo - level' probe, the pump automatically restarted until the dewar was again full. The reaction bath was inserted in the refrig-
To Recorder

Transducer

Pushrod

Isopentane

Heater

Liquid N2

FIG. 16  Cryostat Assembly (Schematic).
erant dewar. The bath was made of copper to give good conductivity, thus minimising heat-transfer delays, and was jacketed with an electrical heating coil, the operation of which will be described later. The reaction bath was filled with iso-pentane, this being a stable liquid at the required subzero temperatures, having a fairly low evaporation rate, and being non-corrosive. The isopentane was stirred continuously to give good temperature equalisation. Low conductivity lagging was used where appropriate to reduce heat losses. Good bath-temperature control was obtained using a resistance heater with variable output power. This consisted of a resistance coil, immersed in the reaction bath, forming one arm of a Wheatstone bridge circuit, the other arm containing a very sensitive rheostat. As the reaction-bath temperature decreases, the coil resistance decreases, below that of the rheostat. At this point, the imbalance current in the bridge circuit falls to zero, changes polarity and begins to increase again. The imbalance current is detected by a device sensitive only to current of the 'correct' polarity. When a current of the 'correct' polarity begins to pass, the heating coil around the reaction bath is automatically energised, the wattage being determined by the magnitude of the imbalance current in the bridge. Heating continues until the bridge again balances, when the current to the coil falls to zero. The bath temperature thus gradually stabilises at a temperature determined by the rheostat setting; the actual bath temperature was displayed on a digital indicator connected to a platinum resistance thermometer immersed in the bath. Using this technique, any desired reaction temperature could be obtained by suitable choice of rheostat setting; the temperature could then be held constant to within $\pm 0.1^\circ C$ for a period of several hours.
3.3.2 Dilatometric Apparatus

Several methods of monitoring the progress of the austenite → martensite reaction were initially considered, namely:

1) Resistometric techniques
2) Magnetometry
3) Dilatometry

A dilatometric method was finally chosen since this enables constant monitoring of the transformation kinetics, using fairly simple equipment, and is less likely to be affected by the proximity of strong magnetic fields and high electric currents. In addition, the volume change accompanying the fcc → bcc reaction in the alloy under investigation is large enough to be observed by dilatometry without recourse to excessively sensitive instrumentation.

The specimen-holder was designed to give rigid mechanical support to the specimen, whilst allowing free access and circulation of the quenching medium. This ensures rapid cooling of the specimen to the reaction temperature. A low conductivity silica push rod (to minimise heat flux from the specimen) was positively located on the top of the specimen (see Figure 16), and transmitted any changes in specimen length to a sensitive linear voltage displacement transducer (capable of measuring $\frac{AL}{L} \geq 10^{-6}$) mounted at the top of the specimen holder. The transducer was enclosed in a constant-temperature vessel to minimise any effect of ambient temperature fluctuations. The complete assembly could be rapidly lowered, in order to quench specimens into the bath.

The voltage output from the transducer is proportional to the change in length of the specimen and hence to the amount of martensite formed. The signal was too weak for direct monitoring, and was therefore amplified and displayed on a Rikadenki pen recorder with pre-set chart-drive
speeds. This enabled displacement versus time curves to be determined. In order to convert these to percentage transformation versus time, the transducer signal required calibration. This was achieved in the following way:

Specimens were mounted in the dilatometer and each was quenched to -60° C for different times, giving varying amounts of transformation. The transducer output to the chart recorder was noted for each specimen, and the actual amount of martensite in each specimen was then determined using a Quantimet image-analysing microscope. This instrument can detect very accurately the relative proportions of two phases provided that the phases are strongly contrasted.

In the alloy under investigation, the martensite is heavily attacked by a Nital etch, whereas the austenite is virtually unaffected. This produces a marked differentiation between the two phases, allowing determination of their relative proportions to within 0.2%. The percentage transformation in each specimen, with a small correction for surface martensite (see Section 3.4.1) was then plotted against the corresponding output signal from the transducer. This gave an almost linear calibration curve over the transformation range of most interest, as shown in Figure 17, allowing simple conversion of measured dilation rates to transformation rates.

3.3.3 Measurement of Magnetic Field Strength

The magnetic fields employed were generated by a d.c. Newport electromagnet with 10 cm diameter poles. Using conical, plane-faced pole pieces, magnetic fields of up to 20 kOe were available. The dilatometer was arranged such that, after quenching in the reaction vessel, specimens were located accurately and reproducibly in the centre of the magnet gap,
Fig. 17 Calibration curve for the dilatometer.
thereby ensuring a uniform field distribution around them. The magnetic field was varied by means of a rheostat controlling the current through the magnet coils, which were water-cooled.

The magnetic field strength $H$ was measured by means of a Hall probe in conjunction with a Bell 120 Gaussmeter. The operation of the Hall probe may be understood as follows, with reference to Figure 18.

The sensing probe makes use of the 'Hall Effect' in a thin wafer of semiconducting material accurately aligned at right angles to the magnetic flux. The control current $I_c$ passes through the long dimension of the rectangular indium arsenide wafer. When placed in a magnetic field $H$, some of the charge carriers of the semiconductor are deflected across the crystal resulting in the Hall voltage $E_H$ which appears across the voltage leads. The Hall voltage is directly proportional to the magnetic flux perpendicular to the crystal face. When correctly calibrated against a standard, the probe gives accurate measurement of field strengths from 50 Oe to $3 \times 10^4$ Oe.

3.4 Preliminary Experiments

3.4.1 Surface Martensite Formation

It was found that considerable amounts of surface martensite were formed athermally during quenching of specimens to the isothermal reaction temperature. This is probably due to the formation of a thin oxidised layer during specimen heat treatment. Similar effects were observed in Fe – Ni – Mn alloys by Shih et al (1955) and Raghavan and Cohen (1965).

The effect of surface martensite prior to isothermal transformation is to supply autocatalytic embryos at the start of transformation, hence wiping out the normal incubation period and leading to high initial transformation rates. Since the formation of prior martensite affects the
Fig. 18  Hall probe used to measure magnetic field strength.  (Schematic).
observed isothermal transformation kinetics, it was decided to investigate both the extent of surface martensite formation, and means whereby its occurrence could be prevented, or at least minimised.

Specimens (heat treated as described in Section 3.2) were quenched to various temperatures in the transformation range of interest (\(-50^\circ C\) to \(-90^\circ C\)), held isothermally for 30 seconds, then upquenched rapidly into water at \(50^\circ C\). This was repeated in a magnetic field of 20 kOe. The samples were then examined metallographically and the amount of surface martensite was determined. Occasionally, a very small amount of martensite in the interior regions was seen; this was assumed to be the product of isothermal transformation during the short period of holding at the reaction temperature, and was ignored.

The experimental data are given in Table IV. It can be seen that the amount of surface martensite increased as the temperature was lowered. A magnetic field of 20 kOe caused a significant increase in the amount of martensite formed at each temperature. It was thought that such large amounts of athermal transformation could seriously affect the validity of experimentally observed isothermal kinetic data; hence a means of suppressing surface martensite was sought.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>% Martensite H = 0</th>
<th>% Martensite H = 20 kOe</th>
</tr>
</thead>
<tbody>
<tr>
<td>-50</td>
<td>&lt; 1</td>
<td>~ 1</td>
</tr>
<tr>
<td>-60</td>
<td>1.5</td>
<td>2</td>
</tr>
<tr>
<td>-70</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>-80</td>
<td>3</td>
<td>7.5</td>
</tr>
<tr>
<td>-90</td>
<td>10</td>
<td>16</td>
</tr>
</tbody>
</table>

Table IV Amount of Surface Martensite formed at Various Temperatures with and without a Magnetic Field
Surface martensite could be suppressed almost completely by polishing the specimen surface, firstly using silicon carbide fine abrasive, with a final polish using a slurry of alumina powder and water. After this surface treatment, only 1.5% martensite was formed after quenching to -80°C in a magnetic field of 20 KOe with correspondingly smaller amounts formed at higher temperatures. Surface transformation could be completely suppressed at temperatures in the experimental range by electrodeposition of a copper layer on the pre-polished specimens. It was not considered worthwhile to carry out such a lengthy preparation on the large number of specimens required for the experimental programme; these were used in the polished condition.

A small correction for surface martensite was applied to the data used in the calibration of the experimental dilatometer (Section 3.3.2)

3.4.2 Effect of Magnetic Field Cycling

The major aim of the experimental work was to determine the effect of applied magnetic fields on transformation kinetics. A short series of experiments was performed in order to determine whether the mode of field application affected the results.

The range of available field strengths was 0 - 22 KOe. Various methods of imposing magnetic fields during transformation were investigated as follows:

a) Single, sudden applications of the desired field strength, followed by removal of the field.

b) Slow increase of the field strength from zero to the desired value.

c) Stepped increases in field strength, with kinetics measurements taken at intermediate stages as required.

d) Sudden removal or reduction of field strength.

e) Stepped decreases in field strength with kinetics measurement where appropriate.
The data obtained from these experiments showed that the magnetic effect, for a given field strength, was independent of the mode of application of the magnetic field, and independent of any previously applied magnetic field.

3.5 Main Experimental Methods and Results

3.5.1 Basic Transformation Kinetics of Fe - 26 Ni - 2 In

Specimens were inserted in the dilatometer and quenched to the desired isothermal reaction temperature. The progress of transformation was monitored as previously described, and transformation versus time graphs were constructed from the experimental data. Typical examples for various transformation temperatures are shown in Figure 19.

The temperature range available for simple experimental investigation was rather limited; above $-55^\circ$ C the incubation time was long ($\sim 15$ minutes) and the transformation was sluggish and incomplete, whilst below $-80^\circ$ C transformation was too rapid to be accurately monitored. It was noted that, as the reaction temperature was lowered below $-30^\circ$ C, the kinetics became indistinguishable from an athermal or even a bursting mode. Attention was therefore confined to four temperatures in the above range, namely $-60^\circ$ C, $-65^\circ$ C, $-70^\circ$ C, and $-80^\circ$ C.

The shape of the transformation $(f)$ versus time $(t)$ curves (Figure 19) suggested that a logarithmic law was in operation. The experimental data were therefore replotted as a function of $\log(t)$ and a linear relationship was found, down to the lowest measurable amount of transformation, as shown by Figure 20. Extrapolation of these graphs to zero transformation yielded values of an incubation time for transformation $(t_o)$ at each experimental temperature. Values of $t_o$ are given in Table V. Since $f$ was found to be directly proportional to $\log(t)$, it follows that $\log(f)$
Fig. 19  Transformation kinetics of experimental alloy at various temperatures.
Fig. 20  Percentage transformation versus log.(time) curves for the experimental alloy.
is directly proportional to $-f$. (Dotted quantities, e.g. $\dot{f}$, refer to the first derivative with respect to time, i.e. $\frac{df}{dt}$.) A plot of $\log(\dot{f})$ versus $f$ may hence be extrapolated to zero transformation ($f = 0$), and yields the value of the initial transformation rate $f_0$, as shown in Figure 21. Values of $f_0$ obtained in this manner are given in Table V. The techniques used to evaluate $t_0$ and $f_0$ will be discussed in Section 4.

In martensitic transformations, the growth of nuclei to macroscopic plates of martensite takes place extremely rapidly; the observed transformation rate may hence be assumed to be nucleation controlled. In this case, the rate of transformation $\dot{f}$ at any time may be related to the rate of nucleation $N$ in the following way:

$$\dot{f} = N \bar{v}$$  \hspace{1cm} \text{Equation (11)}

where $\bar{v}$ is the mean volume of martensite produced by each nucleation event.

Hence the fraction transformed at any time $f_t$ is given by:

$$f_t = N \bar{v} t$$  \hspace{1cm} \text{Equation (12)}

assuming that $t$ is sufficiently small that $\dot{N}$ may be regarded as constant.

The graphical techniques outlined above have enabled the transformation rate at a very low value of $f$ to be evaluated, together with the time ($t_0$) taken to transform this small amount of austenite. Assuming that transformation prior to time $t_0$ is negligible compared with the total transformation at time ($t_0 + 1$) sec, the nucleation rate $\dot{N}$ is given by:

$$\dot{N} = \frac{f_{t_0} + 1}{\bar{v} (t_0 + 1)}$$  \hspace{1cm} \text{Equation (13)}
Figure 21: Percentage transformation versus log.(transformation rate) curves for the experimental alloy.
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Incubation Time ($t_0$) (sec)</th>
<th>Initial Transformation Rate ($f_0$) (pct/sec)</th>
<th>Initial Nucleation Rate ($N_0$) (per cm$^3$ per sec)</th>
<th>Activation Energy of Nucleation (ΔW) (cal/mole)</th>
<th>Chemical Driving Force (ΔG) (cal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-60</td>
<td>336</td>
<td>0.014</td>
<td>417</td>
<td>14,900</td>
<td>-342.8</td>
</tr>
<tr>
<td>-65</td>
<td>156</td>
<td>0.06</td>
<td>7,828</td>
<td>13,700</td>
<td>-348.7</td>
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<tr>
<td>-70</td>
<td>108</td>
<td>0.102</td>
<td>9,358</td>
<td>13,000</td>
<td>-354.5</td>
</tr>
<tr>
<td>-80</td>
<td>29</td>
<td>0.316</td>
<td>103,783</td>
<td>11,400</td>
<td>-365.9</td>
</tr>
</tbody>
</table>

Table V Variation in Isothermal Transformation Parameters with Temperature in Fe - 26 Ni - 2 Mn
In the early stages of transformation, while partitioning effects (see Section 1.2) remain negligible, it is a reasonable assumption that every nucleation event causes the same volume of martensite to form. The volume transformed per event depends however on the austenite grain size; the finer the grain size, the more nucleation events are required to form a given volume of martensite. Given the mean grain size of the material, together with an accurate metallographic analysis of the morphology (i.e. thickness-to-length ratio) of the martensite plates, reasonable values for $\bar{v}$ can be evaluated (e.g. Pati and Cohen, 1969; Mucumtrtie and Magee, 1970) for any given alloy. This then allows calculation of $\dot{N}$ via equation 13. The resulting values of $\dot{N}$ obtained from kinetic data at various temperatures are given in Table V.

The activation energy $\Delta W$ for martensite nucleation is given by an Arrhenius-type equation following Shih et al (1955):

$$\dot{N} = n_i \cdot \bar{v} \exp \left(\frac{-\Delta W}{RT}\right)$$

Equation (14)

where $n_i$ is the concentration of martensite embryos

$v$ is the process attempt frequency

Various values for the above parameters have been proposed in the literature. On the assumption that there was one potent embryo per grain, Shih et al (1955) estimated $n_i$ as $\approx 10^5$ per cm$^3$ and this value has recently been supported by Magee (1971). Raghavan and Entwisle (1965) however have proposed that $n_i \approx 10^7$ per cm$^3$, based on observations of transformation in small particles, and this value has been found to give reasonable values of $\Delta W$ (Entwisle, 1968; Pati and Cohen, 1969; 1971). This value has been adopted in calculations based on the present experimental work.

The process attempt frequency $v$ has usually been taken to be
equal to the lattice vibration frequency $10^{13}$ per sec. Magee (1970) has recently proposed the value $v = 10^{11}$ per sec, arguing that the nucleation process involves dislocation motion and that dislocation kinetic processes generally have attempt frequencies about two orders of magnitude smaller than the lattice vibration frequency. Magee's value has been adopted for the present calculations.

The nucleation activation energy $\Delta W$ at various temperatures, calculated from the experimental kinetic data, using equation (14) are given in Table V. In Table VI, for comparison, are $\Delta W$ values found in similar alloys by some other workers. (The values due to Pati and Cohen were originally based on $v = 10^{13}$ per sec, and have been re-calculated using $v = 10^{11}$ per sec to allow a proper comparison with the present results.)

Also listed in Table V are the free-energy changes accompanying transformation, at each temperature. These were calculated employing the empirical relationship of Imai and Izumiyama (1963).

<table>
<thead>
<tr>
<th>Alloy (base Fe)</th>
<th>Temperature $^\circ$K</th>
<th>Activation Energy cal/mole</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.3 Ni 3.8 Mn</td>
<td>134</td>
<td>9,924</td>
<td>Entwisle (1968)</td>
</tr>
<tr>
<td>22.6 Ni 3.3 Mn</td>
<td>204 – 234</td>
<td>12,876 – 17,178</td>
<td>&quot;</td>
</tr>
<tr>
<td>22.4 Ni 3.6 Mn</td>
<td>77.8 – 203</td>
<td>5,066 – 14,701</td>
<td>&quot;</td>
</tr>
<tr>
<td>26 Ni 2 Mn</td>
<td>193 – 213</td>
<td>11,400 – 14,900</td>
<td>Present Work</td>
</tr>
<tr>
<td>26 Ni 3 Cr</td>
<td>143 – 193</td>
<td>10,300 – 16,300</td>
<td>Jones and Entwisle (1971)</td>
</tr>
</tbody>
</table>

Table VI - Activation Energy of Martensite Nucleation determined Experimentally, for Various Fe – Ni Alloys
3.5.2 Effect of Magnetic Fields on Transformation Kinetics

Specimens were placed in the dilatometer and quenched to the desired reaction temperature, as described previously. At various times during subsequent isothermal transformation, the samples were subjected to steady magnetic fields, whose strength could be varied as desired.

It was found that magnetic fields stimulated an almost immediate increase in transformation rate, as shown schematically in Figure 22. The magnetic effect was defined as the ratio of the field-affected transformation rate $f_H$ immediately after application of a magnetic field, and the transformation rate immediately before application of a field $f$.

(A small interval of time was required in practice before evaluation of $f_H$, in order to allow a steady state value to be obtained.) It was found that the magnetic effect increased with increasing field strengths up to 20 kOe and was independent of the amount of martensite present (i.e. transformation time) up to about 40% transformation, and hence independent also of the initial (zero-field) transformation rate $f$.

A major advantage of the experimental method is that transformation kinetics both with and without a magnetic field are determined using the same specimen, thereby eliminating any errors due to compositional and microstructural differences between samples. The data obtained from different specimens were remarkably uniform, indicating that although different samples might show appreciable differences in their 'basic' transformation kinetics, the magnetic effect was independent of these variations.

