THE EFFECT OF MAGNETIC FIELDS ON
TRANSFORMATIONS IN STEELS

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by

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Studies have been made on the effect of a magnetic field of 16 K. Gauss on the martensitic transformation of two steels (Fe 1C 1.5Cr and Fe 0.3C 2.8 Ni 0.6Cr and 0.6Mo). The transformation was followed metallographically using the Greninger and Troiano technique. A magnetic field of 16 K. Gauss raises the $M_s$ by $\sim 5^\circ$C and shifts the entire transformation curve to higher temperatures. A thermodynamic model has been proposed to explain the $M_s$ shift, and it is shown how useful thermodynamic functions, such as the entropy of transformation $\Delta S^{\gamma \rightarrow \alpha}$, can be derived experimentally from such shifts.

An attempt has been made to evaluate the latent heat of martensite formation for the Fe 1C 1.5Cr alloy from the recalescence effects associated with the periodic application of a field below the $M_s$. The heat of transformation value combined with the entropy of transformation yields a value of 260 $\pm$ 100 cals/gm mole for the driving force $\Delta F^{\gamma \rightarrow \alpha}$ at the $M_s$, in good agreement with available theoretical calculations.

Hardness measurements on quenched steels (0.4C 1.4C and 10 1.5Cr) show that quenching in a magnetic field gives an increase in hardness of 20-30 V.P.N., which is largely associated with the extra martensite formed when the transformation takes place in a field. The effect of quenching in a magnetic field on the subsequent kinetics of the decomposition of martensite during the first stage of tempering has been investigated for two steels (1.4C and Fe 10 1.5Cr), using dilatometry and differential Hall Probe technique. Quenching in a magnetic field delays the decomposition of martensite during subsequent tempering, and this has been associated with a decreased driving force for the nucleation of $\xi$-carbide.
ACKNOWLEDGEMENTS

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The role of magnetic forces upon the relative stabilities of the various allotropes of iron has been increasingly recognised in recent years and it is generally accepted that b.c.c. $\alpha$-iron is stable at room temperature only because of a significant ferromagnetic contribution to its free energy. Recent studies on the effect of pressure on phase transformations in pure iron have confirmed that there is a relatively small difference in energy between alternative modifications of crystal structure, each of which having its characteristic magnetic energy component. There has however been much less study of the effect of superimposing an external magnetic field during phase transformations on the relative stabilities of these phases. Since the free energy contribution of the stability of a ferromagnetic phase due to the superimposition of an external field is only of the order of several calories per mol the effect of a magnetic field on phase transformations has generally been considered as potentially negligible. Nonetheless evidence has accumulated in recent years that the superimposition of a magnetic field has considerable influence on transformations in steels during quenching and tempering, although there has been relatively little effort made to find a consistent pattern in the results. At the same time there has emerged in recent years a growing body of evidence in various fields of phase transformations which shows that, under certain conditions, a small amount of energy supplied to the system from an external agency during the phase transformation, may tilt the balance and significantly alter the pattern of the transformation. The aims of the present investigation may, then, be stated as:

1) Investigating whether a magnetic field has a consistent effect on transformations in steels during quenching and tempering.

2) To rationalise the existing evidence in the field and present a comprehensive theoretical framework for the results.

3) To study any associated effects on mechanical properties.
The martensitic transformation was chosen as the starting point because the martensitic transformation, being diffusionless in nature, is easily amenable to simple thermodynamic formalism. Also, in view of the complex nature of tempering reactions in steels, it was felt that a thorough analysis of the role played by a magnetic field on the martensite transformation would act as a starting point to a subsequent analysis of changes in hardness and on tempering produced by the application of a magnetic field during quenching.
SECTION 2  LITERATURE REVIEW

2.1  Effects of magnetic fields on Steel transformations

2.1.1  Introduction

A number of papers have been published in recent years on the effect of magnetic fields on the transformation in steels during quenching and tempering and on the resulting structure and properties; a detailed review does not however appear to have been published so far. As most of the information that is available is rather scattered, an attempt will be made to present the results as clearly and comprehensively as possible, giving wherever possible full details about experimental techniques, and an assessment of the current position in this field.