Various magnetic-field switching cycles were experimented with (see Section 3.4.2) and it was found that the magnetic effect depended only on the applied field strength and was not affected by previously applied fields of different strength. It was thought that remanent
Fig. 22  Effect of magnetic field on transformation kinetics (Schematic).
magnetisation after initial field application could affect the result of subsequent applications, but experiments using consecutive applications of magnetic fields of the same strength but opposite polarity showed that remanent effects were negligible.

The experimental data given in Table VII were obtained by stepped increments of 5 kOe from $H = 0$ to $H = 20$ kOe. Measurements were made in this manner at least twice during transformation of each specimen, wherever possible.

3.6 **Subsidiary Experiments**

**Magnetic Embryo Detection**

The most successful models for martensite nucleation (Kaufman and Cohen, 1958; Raghavan and Cohen, 1972a) are based on the existence of martensite embryos in austenite above the $M_S$ temperature. The size of these embryos determines their potency and hence the temperature at which they can be 'triggered' to form martensite plates. Kaufman et al (1960) studied the effect of high pressure applied during annealing of Fe-Ni alloys in the austenitic state on the $M_S$ temperature observed during subsequent cooling at atmospheric pressure. Their hypothesis was that high pressure should reduce the size of martensite embryos formed in austenite, thereby lowering the $M_S$ temperature. Suppression of $M_S$ was observed, lending support to their idea. Despite this indirect experimental support for pre-existing embryos, none has ever been identified with certainty by direct electron microscopy. Subsequent experiments by Radcliffe and Schatz (1962) indicated that the suppression of $M_S$ by cooling under high pressure could be explained by thermodynamic changes. This casts some doubt on the validity of Kaufman, Leyenaar and Harvey's (1960) explanation in terms of embryo effects.

By analogy with Kaufman's high pressure experiments, it may be
Table VII (continued overleaf)

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Specimen Number</th>
<th>MAGNETIC EFFECT : (INITIAL RATE / RATE IN MAGNETIC FIELD H)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>H = 5 K0e</td>
</tr>
<tr>
<td>-60</td>
<td>a</td>
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<tr>
<td></td>
<td>a</td>
<td>-</td>
</tr>
<tr>
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<tr>
<td></td>
<td>b</td>
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<tr>
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<td>1.3</td>
</tr>
<tr>
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<tr>
<td></td>
<td>l</td>
<td>1.3</td>
</tr>
<tr>
<td>Temperature °C</td>
<td>Specimen Number</td>
<td>MAGNETIC EFFECT (INITIAL / RATE IN MAGNETIC FIELD H)</td>
</tr>
<tr>
<td>---------------</td>
<td>-----------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td></td>
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<td>$H = 5$ Koe</td>
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<tr>
<td>-70</td>
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<td></td>
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</tr>
<tr>
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<td>r</td>
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<tr>
<td>-80</td>
<td>s</td>
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<td></td>
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<tr>
<td></td>
<td>w</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Table VII (continued)  Variation of Magnetic Effect in Fe 26 Ni 2 Mn with Temperature and Magnetic Field Strength
expected that the size of martensite embryos could be increased by the application of magnetic fields. The temperature range in which magnetic annealing can affect the size of martensitic embryos is, however, small; firstly, the temperature must be high enough to allow sufficient atomic mobility for equilibrium embryo formation i.e. above the freeze-in temperature. Secondly, the temperature must be below the Curie point of the martensite (Since the ferrite is not a stable phase at the temperature envisaged, the Curie point will be virtual).

In order to make sure of fulfilling both the above conditions, samples were annealed at 25°C temperature intervals between 450°C and 800°C for 15 minutes in a magnetic field of 19kOe followed by cooling to room temperature in a jet of argon. The specimens were then placed in the dilatometer and their $M_S$ temperature measured during cooling at 1°C/min. Apart from the usual experimental scatter in measured $M_S$ temperatures, no effect of magnetic annealing could be detected.

Under ideal conditions, a magnetic field of 19 kOe could be expected to stabilise ferrite relative to austenite, in the experimental alloy, by about 4 - 5 cal/mole. A magnetic effect of this magnitude should raise the $M_S$ temperature by about 6 - 10°C. From the experimental results, there is no evidence that ferromagnetic embryos exist in austenite.

It is possible however, that the degree of ferromagnetism in the embryos at high temperatures may be much less than that calculated for ideal conditions; alternatively it may be completely incorrect to attempt to apply the bulk magnetic properties of the bcc phase to martensitic embryos.

Similar experiments have been recently reported by Korenko (1973). He also found no evidence to suggest that magnetic fields applied in the austenitic region affected embryo potency and subsequent transformation behaviour.
CHAPTER 4

Model A
Singly Activated
Process From
Initial Sites

Extrapolative
Technique used
Method I

Method I Results
\(N, n, \Delta W\)
Table V

Results of
Magnetic Expts
Table X

Compare with
Basic Criteria
of K - C Model

Poor Correlation
With Method I
No

Is \(\Delta W\) Proportional To
\(\Delta G\)?
Yes

Confidence in
Exptl Magnetic
Results

Yes

Does
The K - C - R
Model Improve
the Fit?

Is there
a Quantitative
Fit?
Yes

Model B
Distribution of
Activation Energies

Distribution
Analysis
Method II

Method II Results
\(N, n, \Delta W\)
Table VIII

Method II Results

Compare with
Basic Criteria
of K - C Model

Good Correlation
With Method II

Yes

Abandon
Method I

No

Confirm Method II
+ K - C Model Best
4.1 Introduction

Previous work (e.g. Satyanarayana 1968) has demonstrated that the magnetic effect during transformation may be attributed directly to the field interaction energy $\Delta I_S H$, which results in a net change in the free energy difference between the transforming phases. (The energy changes associated with other magnetic interactions in metals have been shown to be several orders of magnitude lower than $\Delta I_S H$.)

Analysis of the experimental data, on the basis of current martensite nucleation theory, is undertaken in the following sections.

4.2 Significance of the Activation Energy of Nucleation (A W)

The experimental determination of activation energies of nucleation, for martensitic transformations, presents many difficulties. The most important of these stems from the necessity of observing the initial transformation events, since it is only these which reflect the initial concentration of pre-existing embryos. After the transformation has commenced, autocatalytic embryos (or nucleation sites) become operative, and eventually their activation masks the effect of the pre-existing sites. There are two possible solutions to this problem; firstly it can be assumed that autocatalytic sites require the same energy of activation as the initial sites. Alternatively, the transformation kinetics can be investigated in the earliest possible stages, before autocatalysis exerts a major effect.

Most previous workers (e.g. Pati and Cohen, 1969; Korenko, 1973) have adopted the latter method. Their experimentally determined activation energies were usually calculated from the measured length of time required to form $0.2 - 0.3\%$ martensite, using equation (12). It has been shown
however, (Pati and Cohen, 1969) that autocatalysis is not negligible even at \( f < 0.002 \); experimentally determined activation energies hence reflect only the average nucleation rate during the time interval required to form 0.2\% martensite.

A further criticism is that the approach used to calculate \( \Delta W \) assumes that all embryos have identical nucleation barriers. Magee (1971) found that such a concept did not fit kinetic data relating to transformation in very small particles. He showed that the embryos had a distribution of potencies, and calculated that the initial concentration of pre-existing embryos in Fe - Ni - Mn alloys lay between 3 x 10^4 and 2 x 10^5 per cm^3. Most previous workers had assumed a rather larger initial embryo population of about 10^7 per cm^3.

4.2.2 \( \Delta W \) Evaluation - Extrapolative Method I

In the present experimental work a lengthy preparation route for test specimens, designed to completely suppress surface martensite formation has been avoided. Instead, use has been made of the effective linearisation of the experimental \( f \) versus log \( (t) \) data produced by autocatalysis, to extrapolate back to \( f = 0 \) which provides the value of an incubation time \( t_o \) (see Figure 21). The transformation rate at time \( t_o \) can then be obtained from a corresponding plot of log \( (f) \) versus \( f \) (Figure 22). Ignoring any transformation prior to \( t_o \), the activation energy \( \Delta W \) may be calculated from equation (14). The values of \( \Delta W \) obtained in this manner from the experimental data are listed in Table V (Section 3.5.1).

4.2.3 \( \Delta W \) Evaluation - Distributive Method II

Magee showed in 1971 that martensitic transformation in small particles also obeys the law \( f = K \log (t) \); this was attributed to a postulated distribution of activation energies among the nucleation sites.
initially present. The present experimental data may hence also be interpreted on this basis. Using the procedure of Kimmel and Uhlmann (1969), the distribution of activation energies is approximated by the relationship:

\[
\phi(\Delta W) = \frac{[df/d (\ln t)]}{kT} \quad \text{Equation (15)}
\]

where \( \phi(\Delta W) \) is the contribution to the degree of transformation \( f \) from processes having an activation energy between \( \Delta W_1 \) and \( \Delta W_1 + d (\Delta W) \).

The following relationship also holds:

\[
\Delta W_1 = kT(\ln \nu t + E) \quad \text{Equation (16)}
\]

where \( \nu \) is the process attempt frequency and \( E \) is Euler's constant (\( E = 0.577\ldots \)).

The minimum value of the activation energy of nucleation (\( \Delta W_{\min} \)) is given by Equation (16), when \( t \) is assigned the value of \( t_0 \), the incubation time, derived from a plot of \( f \) versus \( \log (t) \) and given in Table V. Values of \( \Delta W_{\min} \) for the experimental alloy are given in Table VIII, together with those obtained using the previously outlined extrapolative Method I (Section 3.5.1).

The slopes of the \( f \) versus \( \log (t) \) plots at different temperatures (Figure 21) may be used to determine the concentration of nucleation sites having activation energy \( \Delta W_{\min} \), by substitution into Equation (15). This value, \( n_{\min} \), may then be used to evaluate the initial nucleation rate via the relationship:

\[
N = n_{\min} \nu \exp - \frac{\Delta W_{\min}}{RT} \quad \text{Equation (17)}
\]

The value of \( n_{\min} \) may be regarded as a more reliable value for the initial
<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>ΔW (Method I) cal/mole</th>
<th>ΔW min (Method II) cal/mole</th>
<th>n_i cm⁻³</th>
<th>n min * cm⁻³</th>
<th>Ņ (Method I) cm⁻³ sec⁻¹</th>
<th>Ņ (Method II) cm⁻³ sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>-60</td>
<td>14,900</td>
<td>13,500</td>
<td>10⁷</td>
<td>7 x 10⁷</td>
<td>4.2 x 10²</td>
<td>1.2 x 10⁵</td>
</tr>
<tr>
<td>-65</td>
<td>13,700</td>
<td>12,900</td>
<td>10⁷</td>
<td>8 x 10⁷</td>
<td>3.8 x 10³</td>
<td>2.6 x 10⁵</td>
</tr>
<tr>
<td>-70</td>
<td>13,000</td>
<td>12,400</td>
<td>10⁷</td>
<td>10 x 10⁷</td>
<td>9.4 x 10³</td>
<td>5.3 x 10⁵</td>
</tr>
<tr>
<td>-80</td>
<td>11,400</td>
<td>11,300</td>
<td>10⁷</td>
<td>9 x 10⁷</td>
<td>1.04 x 10⁵</td>
<td>16.6 x 10⁵</td>
</tr>
</tbody>
</table>

* Calculated using \( \bar{v} \) (average volume per martensite plate) = 10⁻⁹ cm³ (Pati and Cohen, 1969)

Table VIII  Kinetic Parameters Evaluated From Extrapolative Method (Method I) and Distributive Method (Method II)
concentration of embryos than the estimated value \( n_i \) used by previous workers to evaluate \( \Delta W \) from Equation (14), since \( n_{\text{min}} \) is determined directly from the experimental kinetic data. The calculated values of \( n_{\text{min}} \) and the derived initial nucleation rates, are given in Table VIII, together with those obtained from the extrapolative Method I. The \( n_{\text{min}} \) values are in reasonable agreement with previous estimates of initial embryo population \( (n_i \approx 10^7 \text{ per cm}^3) \); Magee's suggestion that \( n_i \) is about two orders of magnitude lower than this is hence not validated. The nucleation rates calculated using Method II analysis are very consistent with those observed by previous workers e.g. Pati and Cohen (1969).

It is interesting that the disparity between calculations based on the two different methods decreases rapidly with decreasing transformation temperature. This probably occurs because, as the incubation time \( t_0 \) decreases, the error in the extrapolative technique for evaluating \( f_0 \) at time \( (t_0 + 1) \) also decreases. A further point of interest is shown by the \( n_{\text{min}} \) values of Table VIII. These appear to indicate a maximum in the potency distribution of martensite embryos, occurring at \( \Delta W \) values between 12 and 14 K cal/mole. Such a peak in the potency (i.e. size) distribution is quite probable; the experimental data could however, also be explained in terms of a temperature dependence of \( \tau \) which has been discussed by Pati and Cohen (1969).

Although the results of applying the distributive model (Method II) are logical, it should be said that it cannot be ascertained from the present data whether the spectrum of \( \Delta W \) values arises from the presence of autocatalytic embryos of variable potency, or whether the initial nucleation sites themselves posses an intrinsic range of activation energies.

In a later section (Section 4.3.3) it will be shown that the magnitude of the magnetic effect serves to clarify the advantages of the distrib-
utive analysis. The concept of a singly activated process does not successfully account for the observed effect of magnetic fields.

4.3 Discussion of the Magnetic Effect in Relation to the Competing Nucleation Models

4.3.1 Magnetic Effects on K - C Model

As discussed in Section 1.3, the kinetics of isothermal martensite formation are governed by the processes involved in the growth of martensite embryos to a critical size. Beyond this critical point, subsequent growth to form a macroscopic martensite plate has a very low effective activation energy, the growth rate being determined only by the maximum rate at which dislocations can move through the austenite. For this reason, magnetic fields can be regarded as having a negligible influence on the growth kinetics of critically sized nuclei (the magnetic effect on the shear modulus being small). Magnetic fields are hence considered to exert an influence only on the operational nucleation of subcritical embryos.

The validity of the Kaufman - Cohen (K - C) nucleation model will now be tested by determining its predictive capacity in relation to the experimental data obtained during isothermal transformation in a magnetic field.

K - C (1958) proposed the following relationship governing the growth of pre-existing martensite embryos:

$$\Delta W = 0.04 \left( \frac{\sigma}{A} \right)^{\frac{1}{4}} \left[ 3 \sigma r^{3/2} + \Delta G \left( \frac{\sigma}{A} \right)^{\frac{1}{4}} r^2 \right] \text{ Equation (5)}$$

Writing Equation (5) as:

$$\Delta W = K_1 + K_2 \Delta G \text{ Equation (5b)}$$
(assuming that the non-chemical free-energy parameters are independent of the experimental variables) we may obtain an expression for the activation energy of nucleation in a magnetic field \( H \):

\[ \Delta W_H = K_1 + K_2 \Delta G_H \quad \text{Equation (18)} \]

where \( \Delta G_H = \Delta G + \Delta I_S H \quad \text{Equation (7)} \)

Subtracting Equation (7) from Equation (5b) we find:

\[ \Delta W - \Delta W_H = K_2 \Delta I_S H \quad \text{Equation (19)} \]

where from Equation (5):

\[ K_2 = \frac{0.04 \sigma \tau^2}{A} \quad \text{Equation (20)} \]

The rate of nucleation of martensite embryos i.e. the rate at which critically-sized nuclei appear is given by:

\[ N = n_i \nu \exp \left( -\frac{\Delta W}{RT} \right) \quad \text{Equation (14)} \]

In a magnetic field the nucleation rate becomes:

\[ N_H = n_i \nu \exp \left( -\frac{\Delta W_H}{RT} \right) \quad \text{Equation (14b)} \]

Hence we may obtain the ratio of the nucleation rate in a magnetic field to the corresponding zero-field nucleation rate:

\[ \ln \left( \frac{N_H}{N} \right) = \frac{\Delta W - \Delta W_H}{RT} \quad \text{Equation (21)} \]
Combining equations (21) and (19) we obtain:

\[ \ln \left( \frac{N_H}{N} \right) = 0.04 \sigma r^2 \frac{\Delta I_S}{A \cdot R \cdot T} \]  

Equation (22)

In the present experiments, the transformation rates are measured immediately before and after the application of a magnetic field, yielding values of the ratio \( \frac{f_H}{f} \). Since the growth rate of critical nuclei is not a rate-determining step, the ratio \( \frac{f_H}{f} \) is equal to that of the corresponding nucleation rates \( \frac{N_H}{N} \). Equation (22) may therefore be written:

\[ \ln \left( \frac{f_H}{f} \right) = 0.04 \sigma r^2 \frac{\Delta I_S}{A \cdot R \cdot T} \]  

Equation (22b)

It may be seen that the K - C model predicts, through Equation (22b), a linear dependence of \( \ln \left( \frac{f_H}{f} \right) \) on \( H \). When the experimental data were plotted in this form (Figure 23) a straight line was obtained at each reaction temperature, thus providing direct confirmation of one basic requirement of the K - C model.

It is now necessary to determine whether the model is capable of predicting the absolute magnitude of the magnetic effect. This may be achieved by substitution of reasonable values of \( \sigma, r \) and \( A \) (e.g. Pati and Cohen, 1969) into Equation (19) together with the measured value of \( \Delta I_S \) (1500 Gauss cm\(^{-1}\), which is equivalent to 0.25 cal mole\(^{-1}\) KOe\(^{-1}\) for the experimental alloy). Using a field strength of 20 KOe this gives \( \Delta W - \Delta W_H \) (calculated) = 400 cal mole\(^{-1}\) which, when inserted
Fig. 23 Effect of magnetic fields on the transformation kinetics of the experimental alloy at -60°C.
in Equation (21), yields a predicted \((K - C)\) value for
\[
\ln \left( \frac{\dot{N}_H}{\dot{N}} \right)
\]
or
\[
\ln \left( \frac{\dot{f}_H}{\dot{f}} \right)
\]
The predicted values at various temperatures are listed in Table IX and may be compared with those obtained experimentally. The agreement is generally good. The temperature dependence of \(\ln \left( \frac{\dot{f}_H/\dot{f}}{f_{\text{obs}}} \right)\) is opposite to that predicted by the K - C model; this is however, not entirely unexpected in view of the initial assumption that the non-chemical energy parameters \(\sigma, r\) and \(A\) are independent of temperature.

Table IX  Comparison Between Observed and Calculated Magnitudes of the Magnetic Effect

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>(\ln \left( \frac{\dot{f}<em>H/\dot{f}}{f</em>{\text{obs}}} \right)) OBS</th>
<th>(\ln \left( \frac{\dot{f}<em>H/\dot{f}}{f} \right)</em>{\text{CALC}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>-60</td>
<td>1.12</td>
<td>0.97</td>
</tr>
<tr>
<td>-65</td>
<td>0.95</td>
<td>0.99</td>
</tr>
<tr>
<td>-70</td>
<td>0.88</td>
<td>1.02</td>
</tr>
<tr>
<td>-80</td>
<td>0.81</td>
<td>1.07</td>
</tr>
</tbody>
</table>

Having shown that the experimental data give reasonable fit with the K - C model, we may now utilise them to derive the observed shift in the activation energy of nucleation \((\Delta W - \Delta W_H)\) due to a magnetic field at various temperatures, using Equation (22). Values of \(\Delta W - \Delta W_H\) (observed) for \(H = 20\) K0e are given in Table X.
Table X Variation in the Activation Energy Change due to a Magnetic Field of 20 K0e at Different Temperatures

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>ΔW - ΔWH (observed) cal/mole</th>
<th>ΔW - ΔWH (calculated) cal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>-60</td>
<td>470</td>
<td>400</td>
</tr>
<tr>
<td>-65</td>
<td>390</td>
<td>400</td>
</tr>
<tr>
<td>-70</td>
<td>330</td>
<td>400</td>
</tr>
<tr>
<td>-80</td>
<td>300</td>
<td>400</td>
</tr>
</tbody>
</table>

4.3.2 Interpretation of Magnetic Data - Method I

As previously noted, the K – C model predicts a linear relationship between ΔW and the chemical driving force ΔG (Equation 5). Previous workers e.g. Entwisle (1968); Pati and Cohen (1969) plotted observed ΔW values (for transformation at different temperatures) against the corresponding calculated ΔG values. Both claimed that a single linear law was obeyed for all alloys, verifying the general form of Equation (5). The slope and intercept of this line was used to evaluate the most-potent embryo radius (r) and its interface energy (σ). The present experimental ΔW values (MethodI; see Table VIII) when plotted in the same way exhibited a distinct curvature, despite the small range of ΔG values. Detailed examination of the earlier work revealed that in fact similar curvature was present (Figure 24) and that the data for different alloy compositions fell on distinctly separate curves of the same general form. The most obvious explanation for this is that the values of σ and r are dependent to some degree on both temperature and composition – a reasonable hypothesis.
Variation of activation energy of nucleation with transformation driving force.
A measure of this variation of $\sigma$ and $r$ with temperature may be obtained from the experimental data for the magnetic effect on transformation kinetics. The linear relationship found between $\ln \left( \frac{f_H}{f} \right)$ and $H$ means that the observed shift in activation energy due to a magnetic field ($\Delta W - \Delta W_H$) is proportional to the shift in driving force due to the field $\Delta I_{SH}$. By combining the observed zero-field $\Delta W$ (Model I) values with the observed $\Delta W$ shift in a magnetic field, and plotting these against corresponding values of $(\Delta G + \Delta I_{SH})$, Equation (5) may be solved to obtain $\sigma$ and $r$ at each experimental temperature. This is illustrated in Figure (25). The range of $\sigma$ and $r$ values obtained in this manner is given in Table XI, together with values quoted by other workers. (The range quoted by Pati and Cohen, (1969) does not signify any temperature dependence; this merely expresses confidence limits for the best fitting line through their data.)

<table>
<thead>
<tr>
<th>Temperature Range °K</th>
<th>$\sigma$ erg/cm²</th>
<th>$r$ cm x 10⁻⁶</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>77.8 - 233.6</td>
<td>132</td>
<td>2.03</td>
<td>Entwistle (1968)</td>
</tr>
<tr>
<td>77.8 - 233.6</td>
<td>120 - 130</td>
<td>1.8 - 2.0</td>
<td>Pati &amp; Cohen (1969)</td>
</tr>
<tr>
<td>193 - 213</td>
<td>109 - 112</td>
<td>1.85 - 2.1</td>
<td>Present Work (Method I)</td>
</tr>
<tr>
<td>193 - 213</td>
<td>108</td>
<td>2.25</td>
<td>Present Work (Method II)</td>
</tr>
<tr>
<td>213</td>
<td>-</td>
<td>3.5</td>
<td>Present Work (K - C - R Model)</td>
</tr>
</tbody>
</table>

Table XI Embryo Parameters for Fe – Ni – Mn Alloys Reported by Different Workers
Fig. 25  Variation of activation energy of nucleation with applied magnetic energy at different temperatures. (Method I).
The data for the present investigation appear to indicate a very small temperature dependence of the interfacial energy $\sigma$ whilst the most-potent embryo radius $r$ increases with increasing temperature. This is reasonable since at lower temperatures, smaller embryos become active.

4.3.3 **Interpretation of Magnetic Data - Method II**

Thus far, no account has been taken of the significance of $\Delta W$ values obtained from experimental data by the distributive analysis (Method II), which are quoted in Table VIII. One of the criticisms noted in the previous section was that $\Delta W$ values from Method I (and those obtained by previous workers) did not vary linearly with corresponding values of the transformation driving force. Hence one of the criteria of the K - C model was not satisfied.

When the $\Delta W$ (Model II) values were plotted in this manner, however, almost perfect linearity was observed as shown in Figure 26. Additionally when combined with observed $\Delta W$ shifts due to a magnetic field of 20 K0e at each reaction temperature, all the data were seen to fit on a single straight line. The Method II analysis hence accounts perfectly for kinetic changes due to either changes in transformation temperature or to applied magnetic fields. In this respect it offers clear advantages over the singly-activated process postulated by previous workers, and used in the Method I analysis.

The slope and intercepts of the line shown in Figure 26, combining basic kinetic and magnetic data have been used to evaluate $\sigma$ and $r$ from Equation (5). The derived values are:

$$\sigma = 108 \text{ erg/cm}^2$$

$$r = 2.25 \times 10^{-6} \text{ cm}$$

The almost perfect linearity observed between $\Delta W$ and $\Delta G$ indicate that the embryo parameters $\sigma$ and $r$ are independent of both temperature and
Fig. 26 Variation of activation energy of nucleation with the chemical and magnetic driving force. (Method II).
magnetic field over the experimental range.

The basic K - C model, when applied to data obtained from Method II calculations is now seen to give good quantitative prediction of both basic isothermal transformation kinetics and effects due to applied magnetic fields. The more recent K - C - R (1972) model, which is an elaboration of the basic K - C model, provides a more detailed description of possible embryo growth processes. The present experimental data (Method I analysis) can be fitted to the K - C - R model at -60°C assigning $\rho^* = 4.8 \times 10^{-8}$ cm and $r = 3.5 \times 10^{-6}$ cm. Unfortunately the observed variation of $\Delta W$ with temperature does not then fit the K - C - R predictions, neither does the observed variation of $\Delta W$ with magnetic field strength. Substitution of Method II $\Delta W$ values does not improve the position. It is not clear why the K - C - R model shows these deficiencies over the simpler K - C approach; possibly the postulate that the chemical driving force may be resolved into 'stresses' acting in two directions is invalid. Alternatively the assumptions inherent in the mathematical description of the dislocation processes leading to embryo growth may have been oversimplified.
CHAPTER 5 GENERAL PROPERTIES AND TRANSFORMATION PROCESSES OF Fe - Co ALLOYS

5.1 Introduction

Previous chapters have dealt with the nature and kinetics of martensitic reactions, in which no diffusion is necessary to bring about the transformation; there is no compositional difference between parent and product phases. The majority of phase transformations, however, do involve a compositional change during the reaction which is accomplished by a diffusion process. It appears a logical step therefore, to investigate the effect of superimposed magnetic fields on transformations of this type, which have not been previously studied in this way.

5.2 Choice of Alloys

The choice of a suitable alloy system for such an investigation is severely limited by several factors, the most important of these being:

(a) Alloys must undergo a transformation at a high enough temperature to allow an appreciable diffusion rate.

(b) The parent and product phases must differ appreciably in their magnetic properties, at the transformation temperature. (In practise this means that one phase should be ferromagnetic with a high Curie temperature and saturation magnetisation.)

(c) The transformation should involve a readily measurable change in the physical properties.

Requirement (b) is the most difficult to satisfy, since ferromagnetic properties generally deteriorate as the temperature is raised,
with a complete loss of ferromagnetism at the Curie point, which is often below a transformation temperature of interest.

The Iron–Cobalt system (Figure 27) is unique in that an addition of cobalt causes an increase in the Curie temperature off bcc Iron, until it appears to coincide with the bcc + fcc transus line. The loss of magnetism at this point is in fact due to the formation of the paramagnetic fcc phase, and not to a magnetic transformation. There exists, therefore, a virtual Curie temperature for the bcc phase, which lies above the bcc + fcc transition temperature for alloys containing approximately 20–70% Co. Hence during the bcc + fcc transformation in this composition range, any bcc phase remaining will still be ferromagnetic. As the transition temperature is fairly close to the virtual bcc Curie point, the magnetisation will be appreciably less than its room temperature value. However, these alloys possess an intrinsically high magnetisation and a substantial amount remains in the bcc + fcc region.

The main disadvantages of using iron-cobalt alloys stem not from their magnetic properties, but from their mechanical behaviour. Owing to an ordering transformation during cooling, alloys containing 30–60% cobalt are extremely brittle, and very difficult to deform by cold-working. This presents difficulty in producing test specimens, but as the alloy is machinably these can be prepared by a turning operation, although it is a very time-consuming and wasteful process. The alloys can be made workable by the addition of small amounts (~2%) of vanadium; in the present investigation this would have meant undue complications in the analysis of experimental data, so was not considered.

Having chosen Fe–Co alloys as the basis of investigation, their properties of major interest will now be described.
Fig. 27  The fcc/bcc equilibrium in the iron-cobalt system.
5.3  **Constitution of Fe – Co Alloys**

For the purposes of the present experimental work the phase transformation of interest is the bcc ↔ fcc transformation occurring in alloys containing less than 80 wt % Co. The fcc ↔ hcp transformation which occurs at higher cobalt contents will not be discussed further.

The bcc ↔ fcc transformation in a wide range of alloy compositions has been investigated by Stacey and Petty (1971). They found that the structures obtained from transformation of the high temperature phase depended on the alloy composition and also on the cooling rate. At slow cooling rates decomposition occurred by a normal diffusional growth process, leading to the formation of equiaxed grains of the bcc phase. At faster cooling rates, the normal decomposition process involving long range diffusion is suppressed, and the transformation becomes massive in character. The massive transformation temperature was determined as a function of cobalt content by Parr (1967), and was found to lie at least 150° C below the bcc/bcc + fcc phase boundary, with a pronounced minimum at ~ 5 wt % Co. At still faster cooling rates the fcc phase can transform to the bcc structure by a martensitic mechanism.

The other major feature of the constitution diagram is the ordering transformation on cooling, leading to the ordered solid solution CoFe. Consideration of these does not fall within the scope of this thesis; their possible effect on magnetic properties and bcc ↔ fcc transformation will be considered in Section 7.

The ferromagnetic ↔ paramagnetic transformation temperature (Curie temperature) for bcc Fe – Co alloys is also shown in Figure 27, and includes an extrapolation giving the virtual Curie points above the fcc + bcc phase boundary, as determined by Forrer (1930) and Danilenko et al (1962).
For the purposes of the present investigation, it will be assumed that the bcc + fcc and fcc + bcc transformation, under our experimental conditions, take place by an equilibrium nucleation and growth process, governed by long-range diffusion.

5.4 Computed Phase Equilibria in the Fe - Co System

The phase diagram represents the constitution of alloys (as a function of temperature) corresponding to the minimum molar free-energy. Hence in order to compute phase diagrams from theoretical principles, it is essential to be able to calculate the free-energy of all competing phases as a function of temperature and composition. The two-phase regions are determined from the F versus T diagrams by employing the well known common tangency construction, as shown in Figure 28. In physical terms, this is the equilibration of the partial molar free-energy of each phase, leading to the lowest total free-energy state, which is a mixture of two phases; a two-phase mixture can therefore occur despite the fact that the free energy per unit volume of one phase is considerably lower than that of the second phase.

Assuming a regular-solution, the free-energy of the bcc phase $\beta$ in the Fe - Co system can be expressed as:

\[
F^\beta_x = (1 - x) F^\beta_{Fe} + x F^\beta_{Co} + RT \left[ x \ln(x) + (1 - x) \ln(1 - x) \right] + F^\beta_M.
\]

Equation (23)

where $x$ is atomic fraction Co

$F^\beta_{Fe}$, $F^\beta_{Co}$ are the free energies of bcc Fe, bcc Co

$F^\beta_M$ is the excess free-energy of mixing

Calorimetric determination of the enthalpy of mixing of bcc and
Fig. 28  Phase relationships defined by free-energy/composition diagrams.
fcc Fe – Co alloys has been carried out recently by Muller and Hayes (1971). Their data provide a test of the purely mathematical description of the excess energy of mixing proposed by Kaufman and Bernstein (1967)

\[ F_M = x(1-x) \left[ g(1-x) + hx \right] \quad \text{Equation (24)} \]

where \( g, h \) are temperature dependent polynomials. The values of \( g \) and \( h \) for the bcc and fcc phases in Fe – Co alloys, given by Kaufman and Nesor (1973), are listed in the Appendix.

The difference in free-energy between the bcc and fcc forms of iron and cobalt may be estimated from measurements of the latent heat of transformation

\[ \Delta H_{Fe, Co}^\alpha \to \beta \]

using the relationship

\[ \Delta F_{Fe, Co}^\alpha \to \beta = \Delta H_{Fe, Co}^\alpha \to \beta - TAS_{Fe, Co}^\alpha \to \beta \quad \text{Equation (25)} \]

This method assumes that the entropy and enthalpy differences are independent of temperature, but provides a first approximation to \( \Delta F_{Fe, Co}^\alpha \to \beta \) which may then be improved to correlate with existing thermodynamic data.

In the case of bcc cobalt, the heat of transformation cannot be measured directly since the bcc phase is not stable. In this case, the value is deduced by extrapolation of enthalpy values for bcc Fe – Co alloys. This value may then be compared with values calculated from other thermodynamic data (Kaufman, 1972) or by considering magnetic effects (Miodownik, 1970). The agreement is surprisingly good, considering the large number of assumptions involved in these various calculations:

a) Extrapolation to 0°K of experimental data; \( \Delta H_{Co}^\alpha \to \beta \) = 1675 cal/mole
b) Miodownik (1970) calculation; " = 1150 cal/mole
c) Kaufman (1972) calculation; " = 1390 cal/mole
Between 700° K and 1300° K both the Kaufman (1972) and Miodownik (1970) formulations provide the same values for $\Delta F_{Co}^{\alpha \rightarrow \beta}$. Outside this temperature range, the divergence increases, especially at the high temperature. In order to improve the ease of manipulation of $\Delta F_{Co}^{\alpha \rightarrow \beta}$ data by computer, Kaufman (1972) has fitted them to polynomials as a function of temperature, as listed below:

1) Iron, bcc $\rightarrow$ fcc, 1100 $\leq T \leq$ 1800

$$\Delta F_{\beta \rightarrow \alpha} = -1251.2 + 2.2468T - 0.12655 \times 10^{-2} T^2 + 0.2204 \times 10^{-6} T^3 \ldots$$

Equation (26)

2) Iron, bcc $\rightarrow$ fcc, 300 $\leq T \leq$ 1100

$$\Delta F_{\alpha \rightarrow \beta} = 1460 - 0.8274 T - 0.17858 \times 10^{-2} T^2 + 0.1225 \times 10^{-5} T^3 \ldots$$

Equation (27)

3) Cobalt, bcc $\rightarrow$ fcc, 0 $\leq T \leq$ 1800

$$\Delta F_{\alpha \rightarrow \beta} = -1662 + 0.1509 \times 10^{-2} T^2 - 0.6701 \times 10^{-6} T^3 \ldots$$

Equation (28)

In order to use Equation (23) to calculate $F_x^\alpha$ and $F_x^\beta$ for Fe$_x$ - Co$_{(1-x)}$ at a specific temperature, the free energies of the stable allotropic forms of iron and cobalt at that temperature are assigned a value of zero. Then the free energy versus composition curves for bcc and fcc phases at any temperature may be constructed using the above equations.

Calculated (Kaufman, 1972; Miodownik, 1971) values for the free-energy of mixing of bcc alloys are compared with those determined by calorimetric techniques (Muller and Hayes, 1971) in Table XII. Agreement is good, bearing in mind that Muller's results bear a possible error of $\pm$ 200 cal/mole. Similar treatment yields calculated values for the free-energy of mixing of fcc alloys; again agreement between observed and calculated data is good. The enthalpy difference between bcc and fcc phases may be obtained from the above data; experimentally determined
values have been obtained for two alloys by Muller and Hayes (1971) and
these are in good agreement with the calculated data:

\[
\begin{align*}
30.9 \text{ at \% Co (1245° K)} & \quad \Delta H_{\text{OBS}} = 1110 \pm 100 \text{ cal/mole} \\
& \quad \Delta H_{\text{CALC}} = 1210 \text{ cal/mole} \\
50 \text{ at \% Co (1245° K)} & \quad \Delta H_{\text{OBS}} = 1325 \pm 100 \text{ cal/mole} \\
& \quad \Delta H_{\text{CALC}} = 1312 \text{ cal/mole}
\end{align*}
\]

The positions of the phase boundaries defining the equilibrium
between the fcc and bcc single phase regions are computed by determination
of the common tangents to the free-energy versus composition curves for
each phase (see Figure 28). In this manner Kaufman (1972) has calculated
the equilibrium Fe – Co phase diagram, incorporating the fcc/hcp equilibria.
His diagram agrees with that published by Hansen (1958) to within \( \pm 2 \) at. pct.
Co and \( \pm 20^\circ \text{K} \).

<table>
<thead>
<tr>
<th>Composition At.% Co</th>
<th>Free Energy of Mixing Expt. Muller &amp; Hayes</th>
<th>Free Energy of Mixing Calc Kaufman</th>
<th>Free Energy of Mixing Calc. Miodownik</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>-1200 cal/mole</td>
<td>-1186 cal/mole</td>
<td>-1500 cal/mole</td>
</tr>
<tr>
<td>30</td>
<td>-1510</td>
<td>-1546</td>
<td>-</td>
</tr>
<tr>
<td>40</td>
<td>-1660</td>
<td>-1726</td>
<td>-1850</td>
</tr>
<tr>
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<td>+27</td>
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<td>0</td>
</tr>
<tr>
<td>90</td>
<td>-</td>
<td>+468</td>
<td>-</td>
</tr>
</tbody>
</table>

Table XII  Comparison between Observed and Calculated Values for the
Excess Free-Energy of Mixing in bcc Fe – Co Alloys
The techniques used in the present work for calculation of the bcc/fcc phase equilibria will be discussed in Chapter 7.

5.5 Mechanisms and Kinetics of Diffusion Controlled Transformations

5.5.1 The Nucleation Process

The formation of a region of β phase in an α phase matrix at a temperature where the free energy of the β phase ($F_β$) is lower than that of the α phase ($F_α$) entails a net chemical driving force $ΔF_α → β (=F_α - F_β)$ for the $α → β$ transformation. However, it is necessary to create a new surface between the α and β phases, and there may also be a volume change involved. Thus, close to the temperature where $F_β = F_α$ the transformation process does not occur spontaneously, due to the unfavourable surface and volume free energy changes. As the temperature is lowered from $T_0$ ($F_β = F_α$) compositional fluctuations produce small unstable areas of β phase which increase in size as the temperature decreases. As the size of the fluctuations increases, the free energy change attending their formation at first increases, reaches a maximum and then decreases. The fluctuation size giving the maximum free energy change is termed the critical nucleus size. Such a fluctuation has an equal probability of growing or decaying. Fluctuations larger than the critical size are stable and thus provide an area of β phase capable of further growth to form a macroscopic β region. The barrier to nucleation is therefore the maximum free energy change attending nucleus formation of a critical size. The nucleation barrier $ΔF^*$ (or activation energy of nucleation) is dependent on the nucleation mode. In general, nucleation of β phase within a perfect α lattice is uncommon since the surface energy required to create the α/β interface, and the strain energy associated with the atomic matching across the interface are extremely high.
Therefore, nuclei usually form at lattice imperfections such as grain boundaries, dislocations, precipitates etc., where there is energy available to reduce the activation energy barrier. This is termed heterogeneous nucleation. The size of the nucleation barrier in heterogeneous nucleation depends on the nucleation site (e.g. grain boundary, dislocation etc.), the nucleus morphology (e.g. rod, disc, hemisphere etc.) and also on the nature of the nucleus/matrix interface. If there is perfect registry between the lattices of the nucleus and matrix, the nucleus is said to be coherent. In this case, there is a large amount of strain energy involved in forming the nucleus; on the other hand interfacial energy is very low. An incoherent nucleus has complete disregistry of atomic sites across the nucleus/matrix interface. The strain energy involved is negligible but there is a very high surface energy value, often reduced by the incorporation of dislocations into the interface structure.

Theoretical calculation of activation energies of nucleation is difficult due to the large range of possible nucleation sites, and nucleus morphologies. Although calculations are therefore limited to specific idealised nucleation modes which are unlikely to occur in experimental conditions, such calculations are useful in predicting the dependence of the activation energy for nucleation, on the corresponding values of the chemical driving force. This can give some indication of the dominant nucleation mode in phase transformations.

5.5.2 The Growth Process

The driving force for growth is the difference between the chemical potentials of the diffusing species in the parent and product phases respectively, at the transformation interface. The activation energy for growth is the energy required for an atom to leave the parent phase and cross the nucleus/matrix interface, attaching itself to the nucleus. The activation
energy for growth is hence the activation energy for diffusion of the atomic species concerned. Growth proceeds in this manner until interrupted in some way e.g. by the impingement of two growing nuclei.

5.5.3 Nucleation and Growth Kinetics

A brief summary of the most important kinetic parameters will now be given. These will be developed further in Section 7, when analysing the experimental kinetic data.

(a) Nucleation Kinetics

The rate at which critical nuclei are formed is governed by the free-energy of critical nucleus formation $\Delta F_{\text{crit}}$ or $\Delta W$ (i.e. the activation energy of nucleation) and the activation energy $Q$ for the diffusion of atoms to the subcritical embryo. The nucleation rate is given by:

$$N = K \exp\left(-\frac{\Delta W + Q}{RT}\right)$$  \hspace{1cm} \text{Equation (29)}

where $K$ is an attempt frequency for the process.

(b) Growth Kinetics

The growth rate $G$ is controlled by the diffusion rate of atoms from the parent phase to the critical or supercritical nucleus. At temperatures close to the equilibrium transformation temperature the growth rate may be described in the following way (Fine, 1964):

$$G = K^1 \frac{\Delta F}{RT} \exp\left(-\frac{Q}{RT}\right)$$  \hspace{1cm} \text{Equation (30)}

where $K^1$ is an attempt frequency

$\Delta F$ is the chemical free energy difference between the competing phases.
(c) **Bulk Transformation Kinetics**

A common method of empirically describing isothermal rate processes is given by the following relationship:

\[
f = 1 - \exp \left( \frac{-t}{k} \right)^n \quad \text{Equation (31)}
\]

where \( f \) is the untransformed fraction of parent phase.

By assigning \( n = 1 \) and \( K = 3 \times 10^{-3} \text{ N}^{-1} \), Johnson and Mehl (1939) obtained good correlation with experimental kinetics for the austenite → pearlite transformation in steel.

The value of \( n \) indicates whether the overall reaction rate is controlled by the rate of nucleation or the diffusional growth rate. Alternatively, Cahn (1956) has suggested that the value of \( n \) gives an indication of the distribution of nuclei in the material. Thus \( n \) would take well-defined values, depending on whether nucleation predominated at grain boundaries, dislocations or other sites. The Johnson – Mehl equation has been successfully applied recently by Nilan (1957) in an investigation of the effect of high pressure on isothermal transformation of austenite to ferrite.
6.1 Introduction

It is proposed to separate the experimental work into two sections, considering the effect of magnetic fields firstly on transformation temperatures, and secondly on isothermal transformation kinetics. The transformations under investigation are the bcc $\rightarrow$ fcc transformation and the fcc $\rightarrow$ bcc transformation in binary Fe - Co alloys containing 30, 40 and 50 wt $\%$ cobalt. The bcc phase is designated alpha ($\alpha$) and the fcc phase is designated gamma ($\gamma$).

6.2 Materials Characterisation and Specimen Preparation

Alloys containing 30$, 40$ and 50$ cobalt were vacuum induction melted from elemental iron and cobalt of at least 99.99$ $ purity, by BISRA (Sheffield). Chemical analysis of the three melts is given in Table XIIIB. The ingots were forged and rolled at 850 - 900$^\circ$ C and supplied as 0.25" diameter rod. After the surface scale had been removed by machining, the rod was cut into convenient lengths, degreased, and sealed into silica tubes under a partial pressure of argon. The material was then homogenised for 48 hours at 1200$^\circ$ C and water quenched by crushing the silica tube above the water bath. In the quenched condition all three alloys were brittle, the brittleness increasing with cobalt content, and it was not possible to cold swage them to the required size. It was necessary, therefore, to machine the test specimens - a timeconsuming and wasteful process. (The possibility of partial swaging followed by final machining to size was considered, but this gave little time saving, and it was feared that inhomogeneous deformation was likely to result.) The machined specimens were degreased, again sealed in silica capsules
<table>
<thead>
<tr>
<th>Nominal Composition</th>
<th>Analysed Composition (wt %)</th>
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<td></td>
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<td>.027</td>
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<tr>
<td>Fe-50% Co</td>
<td>.04</td>
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</table>

+ by difference

Table XIIIB

Analysed Composition of the Experimental Alloys
under argon, annealed 2 hours at 1150°C and water quenched.

Metallographic examination of the three alloys showed that whilst the 40% and 50% cobalt compositions consisted of coarse equi-axed ferrite grains, the 30% cobalt alloy contained large regions of massive ferrite with typical ragged interfaces. It was found that the massive transformation could be prevented by quenching the material in oil instead of water; all the 30% Co specimens were therefore re-annealed for 30 minutes at 1150°C and oil quenched. This produced a microstructure similar to that found for the other alloys. The grain sizes of all three alloys fell in the range 1.5 - 2.5 mm average diameter. The 50% Co alloy contained a very small amount of second phase distributed in the grain boundaries. This was attributed to carbide formation as this alloy contained rather more carbon than the others. No microstructural evidence of inhomogeneity resulting from the hot working, or final machining was found.

6.3 Apparatus

A dilatometric method was again adopted for monitoring the phase transformations since this technique had performed very satisfactorily in the previous low temperature experiments. Other possible techniques such as resistivity measurement or magnetisation methods did not appear to offer any particular advantages, and would have necessitated more complex measuring apparatus.

6.3.1 Specimen Heating

The bcc → fcc transformation in the composition range under investigation occurs over the temperature range 980°C - 1020°C; the dilatometer must therefore be designed to operate between 950°C and 1100°C, the upper temperature being sufficiently high to ensure rapid austenitising.

The choice of heating method was governed not only by this factor,
but also by the restricted space available for a furnace between the 
magnetic pole-pieces; only 1.25 - 1.5 cm maximum. Increasing the pole 
piece separation gives a very rapid decrease in available field strength 
unless pointed pole pieces are employed. These are not suitable as they 
do not provide a large enough region of constant flux. Four heating 
methods were considered namely:

(a) Direct resistance heating
(b) Induction heating
(c) Indirect resistance heating
(d) Radiation heating

The first two methods were rejected almost immediately because it was 
not considered desirable to have electrical currents flowing in the 
specimen in the presence of strong magnetic fields. In addition, 
induction heating requires bulky ancillary apparatus and creates large 
electrical and magnetic interference. Radiation heating appeared to 
provide an elegant solution to the problem. A radiation furnace was 
constructed, having a 1 KW projector lamp as the energy source. The 
lamp was positioned with its filament located at the near focus of an 
elliptical reflector. In this way the radiation from the lamp was 
concentrated at the second focus, and could be used to heat a specimen. 
Preliminary tests showed that a specimen of the required dimensions 
could be heated to 1200°C inside a large bore evacuated glass tube. 
Unfortunately the heating efficiency was severely reduced when the specimen 
was enclosed in narrow bore tubing suitable for the dilatometer. This 
was due to the fact that the radiant beam could not be focussed on the 
specimen without losing energy in the glass. In addition, it was not 
possible to position a mirror of the initial size used between the existing 
magnet pole-pieces due to the small distance between the energising coils.
When part of the reflecting surface was cut away to allow access between the coils, the reflecting efficiency was markedly reduced. Various unsuccessful attempts were made to increase the heating power. A 2 KW lamp was tried, but the gain in lamp output was almost completely offset by a reduction in focussing ability due to the larger filament size. It was also very difficult to ensure effective cooling of such a high power source. In view of these difficulties, radiation heating was reluctantly abandoned in favour of some form of electrical heating coil.

It was decided to wind the coil on a close-fitting sliding silica sleeve around the dilatometer tube. The sleeve had a long, evenly grooved centre section where the specimens were situated, thus ensuring that the heat distribution was at its most uniform. The coil windings were of platinum since this is chemically inert at high temperatures, is not ferromagnetic, has a high melting point and does not undergo any phase changes which could lead to a deleterious change in properties. It was necessary to energise the coil with direct current since, in a magnetic field, alternating current produced 50 Hz vibrations of sufficient amplitude to cause fatigue failure of the platinum wire. The power required to attain specimen temperatures up to 1050°C was 0 - 13 A at 30 V, or 0.- 400 W. In order to achieve constant current, heavy-duty lead-acid accumulators were employed. Using these it was possible to maintain a steady current (and hence steady temperature) for approximately 20 minutes, which is sufficient for the duration of a complete experiment.

6.3.2 Experimental Measurements

The specimen temperature was measured by a Pt - Pt 13% Rh thermocouple which was fixed in the dilatometer so that it located reproducibly into the drilled specimens. The thermocouple was connected to a digital
thermometer accurate to $\pm 0.5^\circ C$. The temperature gradient between the centre and each end of the specimen, at $1000^\circ C$ was found to be $1^\circ C \pm 0.5^\circ C$, decreasing as the specimen temperature decreased.

Changes in specimen length during experiments were transmitted to a linear-voltage displacement transducer via a silica pushrod and a sliding vacuum-seal spindle. The transducer output was amplified by a Sangamo-Weston C52 transducer meter, and displayed as a function of time on a potentiometric pen-recorder.

The dilatometer assembly is detailed in Figure 29, and the complete experimental arrangement is shown in Figure 30.

6.4 Experimental Methods

6.4.1 The A T Effect

A specimen was inserted into the dilatometer, with the hollow portion firmly located over the thermocouple. The silica pushrod and sliding vacuum seal were then inserted to give positive contact between the specimen tip and the transducer sensor. The apparatus was then evacuated, and flushed twice with high purity argon. The transducer meter was adjusted to give a fiducial point on the chart recorder. After allowing about 10 minutes for thermal and mechanical stabilisation of the transducer assembly, the heating coil was energised to give an overall heating rate of $170^\circ/min$ with a final temperature approximately $50^\circ$ lower than the anticipated bcc $\rightarrow$ fcc reaction temperature. Further heating was then effected very slowly, and the temperature was again stabilised for a few minutes approximately $10^\circ$ below the anticipated reaction temperature. Fine control of the heater current allowed the temperature to be raised in $2^\circ$ increments with intermediate isothermal holding. The
Fig. 29 Details of experimental high temperature dilatometer.
Fig. 30  General view of experimental apparatus.
onset of the bcc + fcc transformation was evidenced by a change from specimen expansion to contraction. The temperature $T_1$ at which this occurred was noted.

A magnetic field of 19 kOe was then applied to the specimen, whereupon the bcc + fcc reaction stopped. After a short isothermal stabilising period (~2 min) heating in 2° increments was continued as before until the transformation recommenced. The temperature $T_H$ at which this occurred was noted. The difference between $T_H$ and $T_1$ is the amount by which the bcc + fcc transformation temperature has been raised by a magnetic field.

The $\Delta T$ effect for the reverse fcc + bcc transformation was evaluated in a similar manner. In this case, however, very slow cooling from the austenite region was employed, and the transformation temperature in a magnetic field $T_H^1$ was measured first. The magnetic field was then switched off, and cooling was continued until the transformation recommenced at $T_1^1$. Hence the $\Delta T$ effect is given by:

$$\Delta T^{\alpha \rightarrow \gamma} = T_H - T_1$$

$$\Delta T^{\gamma \rightarrow \alpha} = T_H^1 - T_1^1$$

6.4.2 The Kinetic Effect

Transformation rates were deduced directly from the dilatometric data, as rates of expansion or contraction. The ratio of transformation rates with and without an applied magnetic field may then be readily determined.

Although the use of length-changes in evaluating the magnetic effect on kinetics is perfectly justified (assuming transformation isotropy), it was thought worthwhile to attempt conversion of these to absolute reaction
rates. This proved to be impossible by the metallographic techniques used successfully in Chapter 3 for martensitic transformations. Specimens were reacted for various times both on heating through the alpha plus gamma region, and on cooling from the gamma region, followed by argon gas quenching in the dilatometer. Metallographic examination of such specimens did not reveal any difference in structure between the isothermally transformed regions, and those which had transformed on cooling.

It was envisaged that a faster cooling rate from the reaction temperature might reveal microstructural differences. In order to check this, a 3 inch length of the 40% Co alloy rod was placed in a temperature gradient such that one end was in the gamma region, whilst the other was in the alpha region. After 15 minutes the rod was quickly water quenched. A longitudinal section was then polished and examined metallographically. Unfortunately, it was still not found possible to distinguish between regions which had been alpha-phase prior to quenching, from those in which alpha had formed from the gamma phase during the quench. Attempts to relate dilatometric data to amounts of transformation were therefore abandoned.

6.5 Experimental Results

6.5.1 The $\Delta T$ Effect

Since the $\Delta T$ effect is intrinsically small, even an error of 1 degree in the measured values is substantial. In view of this it was decided not to perform experiments using field strengths other than the maximum obtainable. Accordingly, all the $\Delta T$ values listed in Table XIII were measured in a field of 19 kOe. These are accurate only to within $^{+}0.5^\circ C$. $^{-}$
Table XIII  Effect of Magnetic Field of 19 K0e on Transformation Temperatures of Fe - Co Alloys

<table>
<thead>
<tr>
<th>Specimen Number</th>
<th>Composition</th>
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<th>$\Delta T (\gamma + \alpha)$</th>
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<td>°C</td>
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### Table XIV (a)  
**FCC → BCC Transformation in 30% Co - Fe**

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<th>Field Strength</th>
<th>Initial Rate ( f_0 )</th>
<th>Field Rate ( f_H )</th>
<th>Zero-Field Rate ( f )</th>
<th>( f/f_H ) (or ( f_H/f ))</th>
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### Table XIV (b)  
**BCC → FCC Transformation in 30% Co - Fe**

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<th>Field Strength</th>
<th>Initial Rate ( f_0 )</th>
<th>Field Rate ( f_H )</th>
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### Table XIV (c)  
**FCC + BCC Transformation in 40% Co - Fe**

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### Table XIV (d)  
**BCC + FCC Transformation in 40% Co - Fe**

<table>
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<tr>
<th>Field Strength (kOe)</th>
<th>Initial Rate (k)</th>
<th>Field Rate (kH)</th>
<th>Zero-Field Rate (k)</th>
<th>f/fH (or fH/f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
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<tr>
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</tr>
<tr>
<td>19</td>
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<td>0.35</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>0.30</td>
<td>0.72</td>
<td>2.4</td>
</tr>
<tr>
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<td>0.29</td>
<td>0.66</td>
<td>2.3</td>
</tr>
<tr>
<td>9</td>
<td>0.71</td>
<td>0.49</td>
<td>0.69</td>
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<tr>
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<td>0.42</td>
<td>0.56</td>
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<td>0.59</td>
<td>0.83</td>
<td>1.4</td>
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### Table XIV (e)  
**FCC → BCC Transformation in 50% Co – Fe**

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<th>Field Strength (kOe)</th>
<th>Initial Rate (fo)</th>
<th>Field Rate (fH)</th>
<th>Zero-Field Rate (f)</th>
<th>f/fH (or fH/f)</th>
</tr>
</thead>
<tbody>
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<td>19</td>
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<tr>
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<td>0.59</td>
<td>1.42</td>
<td>0.61</td>
<td>2.33</td>
</tr>
<tr>
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<td>0.53</td>
<td>1.30</td>
<td>0.56</td>
<td>2.32</td>
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<tr>
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<td>0.42</td>
<td>0.88</td>
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</tr>
<tr>
<td>19</td>
<td>0.34</td>
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</tr>
<tr>
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<td>1.0</td>
<td>0.58</td>
<td>1.72</td>
</tr>
<tr>
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<td>0.45</td>
<td>1.18</td>
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<tr>
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<td>0.53</td>
<td>0.78</td>
<td>0.55</td>
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</tr>
<tr>
<td>9</td>
<td>0.41</td>
<td>0.55</td>
<td>0.42</td>
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</tr>
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<td>0.81</td>
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</tr>
<tr>
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<td>0.48</td>
<td>0.66</td>
<td>0.48</td>
<td>1.37</td>
</tr>
<tr>
<td>9</td>
<td>0.53</td>
<td>0.74</td>
<td>0.53</td>
<td>1.39</td>
</tr>
<tr>
<td>9</td>
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<td>0.84</td>
<td>0.62</td>
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</tr>
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</table>

### Table XIV (f)  
**BCC → FCC Transformation in 50% Co – Fe**

<table>
<thead>
<tr>
<th>Field Strength (kOe)</th>
<th>Initial Rate (f)</th>
<th>Field Rate (fH)</th>
<th>Zero-Field Rate (f)</th>
<th>f/fH (or fH/f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>0.5</td>
<td>0.29</td>
<td>0.47</td>
<td>1.62</td>
</tr>
<tr>
<td>19</td>
<td>0.38</td>
<td>0.22</td>
<td>0.36</td>
<td>1.64</td>
</tr>
<tr>
<td>19</td>
<td>0.72</td>
<td>0.41</td>
<td>0.70</td>
<td>1.69</td>
</tr>
<tr>
<td>19</td>
<td>0.58</td>
<td>0.35</td>
<td>0.55</td>
<td>1.56</td>
</tr>
<tr>
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<td>0.63</td>
<td>0.36</td>
<td>0.63</td>
<td>1.75</td>
</tr>
<tr>
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<td>0.28</td>
<td>0.44</td>
<td>1.55</td>
</tr>
<tr>
<td>19</td>
<td>0.77</td>
<td>0.45</td>
<td>0.75</td>
<td>1.68</td>
</tr>
<tr>
<td>19</td>
<td>0.39</td>
<td>0.21</td>
<td>0.37</td>
<td>1.78</td>
</tr>
<tr>
<td>9</td>
<td>0.58</td>
<td>0.51</td>
<td>0.57</td>
<td>1.12</td>
</tr>
<tr>
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<td>0.51</td>
<td>0.45</td>
<td>0.51</td>
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<tr>
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<td>0.68</td>
<td>0.58</td>
<td>0.67</td>
<td>1.15</td>
</tr>
</tbody>
</table>
7.1 Introduction

The experimental results have shown that applied magnetic fields influence the fcc → bcc and bcc → fcc transformations in Fe - Co alloys containing 30 - 50 pct Co. The following effects have been observed:

a) For a given alloy composition, the temperature at which phase transformation commences is raised by applied magnetic fields. This phenomenon has been termed the 'ΔT Effect'.

b) Magnetic fields applied during the course of isothermal phase transformation alter the rate of transformation. This phenomenon has been termed the 'Kinetic Effect'.

In order to simplify the detailed discussion of experimental data, these two phenomena will be considered separately.

7.2 The ΔT Effect

7.2.1 Introduction

The present experimental work on transformations in Fe - Co alloys has demonstrated that the magnetic effect is not confined to diffusionless shear transformations. In qualitative terms the experimental results are logical; magnetic fields have been shown to increase the stability of the bcc ferromagnetic phase, as evidenced by an increase in the bcc → fcc transformation temperature. It now remains to investigate whether the observed magnitude of the ΔT Effect in the experimental alloys is consistent with theoretical expectations.

7.2.2 Phase Equilibria and Magnetic Effects

In order to predict the effect of magnetic fields on phase trans-
formation temperatures in the experimental alloys, it is first necessary
to determine the position of the bcc and fcc phase field boundaries under
zero-field conditions and secondly after superimposition of a magnetic
field of the required strength. This was achieved by computer calculation;
the general methods used are described in detail in Section 6.6. Direct
substitution of phase stability data for the Fe - Co system yields the
computed phase diagram under zero-field conditions.

In order to calculate the modified phase diagram in the presence
of a magnetic field, it is necessary to invoke a quantitative model
describing the effect of magnetic fields on phase stability. In a previous
part of this thesis (Section 4) it was demonstrated that experimental data
were adequately accounted for by postulating a magnetic free-energy com­
ponent $\Delta I_{S,H}$ stabilising a ferromagnetic phase, in a magnetic field.
It is hence logical to recalculate the Fe - Co phase diagram assuming
that the bcc phase is stabilised by a similar magnetic free energy
increment.

As an initial approximation, the magnetic energy for all alloys
was assigned a fixed value based on the room-temperature magnetisation
of the 70 Fe/30 Co alloy. For a magnetic field of 20 K0e, the value of
$\Delta I_{S,H}$ is approximately 5 cal/mole. The modified phase diagram calculated
using this figure, when compared with the normal diagram, showed that
the experimental $\Delta T$ values were of the correct order of magnitude.

In order to obtain a more accurate assessment of the predicted
change in the phase diagram due to a magnetic field, a more sophisticated
expression for the magnetic energy was employed. This takes into account
the considerable variation of saturation magnetisation with both temper­
ature and composition. The compositional dependence was obtained as a
continuous variable by a computer procedure which yielded the best fitting
polynomial based on experimental data. The magnetisation for a given composition, obtained in this manner, was then calculated as a function of temperature using the approximate relationship:

$$\beta_T = \beta_0 \left[ 1 - \left(\frac{T}{T_C}\right)^6 \right]$$  

Equation (32)

where $\beta_0$, $\beta_T$ are magnetisation values at $0^\circ$ K, $T^\circ$ K and $T_C$ is the Curie Temperature in deg. K.

The $T_C$ values for any composition were obtained by a further computer curve-fitting procedure based on published experimental data.

The position of the bcc and fcc phase-field boundaries calculated for a magnetic field of 19 Koe are shown, relative to their zero-field position, in Figure 31. From these data, the $\Delta T$ values at 19 Koe may be readily obtained and are in reasonable agreement with experimental data, with the exception of the observed $\Delta T$ value for the fcc $\rightarrow$ bcc transformation in the 30% Co alloy, which is significantly greater than predicted (Table XVI). The observed variation of $\Delta T$ with composition for both transformations is shown in Figure 32. A major point of interest is that $\Delta T$ (fcc $\rightarrow$ bcc) is significantly higher than $\Delta T$ (bcc $\rightarrow$ fcc). A detailed examination of the computed free-energy data for Fe - Co alloys as a function of temperature and composition was therefore carried out in order to determine whether the observed variation of $\Delta T$ with composition could be accounted for, together with the observed differences in the magnitude of $\Delta T$ between the fcc $\rightarrow$ bcc and bcc $\rightarrow$ fcc transformations.

7.2.3 Computed Phase Stability Data

The free-energies of both the fcc and bcc phases were computed as a function of composition at intervals of 1 at. % Co from 0 - 100% Co; and as a function of temperature at intervals of $1^\circ$ K. This permitted
Fig. 31 Computed $\alpha/\gamma$ equilibrium with and without a magnetic field of 19 K0e.
Fig. 32  Variation of observed ΔT values with composition, for a magnetic field of 19K0e.
very accurate determination of the positions of the (fcc + bcc)/bcc and (fcc + bcc)/fcc phase boundaries for any alloy composition. This procedure was repeated to determine the position of the phase boundaries in a magnetic field of 19 K0e. This is shown schematically in the sketch below, which includes the critical transformation temperatures for an alloy containing 7% Co.

The experimental $\Delta T$ effect is defined as:

$$\Delta T (\gamma \rightarrow \alpha) = T_{\alpha \rightarrow \gamma} (H) - T_{\alpha \rightarrow \gamma}$$

$$\Delta T (\alpha \rightarrow \gamma) = T_{\gamma \rightarrow \alpha} (H) - T_{\gamma \rightarrow \alpha}$$

(The apparent discrepancy in subscript notation above arises because $T_{\alpha \rightarrow \gamma}$ has been defined as $T (\alpha \rightarrow 100\% \gamma)$ whereas the observed $\Delta T$ values relate to the initial formation of the new phase at the limit of the two-phase region.)

The computed critical transformation temperatures for the experimental alloys are given in Table XV. These may be utilised to give the corresponding computed $\Delta T$ values, which are given in Table XVI, together with those observed experimentally.
### Table XV  Computed Critical Transformation Temperatures in Zero Field, and in a Field of 19K0e

<table>
<thead>
<tr>
<th>Field Strength KOe</th>
<th>Composition At. % Co</th>
<th>Critical Transformation Temperature $T_{\alpha \rightarrow \gamma}$ ($^\circ K$)</th>
<th>$T_{\gamma \rightarrow \alpha}$ ($^\circ K$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>1246</td>
<td>1244</td>
</tr>
<tr>
<td>0</td>
<td>38</td>
<td>1260.5</td>
<td>1259.2</td>
</tr>
<tr>
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<td>1262.3</td>
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<td>1250</td>
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<tr>
<td>19</td>
<td>38</td>
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<tr>
<td>19</td>
<td>49</td>
<td>1268.5</td>
<td>1268.1</td>
</tr>
</tbody>
</table>

### Table XVI  Comparison between Computed and Observed $\Delta T$ Values

<table>
<thead>
<tr>
<th>Composition At. % Co</th>
<th>$\Delta T (\gamma \rightarrow \alpha)$ $^\circ K$</th>
<th>$\Delta T (\alpha \rightarrow \gamma)$ $^\circ K$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Computed</td>
<td>Observed</td>
</tr>
<tr>
<td>29</td>
<td>4.2 ($^+ 0.05$)</td>
<td>4.7 ($^+ 0.5$)</td>
</tr>
<tr>
<td>38</td>
<td>5.3</td>
<td>5.9</td>
</tr>
<tr>
<td>49</td>
<td>5.8</td>
<td>5.0</td>
</tr>
</tbody>
</table>
The general order of magnitude of the computed and observed values is in good agreement, thereby giving general support to the model used to account for the magnetic effect. However, the calculated $\Delta T$ values indicate that a magnetic field would have a similar effect on both the $\alpha \rightarrow \gamma$ and $\gamma \rightarrow \alpha$ transformations, whereas the experimental data show that the $\Delta T$ effect is considerably greater for the $\gamma \rightarrow \alpha$ transformation.

It was thought that an explanation of this discrepancy could be obtained by detailed consideration of the transformation thermodynamics. The free-energy changes accompanying transformation in the narrow $\alpha + \gamma$ region are difficult to evaluate; accordingly the free-energy change $\Delta F_{\gamma \rightarrow \alpha}$ or $\Delta F_{\alpha \rightarrow \gamma}$ involved during the $100\% \gamma \rightarrow 100\% \alpha$ and $100\% \alpha \rightarrow 100\% \gamma$ transformations respectively was calculated. ($\Delta F_{\gamma \rightarrow \alpha}$ is defined as the difference in free energy between unit volumes of $\gamma$ and $\alpha$ phase of the same composition, at $T_{\gamma \rightarrow \alpha}$). The $\Delta F$ values in zero-field and in a magnetic field of 19 Koe are given in Table XVII.

<table>
<thead>
<tr>
<th>Field Koe</th>
<th>Composition At. % Co</th>
<th>Free Energy of Transformation $\Delta F_{\alpha \rightarrow \gamma}$</th>
<th>$\Delta F_{\gamma \rightarrow \alpha}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>29</td>
<td>1.5 cal/mole</td>
<td>0.5 cal/mole</td>
</tr>
<tr>
<td></td>
<td>38</td>
<td>1.3 cal/mole</td>
<td>0.4 cal/mole</td>
</tr>
<tr>
<td></td>
<td>49</td>
<td>$\sim0.1$ cal/mole</td>
<td>$\sim0.1$ cal/mole</td>
</tr>
<tr>
<td>19</td>
<td>29</td>
<td>1.3 cal/mole</td>
<td>1.4 cal/mole</td>
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<tr>
<td></td>
<td>38</td>
<td>1.1 cal/mole</td>
<td>1.2 cal/mole</td>
</tr>
<tr>
<td></td>
<td>49</td>
<td>$\sim0.1$ cal/mole</td>
<td>$\sim0.1$ cal/mole</td>
</tr>
</tbody>
</table>

Table XVII  Free Energy Difference Between $\gamma$ and $\alpha$ Phases at Critical Transformation Temperature
In considering the significance of the $\Delta F$ values, we shall make a simplifying assumption that the nucleation behaviour of both bcc $\rightarrow$ fcc and fcc $\rightarrow$ bcc transformations is similar, such that their thermodynamic requirements for successful nucleation are similar. In this case, the following points have been inferred from the data of Table XVII:

(a) The defined free-energy change accompanying transformation is intrinsically small for all alloys. It may hence be inferred that some undercooling of the fcc $\rightarrow$ bcc transformation, or superheating of the bcc $\rightarrow$ fcc reaction will be necessary in order to provide sufficient driving force to overcome nucleation barriers.

(b) Since the free-energy change in zero field is greater for the bcc $\rightarrow$ fcc transformation, than for the reverse transformation, whilst these become approximately equal in an applied magnetic field of 19 K0e one may expect to observe asymmetry between the required amounts of undercooling and superheating for the respective transformations. This gives expectation of different $\Delta T$ values for the two transformations.

(c) For the bcc $\rightarrow$ fcc transformation, the $\Delta F$ values are approximately equal both in zero field and in a magnetic field of 19 K0e One may hence infer that the experimental $\Delta T$ values should be in good agreement with calculated data, as has been observed.

(d) For the fcc $\rightarrow$ bcc transformation, except for the 50% Co alloy, the $\Delta F$ values are significantly lower in zero-field conditions than in a magnetic field of 19 K0e It may hence be inferred
that the transformation in zero field will take place at an anomalously low temperature, giving rise to increased $\Delta T$ values for the fcc $\rightarrow$ bcc transformation. Again, this is in agreement with the experimental data.

(e) For the fcc $\rightarrow$ bcc transformation in the 50% Co alloy, where $\Delta F$ is approximately the same in zero-field conditions and in a field of 19 kOe the argument given in (c) above applies, and the observed $\Delta T$ is expected to agree closely with the calculated value.*

7.3 The Kinetic Effect

7.3.1 Origin of the Kinetic Effect

In this discussion it will be assumed that both the bcc $\rightarrow$ fcc transformation on heating and the fcc $\rightarrow$ bcc transformation on cooling occur by a diffusional nucleation and growth process, although it is well known that the fcc $\rightarrow$ bcc transformation can also occur in these alloys by either a massive or martensitic reaction depending on the transformation conditions.

Since the kinetics of both nucleation and growth are separately dependent on the value of the chemical driving force for the transformation, magnetic fields may be expected to influence the transformation kinetics when one of the participating phases is ferromagnetic (Figures 33 and 34).

*Footnote
Similar arguments have been applied to the effect of magnetic fields on transformation kinetics (Section 7.3). In this manner, observed differences in kinetics between bcc $\rightarrow$ fcc and fcc $\rightarrow$ bcc transformations may also be accounted for.
Fig. 33 Effect of magnetic fields on the kinetics of the fcc → bcc transformation.
Effect of magnetic fields on the kinetics of the bcc $\rightarrow$ fcc transformation.
The purpose of the present discussion is to determine whether experimental data for the effect of magnetic fields on transformation kinetics may be accounted for using quantitative descriptions of both nucleation and growth. As in the previous section, the theoretical aspects will be considered first, and their application to experimental data will then be discussed.

7.3.2 Predicted Growth Kinetics in a Magnetic Field

The kinetics of diffusional growth are given by the relationship:

\[
G = K \frac{AF}{kT} \exp \left( - \frac{Q}{kT} \right) \tag{33}
\]

where \( Q \) is the activation energy for diffusion
\( \Delta F \) is the chemical driving force per unit volume
\( K \) is a constant
\( G \) is the linear growth rate

Assuming that the activation energy for diffusion is not significantly affected by a magnetic field, we may obtain an expression for the modified growth rate in a magnetic field:

\[
G_H = K \frac{\Delta F_H}{kT} \exp \left( - \frac{Q}{kT} \right) \tag{34}
\]

The inverse ratio of growth rates before and after the application of a magnetic field is hence given by:

\[
\frac{G_H}{G} = \frac{\Delta F_H}{\Delta F} = 1 + \frac{\Delta I_S H}{\Delta F} \tag{35}
\]
7.3.3 Predicted Nucleation Kinetics in a Magnetic Field

During steady state nucleation, the rate at which critical nuclei form \( \dot{N} \) is given by:

\[
\dot{N} = A_0 \exp \left( -\frac{\Delta W + Q}{kT} \right) \quad \text{Equation (36)}
\]

where \( A_0 \) is a frequency factor and \( \Delta W \) is the work of nucleation.

Again assuming that \( Q \) is independent of the magnetic field, the modified nucleation rate in a magnetic field is given by:

\[
\dot{N}_H = A_0 \exp \left( -\frac{\Delta W_H + Q}{kT} \right) \quad \text{Equation (37)}
\]

The inverse ratio of nucleation rates before and after the application of a magnetic field may now be written as:

\[
\frac{\dot{N}_H}{\dot{N}} = \exp \left( -\frac{\Delta W_H - \Delta W}{kT} \right) \quad \text{Equation (38)}
\]

The relationship between the work of nucleation and the driving force for transformation depends on the operative nucleation mode (homogeneous or heterogeneous) and on the size and shape of critical nuclei. For the case of homogeneous nucleation of spherical nuclei, and neglecting strain energy, we may write:

\[
\Delta W = \frac{16\pi \sigma^3}{3\Delta F^2} \quad \text{Equation (39)}
\]

where \( \sigma \) is the nucleus/matrix interfacial energy.

The ratio of nucleation rates with and without a magnetic field is given by combining equations 38 and 39.
In the case of heterogeneous nucleation, the expression for the work of nucleation is given by multiplying the equivalent equation for homogeneous nucleation by a factor $f(\theta)$ where $\theta$ is the nucleus/matrix contact angle. When $\theta = 180^\circ$, the matrix does not 'wet' the nucleus and $f(\theta) = 1$. When $\theta = 0$ (i.e. perfect 'wetting'), $f(\theta) = 0$ and the barrier to nucleation disappears. One of the simplest (and most often observed) heterogeneous nucleation modes which can be analysed for solids is that of nucleation at grain boundaries. In the following derivation of nucleation kinetics at a grain boundary it is assumed

(a) that the nucleus is hemispherical,
(b) that it is formed on a grain boundary surface, and
(c) that strain energy may be neglected.

The free energy change involved in forming such a nucleus is given by:

$$\Delta F_n = \frac{2}{3} \pi r^3 \Delta F + 2 \pi r^2 \sigma - \pi r^2 \sigma_n$$

Equation (41)

where $r$ is the nucleus radius

$\sigma$ is the nucleus/matrix interface energy

$\sigma_n$ is the boundary energy per unit area

If we further assume

(d) that the nucleus/matrix interface is incoherent, we may make a simplifying assumption that $\sigma = \sigma_n$

Equation (41) then reduces to:
\[ \Delta F_n = \frac{2}{3} \pi r^3 \Delta F + \pi r^2 \sigma \quad \text{Equation (42)} \]

The work of nucleation \( \Delta W \) is given by the value of Equation (42) when

\[ \frac{d (\Delta F_n)}{dr} = 0 \]

that is

\[ \Delta W = \frac{\pi \sigma^3}{3 \Delta F^2} \quad \text{Equation (43)} \]

7.3.4 Effect of Nucleation and Growth on Bulk Transformation

The bulk kinetics of transformation reflect the influence of both nucleation and growth, but the inter-relationship between the three parameters is still not well understood. Quantitative treatment is extremely complex, and is difficult to check by direct experimentation, since in situ observation of nucleation in solids is almost impossible. Some simple cases however, lend themselves to quantitative analysis, and three of these will now be briefly discussed.

(a) Nucleation Controlled Transformation

In this case it is assumed that the rate of transfer of atoms from the parent phase to the nucleus is very rapid. Hence the rate of bulk transformation depends only on the rate at which critical nuclei come into existence. Additionally magnetic effects on growth kinetics may be ignored.

Using these assumptions we may obtain an expression for the change in transformation rate due to a magnetic field:

\[ \ln \left( \frac{\dot{f}_H}{\dot{f}} \right) = \frac{C}{kT} \left[ \frac{1}{\Delta F^2} - \frac{1}{\Delta F_H^2} \right] \quad \text{Equation (44)} \]
where \( C \) is a constant.

(b) **Growth Controlled Transformation**

In this case it is assumed that transformation is achieved from a fixed number of nuclei. This can happen if rapid nucleation occurs prior to observable growth for instance in diffusional transformations at low temperatures. Alternatively, if the rate of formation of nuclei is equal to their rate of exhaustion, the number of active growth centres remains constant.

Assuming that a magnetic field does not greatly affect the concentration of critical nuclei, the effect of a magnetic field on the transformation rate is given by:

\[
\ln \left( \frac{f_H}{f} \right) = 3 \ln \left( \frac{\Delta F_H}{\Delta F} \right)
\]

Equation (45)

(c) **Nucleation and Growth Dependent Transformation**

This is important when nucleation continues throughout the transformation process. It is applicable to many phase transformations involving discontinuous precipitation. The rate of transformation at any time \( t \) is given by the Johnson-Mehl equation:

\[
f = \mathcal{N} G^3 t^n
\]

Equation (46)

where \( n \) is a constant, whose value depends on the type of transformation considered.

From equations 40, 45, and 46, we may obtain an expression for the effect of magnetic fields on transformation kinetics at any time:

\[
\frac{\dot{f}_H}{\dot{f}} = \frac{N_H}{N} \left( \frac{\dot{G}_H}{\dot{G}} \right)^3
\]

Equation (47)
Hence \[ \ln \left( \frac{\frac{d}{dt}}{\dot{f}} \right) = 3 \ln \left( \frac{\Delta F_H}{\Delta F} \right) + \frac{c}{kT} \left( \frac{1}{\Delta F^2} - \frac{1}{\Delta F_H^2} \right) \]

Equation (48)

7.3.5 **Comparison with Experiment**

The main trends of the experimental kinetics are as follows:

(a) For each alloy composition, the effect of a magnetic field is greater for the fcc \(\rightarrow\) bcc transformation than for the bcc \(\rightarrow\) fcc transformation.

(b) The accelerating (or retarding) influence of magnetic fields on both transformations increases with increasing field strength.

(c) The magnitude of the field effect (expressed as the ratio of transformation rates) is independent of the initial (zero field) transformation rate.

(d) The magnitude of the field effect is markedly dependent on composition.

In this section it is intended to investigate whether the observed kinetics may be explained by consideration of the theoretical kinetic relationships outlined previously. In order to perform this analysis it is necessary to calculate the driving force for transformation at each experimental reaction temperature both with and without the presence of a magnetic field. The experimental kinetics of the fcc \(\rightarrow\) bcc transformation were measured at 10°C undercooling below the transformation temperature observed during determination of the \(\Delta T\) effect. Similarly, kinetics measurements during the bcc \(\rightarrow\) fcc transformation were taken at 10°C superheating above the observed transformation temperature.
Accordingly, the calculated free energy of transformation was evaluated at 10°C undercooling or superheating respectively. The free-energy of each transformation is defined as the difference in free-energy between unit volumes of $\alpha$ and $\gamma$ phases of the same composition at $(T_{\alpha} + 10)^°K$ or $(T_{\gamma} - 10)^°K$ respectively.

These driving forces $\Delta F^E_{\gamma + \alpha}$ are given in Table XVIII for both zero-field conditions, and in a magnetic field of 19 KOe.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\Delta F^E_{\gamma + \alpha}$ (cal/mole)</th>
<th>$\Delta F^E_{\alpha + \gamma}$ (cal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>At.-% Co</td>
<td>H = 0</td>
<td>H = 19 KOe</td>
</tr>
<tr>
<td>29</td>
<td>11.0</td>
<td>13.1</td>
</tr>
<tr>
<td>38</td>
<td>11.1</td>
<td>16.0</td>
</tr>
<tr>
<td>49</td>
<td>11.8</td>
<td>16.5</td>
</tr>
</tbody>
</table>

Table XVIII Free Energy Change of bcc/fcc Transformations at 10°C Undercooling ($\gamma + \alpha$) or Superheating ($\alpha + \gamma$)

The magnitude of the magnetic energy input for a particular alloy is given by $\Delta F^E (H = 0) - \Delta F^E (H = 19 KOe)$ for the appropriate transformation, and is proportional to the magnetic field strength. This

Footnote
Any discrepancy between calculated and observed absolute transformation temperatures derived from slight inaccuracies in the thermochemical and phase stability data was ignored, as we are dealing with temperature differences rather than absolute values in these calculations.
allows determination of $\Delta F^E$ at any field strength.

In Table XIX are listed the values of some parameters derived from experimental results, and from the data given in Table XIV. These parameters will be used to analyse experimental kinetics using the available theoretical models for nucleation and growth kinetics.

<table>
<thead>
<tr>
<th>Composition At.% Co</th>
<th>Experimental Data</th>
<th>Calculated Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Field Strength (H) K0e</td>
<td>$\ln \left( \frac{\gamma_f}{\gamma^*} \right)$</td>
</tr>
<tr>
<td>29</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>0.438</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>0.912</td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>1.075</td>
</tr>
<tr>
<td>38</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>0.668</td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>1.484</td>
</tr>
<tr>
<td>49</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>0.515</td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>0.789</td>
</tr>
</tbody>
</table>

Table XIX (a) Kinetic Parameters for $\gamma \rightarrow \alpha$ Transformation

The first stage in the analysis of the experimental data was to determine whether the observed transformation kinetics could be accounted for by either growth-controlled or nucleation-controlled transformation criteria.
For the former, it has been shown that:

\[
\frac{\dot{\gamma}}{\dot{\gamma}_H} = \frac{\Delta F^E_H}{\Delta F^E} = 1 + \frac{\Delta I_S H}{\Delta F^E} \quad \text{Equation (35)}
\]

It would therefore be expected that in a growth-controlled transformation, a plot of \((\frac{\dot{\gamma}}{\dot{\gamma}_H})^{\frac{1}{3}}\) Versus \(H\) would be linear. When the experimental data were plotted in this manner, linearity was not observed, and it was concluded that transformation was not growth-controlled. This conclusion was supported by the calculated values of the driving force for transformation; a growth-controlled transformation should obey the relationship

\[
\ln \left( \frac{\dot{\gamma}}{\dot{\gamma}_H} \right) = 3 \ln \left( \frac{\Delta F^E_H}{\Delta F^E} \right)
\]

and this was not found to be the case.

<table>
<thead>
<tr>
<th>Composition At.% Co</th>
<th>Experimental Data</th>
<th>Calculated Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Field Strength H (Ko)</td>
<td>(\ln \left( \frac{\dot{\gamma}}{\dot{\gamma}_H} \right))</td>
</tr>
<tr>
<td>29</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>0.234</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>0.588</td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>0.811</td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>0.811</td>
</tr>
<tr>
<td>38</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>0.315</td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>0.811</td>
</tr>
<tr>
<td>49</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>0.131</td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>0.507</td>
</tr>
</tbody>
</table>

Table XIX (b) Kinetic Parameters for α + γ Transformation
For nucleation-controlled transformations, the transformation kinetics should obey the relationship:

\[
\frac{f_H}{f} = \exp \frac{C}{kT} \left[ \frac{1}{(\Delta F^E)^2} - \frac{1}{(\Delta F_H^E)^2} \right] \quad \text{Equation (44)}
\]

Hence a plot of \( \ln \left( \frac{f_H}{f} \right) \) Versus \( \frac{1}{(\Delta F^E)^2} - \frac{1}{(\Delta F_H^E)^2} \) should be linear. When the experimental data were plotted in this manner (Figures 35 and 36), a reasonable fit was obtained for the fcc \( \rightarrow \) bcc transformation in all the experimental alloys, as well as for the bcc \( \rightarrow \) fcc transformation in the 30\% Co alloy. The fit for the latter transformation in the 40\% Co and 50\% Co alloys was, however, much less significant.

A similar analysis was carried out on the hypothesis that transformation was controlled by both nucleation and growth. Referring to equation (48) it would be expected in this case that a plot of

\[
\ln \left( \frac{f_H}{f} \right) - 3 \ln \left( \frac{\Delta F_H^E}{\Delta F^E} \right) \text{ Versus } \frac{1}{(\Delta F^E)^2} - \frac{1}{(\Delta F_H^E)^2}
\]

would be linear. When the experimental data were plotted in this manner, no improvement was found in the fit for either transformation in any of the experimental alloys.

It was concluded that the experimental data were not compatible with growth controlled transformation, or with nucleation and growth controlled kinetics. It appeared that the model for nucleation-controlled transformation was successful for the fcc \( \rightarrow \) bcc transformation and also for the bcc \( \rightarrow \) fcc transformation in the 30\% Co alloy.
Fig. 35 Plot of kinetic parameters for the fcc $\rightarrow$ bcc transformation (nucleation controlled) in Fe-Co alloys.
Fig. 36  Plot of kinetic parameters for the bcc -> fcc transformation (nucleation-controlled) in 30%Co-Fe.
7.3.6 Utilisation of Experimental Data

The preceding analysis has indicated that theoretical models for nucleation-controlled transformation provide the best correlation with the general trends of the experimental data. Accordingly, the quantitative relationships governing nucleation kinetics will now be employed to evaluate certain of the parameters associated with nucleation of the \( \alpha \rightarrow \gamma \) and \( \gamma \rightarrow \alpha \) transformation in the experimental alloys.

As previously derived, the effect of magnetic fields on a nucleation-controlled transformation is given by:

\[
\frac{\Delta W}{kT} = \frac{1}{(\Delta F^E)^2} - \frac{1}{(\Delta F_H^E)^2}
\]

Hence the slope of a plot of \( \ln \left( \frac{\dot{f}_H}{\dot{f}} \right) \) Versus \( \frac{1}{(\Delta F^E)^2} - \frac{1}{(\Delta F_H^E)^2} \) (Figures 35 and 36) is given by

\[
\frac{\Delta W}{kT} \cdot \frac{c}{kT} = \frac{1}{(\Delta F^E)^2} - \frac{1}{(\Delta F_H^E)^2}
\]

and may hence be used to evaluate the constant \( c \). The value of \( c \) is dependent on the size and shape of the nucleus, and the nature of the interface between the matrix and the nucleus (see Section 7.3.3).

It may be assumed that nucleation is heterogeneous; thus the nucleus morphology is related to the nature of the nucleation site. In the absence of information concerning nucleation of Fe-Co alloys, the data will be analysed in terms of heterogeneous nucleation at grain boundaries - a potent and commonly-encountered nucleation site.

Considering the case of a hemispherical nucleus on a grain boundary, equation (43) gives the appropriate activation energy for nucleation, when multiplied by the contact angle function \( f(\theta) \), as noted in Section 7.3.3. From equations (38) and (43) the value of the constant \( c \) in equation (44)
may be evaluated for this nucleation mode:

\[ C = \frac{\pi \sigma^3 f(\theta)}{3} \quad \text{Equation (49)} \]

The slopes of the straight lines in Figures 35 and 36 are then given from equations (44) and (49):

\[ \text{slope} = \frac{\pi \sigma^3 f(\theta)}{3 kT} \]

These slopes may be used to evaluate an interfacial energy factor \( \sigma^3 f(\theta) \). The relevant data are given in Table XX.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Transformation</th>
<th>Slope ( \times 10^{-2} ) cal²/mole²</th>
<th>Energy Factor ( \sigma^3 f(\theta) ) erg³/cm⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>29 At. % Co</td>
<td>( \gamma \rightarrow \alpha )</td>
<td>4.2</td>
<td>2,459</td>
</tr>
<tr>
<td>29 At. % Co</td>
<td>( \alpha \rightarrow \gamma )</td>
<td>2.7</td>
<td>1,609</td>
</tr>
<tr>
<td>38 At. % Co</td>
<td>( \gamma \rightarrow \alpha )</td>
<td>3.1</td>
<td>1,837</td>
</tr>
<tr>
<td>49 At. % Co</td>
<td>( \gamma \rightarrow \alpha )</td>
<td>2.0</td>
<td>1,188</td>
</tr>
</tbody>
</table>

Table XX  Interfacial Energy Factor \( \sigma^3 f(\theta) \) derived from Nucleation-control Model

The interfacial energy \( \sigma \) may now be determined as a function of the contact angle \( \theta \) given that \( f(\theta) = (2 - 3 \cos \theta + \cos^3 \theta) / 4 \). Selected values are given in Table XXI.
The activation energy of heterogeneous nucleation $\Delta W$ is given by

$$\Delta W = \frac{\pi \sigma^3 f(\theta)}{3\Delta F}$$

Equation (43)

and may now be calculated from the data of Tables XX & XVIII. Values of $\Delta W$ for each transformation considered are given in Table XXII.

### Table XXII  Calculated Activation Energy of Nucleation ($\Delta W$)

<table>
<thead>
<tr>
<th>Transformation and Alloy Composition</th>
<th>Activation Energy for Nucleation ($\Delta W$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma \rightarrow \alpha$ 29 At.% Co</td>
<td>8.41 K cal/mole</td>
</tr>
<tr>
<td>$\alpha \rightarrow \gamma$ 29 At.% Co</td>
<td>6.69 K cal/mole</td>
</tr>
<tr>
<td>$\gamma \rightarrow \alpha$ 38 At.% Co</td>
<td>6.20 K cal/mole</td>
</tr>
<tr>
<td>$\gamma \rightarrow \alpha$ 49 At.% Co</td>
<td>3.56 K cal/mole</td>
</tr>
</tbody>
</table>
The radius of the critically sized nucleus is given by

\[ r_c = \frac{-\sigma}{\Delta F^E} \]  \hspace{1cm} \text{Equation (50)}

Recalling the initial assumptions that

(a) the nucleus/matrix interfacial energy is approximately equal to that of the nucleating site and

(b) nucleation takes place at grain boundaries,

equation (50) may be used to evaluate \( r_c \). Putting \( \sigma = \sigma \) (grain boundary) \( \approx 200 \text{ erg/cm}^2 \), equation (50) yields for the \( \gamma \rightarrow \alpha \) transformation in the 29 At.% Co alloy:

\[ r_c = 303 \times 10^{-8} \text{ cm} \]

Similar results are obtained for the other alloys. This approach to the nucleation problem is clearly lacking in the following respects:

(a) Assuming that the nucleus/matrix interfacial energy is equal to that of grain boundaries (\( \sigma > 200 \text{ erg/cm}^2 \)), very small contact angles (\( \theta < 10^\circ \)) are necessary to explain the observed kinetics. This is unlikely and is inconsistent with the hemispherical nucleus model.

(b) The above assumption also indicates that critical nuclei are greater than \( 600 \times 10^{-8} \text{ cm} \) in diameter. In fact, critical nuclei in solids rarely exceed \( 100 \times 10^{-8} \text{ cm} \) in diameter.

The above criticisms of the nucleation model initially employed appear to infer that the geometric relationships employed are incorrect, or that the nuclei are formed at boundaries or surfaces having a much lower interfacial energy than the normal high angle boundaries. Nucleation
at stacking fault could be cited as an example; this is however unlikely in the present case, owing to the high stacking fault energy of the experimental alloys.

A more generalised nucleation model developed recently by Russell (1969) deals with the coherent nucleation of a single-sided allotriomorph at a grain boundary (see sketch below)

In this case, the curved interface is coherent, whilst the flat interface at the grain boundary is, of course incoherent. The activation energy for nucleation of such an allotriomorph is given by:

\[ \Delta W = \frac{16\pi\sigma^3 f(\theta)}{3\Delta F^2} \]

Equation (51)

where \( \sigma \) refers to the curved, coherent interface.

Using equation (51) and the experimental data, values of \( \sigma \) may be obtained for nucleation using Russell's model. These are given in Table XXIII, at various values of contact angle \( \theta \), together with the corresponding values for the critical embryo radius, which in this case is given by:

\[ r_c = \frac{-2\sigma}{\Delta F} \]

Equation (52)
<table>
<thead>
<tr>
<th>Contact</th>
<th>29 At.% Co $\gamma \rightarrow \alpha$</th>
<th>29 At.% Co $\alpha \rightarrow \gamma$</th>
<th>38 At.% Co $\gamma \rightarrow \alpha$</th>
<th>49 At.% Co $\gamma \rightarrow \alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Angle $\theta^\circ$</td>
<td>$\sigma$</td>
<td>$r_c$</td>
<td>$\sigma$</td>
<td>$r_c$</td>
</tr>
<tr>
<td>10°</td>
<td>85 erg/cm²</td>
<td>$2.6 \times 10^{-6}$ cm</td>
<td>74 erg/cm²</td>
<td>$2.5 \times 10^{-6}$ cm</td>
</tr>
<tr>
<td>20°</td>
<td>40 ' '</td>
<td>$1.2 \times 10^{-6}$ cm</td>
<td>34 ' '</td>
<td>$1.1 \times 10^{-6}$ cm</td>
</tr>
<tr>
<td>30°</td>
<td>25 ' '</td>
<td>$7.6 \times 10^{-7}$ cm</td>
<td>20 ' '</td>
<td>$6.7 \times 10^{-7}$ cm</td>
</tr>
</tbody>
</table>

Table XXIII  Critical Embryo Parameters Derived from Russell's Nucleation Model
From these data, a self-consistent set of embryo parameters may be selected for nucleation using Russell's model. Consider, for example, the fcc → bcc transformation in the 29 At.% Co alloy. In this case, sensible nucleation conditions are obtained for an allotriomorph of critical radius $76 \times 10^{-8}$ cm, having a nucleus/matrix contact angle of $30^\circ$. Such a nucleus would have an interfacial energy (coherent) of $25 \text{ erg/cm}^2$, and an activation energy for nucleation of $8.4 \text{ K cal/mole}$.

In the absence of specific data concerning the morphology and distribution of nuclei in the experimental alloys, the above quantitative conclusions remain uncorroborated. It appears likely however, that the nuclei are partially coherent, as indicated by the low interfacial energies which have been computed. Russell's model of coherent nucleation at grain boundaries provides a sensible fit with the experimental kinetic data, and is preferred to the incoherent nucleation model initially employed.

The inference that nuclei retain coherency even at quite large radii may have some implications with respect to transformation modes in the experimental alloys. In particular, the propensity towards massive transformation in these alloys could be controlled by the interfacial characteristics of nuclei of the product phase. An indication of this has been provided by the failure of attempts to distinguish isothermally-formed equilibrium alphaphase from massive decomposition products formed during quenching.
CHAPTER 8  CONCLUSIONS

1. Magnetic fields have been found to markedly increase the rate of isothermal martensite formation in a Fe - 26\% Ni - 2\% Mn alloy. The observed magnitude of the magnetic effect has been shown to be in good general agreement with that predicted from martensite nucleation theory.

2. The best correlation between calculated data, and the observed variation of transformation kinetics with temperature and magnetic field strength, has been obtained from analyses based on a distribution of activation energies among nucleation sites. The correlation is not as good when, alternatively, all operative sites are assumed to have the same activation energy.

3. Using Kaufman and Cohen's nucleation model the experimental data yielded the following parameters for the most-potent martensite embryos in the experimental alloy:
   
   embryo radius \( r = 2.25 \times 10^{-5} \) cm
   
   interfacial energy \( \sigma = 108 \) erg/cm\(^2\)

4. The distributive analysis of the experimental data (Method II) has indicated that the concentration of most potent sites in the experimental alloy lies between \(10^7\) and \(10^8\) per cm\(^3\), depending on the transformation temperature. Previous estimates of this parameter range from \(10^4 - 10^7\) per cm\(^3\).

5. The present experimental data provide better correlation with the Kaufman-Cohen model, than with the more recent Raghavan-Cohen nucleation model.
6. Magnetic fields have been shown to raise the transformation temperature (ΔT Effect), and influence the kinetics of the bcc → fcc and fcc → bcc transformations in Fe-Co alloys containing 30–50 wt.% Co. The observed magnitude of the ΔT Effect is in good general agreement with that predicted by the phase stability rules of Kaufman, and any small differences between computed and observed ΔT values have been accounted for in terms of slight differences in the thermodynamics of transformation, between the different alloys.

7. Magnetic fields have been shown to accelerate the fcc → bcc transformation, and to retard the bcc → fcc transformation in the experimental alloys. This is consistent with the general model for the origin of the magnetic effect. The experimental kinetic data have been used to evaluate transformation parameters, using models for nucleation-controlled and growth-controlled transformation kinetics. The data were found to be most consistent with nucleation-controlled kinetics.

8. The kinetic data could be correlated satisfactorily with Russell's nucleation model for coherent allotriomorphs. In the case of the 30 wt.% Co alloy, sensible nucleation conditions were satisfied by a coherent allotriomorph of radius $76 \times 10^{-8}$, with a nucleus/matrix contact angle of 30°. The interfacial energy of this nucleus is 25 erg/cm², and its activation energy for nucleation is 8.4 K cal/mole.

9. The implied coherent nature of large nuclei in Fe-Co transformations may be connected with the tendency of the experimental
alloys to transform by the massive mechanism, which is known to depend largely on transformation interface characteristics.
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APPENDIX I - Phase Stability Data

This appendix contains the thermochemical and phase-stability data required for computer calculation of the fcc/bcc constitution in the Fe - Co system.

Also included is a brief description of the technique used for computer determination of common tangents to free-energy/composition curves, and the complete program listings.

1. Phase Stability Data for Fe - Co Alloys

\[
F_Y^{\text{(fcc)}} = (1 - x) F_{Fe}^Y + x F_{Co}^Y + RT \left[ x \ln x + (1 - x) \ln (1 - x) \right] \\
+ x (1 - x) \left[ (1 - x) (-555 + 0.4983 \times 10^{-3} T^2 - 0.10264 \times 10^{-6} T^3 \right. \\
+ x (-235 + 0.13703 \times 10^{-2} T^2 - 0.28228 \times 10^{-6} T^3) \right]
\]

Equation (A1)

\[
F_\alpha^{\text{(bcc)}} = (1 - x) F_{Fe}^\alpha + x F_{Co}^\alpha + RT \left[ x \ln x + (1 - x) \ln (1 - x) \right] \\
+ x (1 - x) \left[ (1 - x) (-8830 + 0.119585 \times 10^{-1} T^2 - 0.518664 \times 10^5 T^3) \right. \\
+ x (-9555 + 0.104454 \times 10^{-2} T^2 - 0.395858 \times 10^{-5} T^3) \right]
\]

Equation (A2)

For \( 0 < T < 1183 \)

\[
F_{Fe}^\alpha = 0
\]

For \( 0 < T < 1100 \)

\[
F_{Fe}^Y = 1460 - 0.8274 T - 0.17858 \times 10^{-2} T^2 + 0.1225 \times 10^{-5} T^3
\]

Equation (A3)

For \( 1100 < T < 1183 \)

\[
F_{Fe}^Y = -(-1251.2 + 2.2468 T - 0.12655 \times 10^{-2} T^2 + 0.2204 \times 10^{-6} T^3)
\]

Equation (A4)

For \( 750 < T < 1768 \)

\[
F_{Co}^Y = 0
\]

For \( 0 < T < 1800 \)

\[
F_{Co}^\alpha = 1662 - 0.1509 \times 10^{-2} T^2 + 0.6701 \times 10^{-6} T^3
\]

Equation (A5)
For $1183 < T < 1673$
\[ F^\gamma_{Fe} = 0 \]

For $1100 < T < 1800$
\[ F^\alpha_{Fe} = -1251.2 + 2.24681 - 0.12655 \times 10^{-2} T^2 + 0.2204 \times 10^{-6} T^3 \]

Equation (A6)

fcc phase denoted by $\gamma$

bcc phase denoted by $\alpha$

$x$ denotes atomic fraction Co

$T$ is temperature ($^0K$)

$F$ is free-energy (cal/mole)

2. Computation of Boundaries of Phase Mixtures from Free Energy Curves for Binary Alloys

Let $F^\alpha (x, T)$ and $F^\beta (x, T)$ be the free energies at $T^0K$ for the $\alpha$ and $\beta$ phases with $x$, the concentration of the alloying element expressed as the atomic fraction as the variable. Let $xy$ be the common tangent, touching these curves at $x^\alpha$ and $x^\beta$ (Figure 28). Between concentrations $x^\alpha$ and $x^\beta$ a mixture of $\alpha$ and $\beta$ phases is the most stable state of the alloy. Our intention is now to determine $x^\alpha$ and $x^\beta$, given $F^\alpha (x, T)$ and $F^\beta (x, T)$ as functions of $x$ for various fixed values of $T$.

The computational procedure is to devise an iterative process, and to arrive at points $x^\alpha$ and $x^\beta$ starting from the point of intersection of the free energy curves. The conditions for tangency are:

\[ m'^\alpha_x = m'^\beta_x = m^s \]

Equation (A7)
when \( m_a \) = the slope of \( F^a(x,T) \) at \( x = x^a \)
\( m_\beta \) = the slope of \( F^\beta(x,T) \) at \( x = x^\beta \)
\( m_s \) = the slope of the straight line joining points \( x^a \) and \( x^\beta \) on the two curves (i.e. the common tangent).

First of all we estimate the value of \( x_o \), the value of \( x \) at the point \( I \), by calculating the differences \( \Delta F = F^\beta(x,T) - F^a(x,T) \); \( I \) is then the point when \( \Delta F \) goes to zero. To determine \( x_o \) we calculate \( \Delta F \) as a function of \( x \) at intervals of \( \Delta x \) (\( \approx 0.01 \) say); A value of \( x_o^1 \) corresponding to \( \Delta F = 0 \) can then be obtained by linear interpolation. As we shall see later, a value of \( x_o \) more accurate than \( x_o^1 \) (\( = x_o \)) is not necessary for the computation of \( x^a \) and \( x^\beta \).

Let \( m_1^a \) and \( m_1^\beta \) be the slopes of curves \( F^a(x,T) \) and \( F^\beta(x,T) \) at \( x = x_o^1 \). The first trial values for \( x^a \) and \( x^\beta \): \( x_1^a \) and \( x_1^\beta \) are both set equal to \( x_o^1 \), while \( m_1^s \) (the first trial value for the slope of the common tangent) is taken as:

\[
m_1^s = \frac{(m_1^a + m_1^\beta)}{2} \quad \text{Equation (A8)}
\]

where \( m_1^a = \left[ \frac{\partial F^a(x,T)}{\partial x} \right]_{x = x_1^a} \quad \text{Equation (A9)} \]

and \( m_1^\beta = \left[ \frac{\partial F^\beta(x,T)}{\partial x} \right]_{x = x_1^\beta} \quad \text{Equation (A10)} \)
These equations thus provide the first approximations for the true slope $m^s$, $m^\alpha$, $m^\beta$ respectively.

The next trial value for $x^\alpha$ namely $x_2^\alpha$ is set so that the slope $m_2^\alpha$ at $x_2^\alpha$ is equal to the first trial slope of the tangent ($m_1^s$).

To obtain the slope $m_2^\alpha$ at $x_2^\alpha$ we use the Taylor expansion:

$$m_2^\alpha = m_1^\alpha + \left(\frac{\partial m^\alpha}{\partial x}\right)_{x_1^\alpha} (x_2^\alpha - x_1^\alpha) + \ldots \quad \text{Equation (A11)}$$

When $m^\alpha =$ slope of the curve $F^\alpha (x, T)$. The higher order terms can be neglected at this stage without any sacrifice of eventual accuracy, because this equation is only used to obtain a running estimate for $x_2^\alpha$. (There may however be some effect on the convergence properties of iterative process.)

Equating $m_2^\alpha$ to $m_1^s$, we obtain from equation (A11):

$$m_1^s = m_1^\alpha + \left(\frac{\partial m^\alpha}{\partial x}\right)_{x_1^\alpha} (x_2^\alpha - x_1^\alpha) \quad \text{Equation (A12)}$$

i.e. $x_2^\alpha = \frac{(m_1^s - m_1^\alpha)}{\left(\frac{\partial m^\alpha}{\partial x}\right)_{x_1^\alpha}} x_1^\alpha + x_1^\alpha \quad \text{Equation (A13)}$

The movement of $x$ along the curve $F^\beta (x, T)$ from $x_1^\beta$, to $x_2^\beta$, is similarly given by:

$$x_2^\beta = \frac{(m_1^s - m_1^\beta)}{\left(\frac{\partial m^\beta}{\partial x}\right)_{x_1^\beta}} x_1^\beta + x_1^\beta \quad \text{Equation (A14)}$$

The iterative procedure is now constructed by setting:
i) \( x_1^\alpha \) to be equal to \( x_2^\alpha \)

ii) \( x_1^\beta \) to be equal to \( x_2^\beta \),

while the new value of \( m_1^s \) is defined by:

\[
m_1^s = \frac{[F^\alpha (x_2^\alpha, T) - F^\beta (x_2^\beta, T)]}{(x_2^\alpha - x_2^\beta)} \quad \text{.... Equation (A15)}
\]

Remembering that \( m_1^s \) is the slope of the straight line joining the points \( x_2^\alpha \) and \( x_2^\beta \), the calculations are now repeated, and the programme is terminated when the terminal values of \( m_2^\alpha \), \( m_2^\beta \) and \( m_1^s \) satisfy the initial requirement:

\[
m_2^\alpha = m_2^\beta = m^s
\]
BEGIN
COMMENT THIS PROGRAM FINDS THE COMMON TANGENT TO THE FREE ENERGY
VERSUS CONCENTRATION CURVES OF BINARY ALLOY SYSTEMS;
COMMENT THIS ALLOWS CALCULATION OF THE PHASE DIAGRAM
FOR THE SYSTEM UNDER CONSIDERATION;
REAL TMIN, DT, Tmax, XMIN, DX, XMAX, T1, T2, T3, FA1T, FA2T,
XA, XB, HA, HB, NS, FA, FB, EPS, DDFA, DDFB,
X12, FMIN, FAT, FBT, ASLOPE, A2SLOPE, B1SLOPE, B2SLOPE, DIF1,
FAT2T, X2, FA2T, DIF2T, FX, DIFFX, DDIFFX;
INTEGER I, J, N1, N2, N, M1, M2, M, K1, K2, K, NP, N,
H1, HAF, HBF,
VECTOR BOOL INT L;
REAL ARRAY AK[1,16], G1, G2[1,2],
CONVALQ[0;1,3],
P, SI, P1, S1[0;3],
AT[1,30], FATX, FBTX[1,30,1,100],
XX, B, TC, H, F[1,50],
X1, N1; AX[1,100];
PROCEDURE E0ZABA(N, X, F, H, K, N, SI, P, L);
VALUE N, K;
INTEGER N, K, N1;
ARRAY X, F, H, SI, P;
BOOLEAN L;
ALGOL
COMMENT: CALCULATIONS MAY BE DONE FOR A MAXIMUM OF 30 TEMPERATURES

COMMENT: CALCULATIONS MAY BE DONE FOR A MAXIMUM OF 100 CONCENTRATIONS;
BEGIN

REAL·PROCEDURE·INPTT(X1,X2,Y1,Y2,Y);
VALUE·X1,X2,Y1,Y2,Y;
REAL·X1,X2,Y1,Y2,Y;
INPTT:=X1+((X2-X1)*(Y-Y1)/(Y2-Y1));
COMMENT: PROCEDURE INPTT GIVES THE INTERPOLATED VALUE OF X;
COPYTEXT ('(1/1)');
NEWLINE (2);
EPS:=READ;
COMMENT: EPS IS THE ACCURACY NEEDED IN FRACTION OF SLOPE;
L:'FALSE'; L:=10; K1:=3;
THIN:=READ; DT:=READ; MAX:=READ;
X[1]:=READ; DX:=READ; XMAX:=READ;
FOR J:=1,2 'DO'
FOR I:=1,2 'DO'
AK[I,J]:=READ;
COMMENT: CONSTANTS AK[I,J] ARE PARAMETERS FOR THE EXCESS FREE ENERGY
OF MIXING; I = 1 FOR THE FIRST PHASE & I = 2 FOR THE SECOND;
I:=0;
FOR I:=1 'STEP' 1 'UNTIL' MAX 'DO'
BEGIN
XX[I]:=READ;
X[I]:=READ;
X[I]:=READ;
W[I]:=READ;
END;
FOR T:=THIN 'STEP' DT 'UNTIL' MAX 'DO'
BEGIN
I:=I+1; AT[I]:=T;
RT:=1.987*T; T2:=T*T; T3:=T2*T;
FOR K:=1,2 'DO'
BEGIN
G1[K]:=AK[K,1]+AK[K,2]*T2+AK[K,3]*T3;
G2[K]:=AK[K,4]+AK[K,5]*T2+AK[K,6]*T3;
END;
COMMENT: EXCESS FREE ENERGY FOR THE KTH PHASE (K=1,2) G1[K] & G2[K];
FAKT:=U;
IF T>1183 'THEN'
FB1T:=1251.2-2.2468*T+0.0012655*T2-0.2204*T3; 'ELSE'
FB1T:=0;
IF T<1000 'THEN'
FB2T:=1662-0.15098*T-2*T2-0.67018*T3;
FAT1 = 1440 - 0.8274 * T - 0.0017858 * T^2 + 0.12258 * 5 * T^3;

\[ \text{IF } T > 1183 \text{ THEN} \]
FA1T := 0;

\[ \text{IF } T \geq 1183 \text{ AND } T \leq 1100 \text{ THEN} \]
FA1T := 1251 - 2 * 2.2468 * T + 0.0012655 * T^2 - 0.22048 - 6 * T^3;

\[ \text{COMMENT! } \text{THE VALUES OF } \text{FA1T, FA2T, FB1T, FB2T AS SPECIFIED ABOVE ARE} \]
\[ \text{VALID IN THE TEMPERATURE RANGE 730 TO 1673 (DEG. ABS.)}; \]

\[ \text{COMMENT! } 1 \text{ IMPLIES IRON, 2 IMPLIES COBALT, A MEAND FCC PHASE} \]
& B MEANS BCC PHASE;

\[ \text{COMMENT! } \text{FA1T: A IMPLIES A\text{-}TH PHASE, 1 IMPLIES FIRST ELEMENT.} \]
\[ \text{SIMILARLY } \text{FA2T, FB1T, & FB2T} \]
\[ \text{THESE ARE THE FREE ENERGY VALUES FOR THE PURE METALS} \]
\[ \text{AT TEMP. } = T ; \]

J := 0;

BOOL INT := 'TRUE';
FA1T := -FA1T + FA2T; FB1T := -FB1T + FB2T;
NA := NU := NI := 0;

\[ \text{FOR } X := XMIN \text{ STEP } DX \text{ UNTIL } XMAX \text{ DO} \]
BEGIN
J := J + 1;
AX(J) := X; X2I := 1 - X; X3I := X * X2I;
FM := RT * (X * LN(X) + X2 * LN(X2));
X2 := 1 - 2 * X; FPA := RT * LN(X/X2);
FA1TX[I,J] := X2 * FA1T + X * FA2T + FM * X3 * (X2 * G1[I] + X * G2[I]);
FB1TX[I,J] := X2 * FB1T + X * FB2T + FM * X3 * (X2 * G1[I] + X * G2[I]);

\[ \text{FOR } IK := 1 \text{ STEP } IX \text{ UNTIL } IN \text{ DO} \]
FK[I,K] := 4 * S0 * RI[I,K] * (1 - T/TCL[I,K])^6;

\[ \text{COMMENT! } \text{EOZABA IS A CURVEFITTING PROCEDURE FOR MAGNETISATION} \]
\[ \text{VERSUS COMPOSITION}; \]
EOZABA(M, XX, E, W, K1, N, SI, P, L); 

NP := N; FX := P[NP] * X * NP;
LORDER; NP := NP + 1;

\[ \text{IF } \text{NP } \text{GE} 0 \text{ THEN} \]
BEGIN
FX := FX + P[NP] * X * NP; 'GOTO' LORDER;
END;

\[ \text{IF } \text{FX } \text{LE} 0 \text{ THEN} \]
LORDMAG; FB1TX[I,J] := FB1TX[I,J] + FX;
DF2 := FA1TX[I,J] - FB1TX[I,J];
AZ SLOPE := FAT + FPA * X3 * (G1[I] + G2[I]) * X2 * (G1[I] * X2 + G2[I] * X); B2 SLOPE := FBT + FPA * X3 * (G1[I] + G2[I]) * X2 * (G1[I] * X2 + G2[I] * X);
NP := N;
D1FFX := NP * P[NP] * X * (NP + 1);
LOK: NP := NP + 1;

\[ \text{IF } \text{NP } \text{GT} 0 \text{ THEN} \]
DIFFX := DIFFX + NP * P[NP] * X + NP; GOTO LOK;
END;

COMMENT E0ZABA IS A CURVE FITTING PROCEDURE FOR
CURIE TEMPERATURE VERSUS COMPOSITION;
E0ZABA(H,XX,TC,H,K1,PI1,K1,P1,L);
N2 := N1; TCX := P1[N2] * X + N2;
LCURIE := N2 := N2;
IF N2 = 0 THEN BEGIN
TCX := TCX * P1[N2] * X + N2;
GOTO LCURIE; END;
IF T = 0 THEN
B2SLOPE := B2SLOPE + DIFFX;
IF J = 1 THEN
BEGIN
IF SIGN(DIF2) = SIGN(DIF1) THEN
BEGIN
N1 := N1 + 1;
CON[N1, 1] := 0;
CON[N1, 2] := 0;
VAL[N1, 3] := INTP(X = 1, Y = 1, X = 1, DIF1, DIF2, 0);
IF NA = 0 AND NB = 0 THEN
CON[N1, 1] := 0;
IF BOOINT THEN
BEGIN
CON[N1, 1] := 0;
VAL[N1, 2] := VAL[N1, 3];
END;
IF N1 THEN
BOOINT := TRUE;
END;
IF SIGN(A2SLOPE) = SIGN(A1SLOPE) THEN
BEGIN
NA := NA + 1;
CON[N1 + 1, 1] := 1;
VAL[N1 + 1, 1] := INTP(X = 1, Y = 1, X = 1, A1SLOPE, A2SLOPE, 0);
IF BOOINT THEN
BEGIN
CON[N1, 2] := 1;
VAL[N1, 2] := VAL[N1 + 1, 1];
END;
NA := NA + 1;
BOOINT := FALSE;
END;
IF SIGN(B2SLOPE) = SIGN(B1SLOPE) THEN
BEGIN
...
CON[N1+1,1]=2
VAL[N1+1,1]=INTPT(AX[N1+1,1],X1,B1,SLOPE1,B2,SLOPE2,0)
'IF' BOOLINT 'THEN'
'BEGIN'
CON[N1,2]=2;
VAL[N1,2]=VAL[N1+1,1];
'ENDIF'

NEWLINE(1);
DIF 1=DIF2;
A1 SLOPE 1=A2 SLOPE2; B1 SLOPE = B2 SLOPE;
'ENDIF' 'COMMENT: CONC CYCLE FINISHES HERE;
PAPERTHROW;
WRTXT('!'NO.%OF%POINTS%OF%INTERSECTION%=%')!);
PRINT(N1,1,0);
'IF' NIF=0 'THEN' 'BEGIN'; SPACE(4);
'FOR' N1:=1 'STEP' 1 'UNTIL' NIF 'DO' 'BEGIN'
PRINT(VA[N1,3],0,4); WRTXT('!'NO.%OF%MINIMUM%POINTS%')!);
'END';
'END';

NEWLINE(1):
WRTXT('!'NO.%OF%MINIMUM%POINTS%=%')!);
PRINT(N1,1,0);
WRTXT('!'NO.%OF%MINIMUM%POINTS%')%'))
PRINT(N1,1,0);
WRTXT('!'NO.%OF%MINIMUM%POINTS%')%'))

NEWLINE(2):
'IF' NIF = 0 'THEN' 'GOTO' ! NOINT;
'FOR' N1:=1 'STEP' 1 'UNTIL' NIF 'DO'
'BEGIN'
'IF' CON[N1,1]=0 'OR' CON[N1,2]=0 'THEN'
'BEGIN'
XA:=X1=VAL[N1,3];
MAT1+RT*LN(XA/(1+XA))*XA*(1-XA)*(-G1[1]+G2[1])+ (1-2*X*X)+(G1[1]*X-XA)*G2[1]*X)
'END';
'END';
IF T 'GE' TCX 'THEN' DDIFX;=0;
M2=N1; 
LCURVE: 'END';
IF T 'GE' TCX 'THEN' DDIFX;=0;
M2=N2; 
LCURVE: 'END';
IF T 'GE' TCX 'THEN' DDIFX;=0;
M2=DDFB + DDIFX;
IF 'DDFA<0' 'OR' 'DDFB<0' 'THEN'
'BEGIN'
WRITE TEXT('THE CURVE IS CONVEX UPWARDS AT THE POINT ' 
OF INTERSECTION CONSIDERED (SEE LINE BELOW FOR THE ' 
SPECIFICATION OF THE POINT)');
'GOTO' LFINISH;
'END';
X1=XA *(MS-MA)/DDFA1
X2=XB *(MS-MB)/DDFB1
FA1 = (1=XA)*FAXA1*RT*(XA+LN(XA)*G1[1]1+AXA*G2[2]);
X1=XA;
NP=0; 
FX=NP*X+NP;
LORDER: NP=NP-1;
IF NP=0 'THEN'
'BEGIN'
FX=FX+NP*X+NP; 
'GOTO' LORDER;
'END';
FB1=(1-XA)*FB1*XB+FB2*RT*(XB+LN(XB)*G1[1]1+AXB*G2[2]);
FB=FB+FX;
MS=(FR-FA)/(XB-XA);
L ENTER: IF 'ABS((MS-HA)/(HS)<EPS 'AND' ABS((MS-MB)/MS)<EPS 'THEN'
'GOTO' LFINISH;
DDFA=RT/(XA+(1-XA))2+(3=XA)+(1=3=XA)*G2[2];
DDFB=RT/(XB+(1-XB))2+(3=XB)+(1=3=XB)*G2[2];
X1=XB;
NP=N2; 
DDIFX;=(NP-1)*NP*P[NP]*X*(NP-2); 
LOOK:
NP=NP-1;
IF NP=2 'GE' 0 'THEN'
'BEGIN'
DDIFX;=DDIFX;*(N-1)*NP*P[NP]*X*(NP-2);
'GOTO' LOOK;
'END';
X1=XB;
N2=N1; 
TCX=P[N2]*X*N2; 
LCURVE: 'END';
IF T 'GE' TCX 'THEN'
'BEGIN'
DDIFX;=0;
DDFB=DDFB + DDIFX;
IF 'DDFA<0' 'OR' 'DDFB<0' 'THEN'
'BEGIN'
WRITE TEXT('THE CURVE IS CONVEX UPWARDS AT THE POINT ' 
OF INTERSECTION CONSIDERED (SEE LINE BELOW FOR THE ' 
SPECIFICATION OF THE POINT)');
'GOTO' LFINISH;
'END';
X1=XA *(MS-MA)/DDFA1
X2=XB *(MS-MB)/DDFB1
```
LIMIT;
PRINT(XA,0,4); SPACE(2);
PRINT(XB,0,4); SPACE(2);
PRINT(XA,0,4); SPACE(2);
PRINT(FA,0,4); SPACE(2);
PRINT(FB,0,4); SPACE(2);
PRINT(HA,0,4); SPACE(2);
PRINT(HB,0,4); SPACE(2);
PRINT(HL,0,4); SPACE(2);
NEWLINE(1);
'END';
'FOR' XN:=0 'STEP' 1 'UNTIL' XN 'DO' 'BEGIN'
PRINT(p1[XN],0,4); SPACE(2); 'END';
'NEWLINE(1);
'END';
'FOR' XN:=0 'STEP' 1 'UNTIL' XN 'DO' 'BEGIN'
PRINT(p2[XN],0,4); SPACE(2); 'END';
'NEWLINE(1);'
LENGTH 3109
S USED 66
L282 EC
```
APPENDIX II  Experimental Errors and Accuracy of Data

a)  Temperature Measurement in High Temperature Dilatometer

The measured specimen temperature was initially found to deviate considerably from the actual value; this was minimised by contouring the specimen cavity to give the best possible contact with the thermocouple bead. The principal heat loss, however, occurs as a result of conduction down the thermocouple leads; here a compromise was necessary since fine-gauge wire with low thermal loss does not possess the required mechanical rigidity.

In order to calibrate the specimen thermocouple, the measured temperatures for the $\gamma \rightarrow \alpha$ transformation were compared with those obtained from the same samples by differential thermal analysis (D.T.A.). The cooling rate for D.T.A. was $2^\circ$C/min.

Using a comparable cooling rate in the dilatometer, reasonable agreement between transformation temperatures as measured by both techniques was achieved, as shown in the table below. This could possibly have been further improved by using a longer furnace with a more extensive "hot zone".

<table>
<thead>
<tr>
<th>Alloy wt % Co</th>
<th>$T^{\gamma \rightarrow \alpha}$ (calc.) $^\circ$C</th>
<th>$T^{\gamma \rightarrow \alpha}$ (DTA) $^\circ$C</th>
<th>$T^{\gamma \rightarrow \alpha}$ (expt) $^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>972 ($\pm 0.5$)</td>
<td>962 ($\pm 2$) *</td>
<td>950 ($\pm 3$) *</td>
</tr>
<tr>
<td>40</td>
<td>987 &quot;</td>
<td>973 &quot;</td>
<td>963 ($\pm 4$)</td>
</tr>
<tr>
<td>50</td>
<td>990 &quot;</td>
<td>979 &quot;</td>
<td>965 ($\pm 3$)</td>
</tr>
</tbody>
</table>

* 95% confidence limits, after three observations.

Since temperature differences rather than absolute values are of major interest in our calculations, any discrepancy between measured and actual temperatures is of minor importance. Where necessary, in calculations, the transformation temperatures as measured by D.T.A. were taken as the reference values.
b) Possible deviations in Magnetic Field due to Heating Coil

In calculating the magnetic effect on Fe-Co transformations the magnetic field induced by the furnace windings was ignored. Such a coil may be regarded as a long solenoid, the magnetic field strength of which is given by:

\[ H = 4 \pi n i \]  
...... Equation (A16)

where \( n \) = number of turns per cm
\( i \) = current in coil

For the experimental heating coil, at maximum power, the field strength \( H_{\text{max}} \) is approximately 300 Oe, which has a negligible effect on calculated values of magnetic free-energy \( \Delta I_s H \), and derived parameters.

c) Accuracy of Experimental and Derived Data

Standard statistical techniques have been used to estimate errors in the experimental and calculated data. In general, scatter in experimental results has given larger probable errors than intrinsic limits of accuracy of measurements. Unless otherwise stated, graphical solutions were obtained by the method of least mean squares. The accuracy of tabulated parameters corresponds to 95% confidence (i.e. the error range quoted is \( 1.96 \times \sigma \), where \( \sigma \) is the standard deviation of the data.)

Accuracy of Nucleation Data (Table V)

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>( t_o ) sec</th>
<th>( f_o ) pct/sec</th>
<th>( N_o ) cm(^{-3}) sec(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-60</td>
<td>± 6.3</td>
<td>± 1.3 \times 10^{-3}</td>
<td>± 32</td>
</tr>
<tr>
<td>-65</td>
<td>± 4.4</td>
<td>± 6.5 \times 10^{-3}</td>
<td>± 312</td>
</tr>
<tr>
<td>-70</td>
<td>± 3.2</td>
<td>± 6.0 \times 10^{-3}</td>
<td>± 310</td>
</tr>
<tr>
<td>-80</td>
<td>± 3.2</td>
<td>± 1.9 \times 10^{-2}</td>
<td>± 2340</td>
</tr>
</tbody>
</table>
These errors are small compared to the uncertainties in the non-experimental parameters e.g. $v, n_i$. It has been estimated (Pati and Cohen, 1969) that $v$ is probably only correct to within a factor of 2. This implies that $n_i$ values are subject to similar error and leads to an estimated uncertainty in $\Delta W$ of $\pm 300$ cal/mole. These errors are much greater than those listed above.

**Accuracy of Data derived from Magnetic Experiments**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$f_H/f$</th>
<th>$\Delta W - \Delta W_H$ cal/mole</th>
<th>$\sigma$ erg/cm$^2$</th>
<th>$r$ cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>-60</td>
<td>$\pm 0.63$</td>
<td>$\pm 8.2$</td>
<td>$\pm 38$</td>
<td>$\pm 12 \times 10^{-7}$</td>
</tr>
<tr>
<td>-65</td>
<td>$\pm 0.20$</td>
<td>$\pm 26$</td>
<td>$\pm 13$</td>
<td>$\pm 6 \times 10^{-7}$</td>
</tr>
<tr>
<td>-70</td>
<td>$\pm 0.18$</td>
<td>$\pm 30$</td>
<td>$\pm 13$</td>
<td>$\pm 6.5 \times 10^{-7}$</td>
</tr>
<tr>
<td>-80</td>
<td>$\pm 0.13$</td>
<td>$\pm 26$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The experimental measurement of $\Delta T$ values involves an uncertainty of $\pm 0.5^\circ C$. The scatter of data however, leads to 95% certainty limits of $\pm 1.5^\circ C$ which is fairly large when compared with the small absolute $\Delta T$ values. The discrepancy between computed and observed $\Delta T$ values for the $\gamma \rightarrow \alpha$ transformation still appears significant especially in the case of the 30% Co alloy.

In the case of kinetics measurements, experimental data ($f_H/f$) are not subject to error introduced by conversion to absolute transformation rates. However, rather more scatter was obtained in the experimental data than for the martensitic transformation and this is the major source of error in derived data.

The estimated 95% limits for data derived from kinetics measurements on Fe-Co transformations (Table XX) are given in the table below, together with embryo parameters from Russell's nucleation model (Table XXIII).
<table>
<thead>
<tr>
<th>Composition wt % Co</th>
<th>Transformation</th>
<th>Slope x $10^{-2}$ cal$^2$/mole$^2$</th>
<th>$\sigma$ (θ=30°) erg/cm$^2$</th>
<th>$r$ (θ=30°) cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>$\gamma \rightarrow \alpha$</td>
<td>± 0.1</td>
<td>+ 1.2</td>
<td>+ 1.2 x $10^{-8}$</td>
</tr>
<tr>
<td>30</td>
<td>$\alpha \rightarrow \gamma$</td>
<td>± 0.15</td>
<td>+ 1.5</td>
<td>+ 1.4 x $10^{-8}$</td>
</tr>
<tr>
<td>40</td>
<td>$\gamma \rightarrow \alpha$</td>
<td>± 0.1</td>
<td>+ 0.8</td>
<td>+ 0.8 x $10^{-8}$</td>
</tr>
<tr>
<td>50</td>
<td>$\gamma \rightarrow \alpha$</td>
<td>± 0.08</td>
<td>+ 1.0</td>
<td>+ 1.1 x $10^{-8}$</td>
</tr>
</tbody>
</table>

The uncertainties listed above are much smaller than those pertaining to the nucleation models employed. In view of the simplified formulation of nucleus morphology and nucleation characteristics, the accuracy of derived embryo parameters is probably of little significance. It would be interesting to extend the work to include phase changes where the nucleation process was more exactly defined. This would allow more confidence in derived values for nucleation parameters.