2.1.2  The effect of Pulsating magnetic fields

(1) Effect on the Ms temperature

The possibility of a strong magnetic field influencing the martensite transformation in steels was first investigated by V.D. Sadovskii et al (1) who observed that a pulsating magnetic field of 350 K. Gauss applied at liquid nitrogen temperatures induced martensite transformation in a fine grained 0.5C 23Ni 1.5Cr steel, which was otherwise in a fully austenitic condition. Pulsating fields were used because intense fields of that magnitude could only be generated in pulses of short duration. Since the length of the coil used for magnetizing the specimens was short compared to the dimensions of the specimens (10 x 10 x 60 mm) the effective field at the ends of the specimens was much weaker compared to that at the centre. This resulted in the formation of a martensitic structure at the centre of the specimen only while the austenitic structure was retained at the ends.

(2) The effect of Field Strength and number of pulses

Fokina and Zavadaski (2) extended this work (1) using an alloy of similar composition (0.5C 22Ni 2Cr), and studied the effect of variables like the strength of the field and the number of pulses on the amount of martensite formed. The transformation was followed by a magnetometric
FIGURE 1  EFFECT OF PULSATING MAGNETIC FIELDS ON MARTENSITIC TRANSFORMATIONS OF 0.5C 22Ni 2Cr STEEL. (2)
FIGURE 2 EFFECT OF A PULSATING MAGNETIC FIELD ON $M_s$ TEMPERATURE OF 0.5C 22Ni 2Cr STEEL. (3)

![Graph showing the effect of a pulsating magnetic field on $M_s$ temperature.]

FIGURE 3 EFFECT OF PULSATING MAGNETIC FIELDS ON MARTENSITIC TRANSFORMATION IN 0.5C 22Ni 2Cr STEEL. (3)

![Graph showing the effect of pulsating magnetic fields on martensitic transformation.]

1. without a field
2. 120 K.G.
3. 170 K.G.
4. 300 K.G.
5. 350 K.G.
method using specimens 25 mm long and 3 mm diameter. Field strengths up to 170 K.Gauss were used at the liquid nitrogen temperatures. It was found that the field has to exceed a minimum value before a martensitic transformation could be induced (Fig. 1). This critical field strength ($H_{crlt}$) which has to be exceeded before the transformation could be induced is analogous with the degree of undercooling required (below $T_0$) when the martensitic transformation is thermally induced. (This is discussed in detail in Section 5.2.1). It can be seen from Figure 1 that once the critical field strength is exceeded, the amount of martensite formed subsequently increases sharply and rises to about 30% in a field strength of 170 K. Gauss. It was also observed that most of the martensite is formed during the first cycle and subsequent pulses induced very little additional transformation (Fig. 1).

(3) Effects below the $M_s$

The effects of strong pulsating magnetic fields at temperatures below $M_s$ for the same steel (0.5C 22Ni 2Cr) was investigated by Fokina Ye.A. et al. (3) also using a magnetometric method. An initial fine grained structure was obtained by a combined thermal and mechanical treatment after which the specimens were austenitized and then subjected to fields of 120, 170, 300 and 350 K. Gauss at various temperatures in the range -40°C to -196°C. The effect of an applied field was again to raise the $M_s$ to higher temperatures (Fig. 2 and Table 1) the average shift being $1/3^\circ$ per K. Gauss.

Table 1E. Effect of magnetic fields on $M_s$ temperature for 0.5C 22Ni 2Cr steel (3).

<table>
<thead>
<tr>
<th>Field Strength in K. Gauss</th>
<th>Shift in $M_s$°C</th>
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<tr>
<td>120</td>
<td>15</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>
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</table>
Table 2 shows the shift in the $M_s$ produced in four different alloys due to a magnetic field of 350 K. Gauss (The shifts in $M_s$ produced by constant magnetic fields are also included in the table and these will be discussed later in Section 2.1.3). The effect of varying the field strength below the $M_s$ resulted in an increase in the amount of martensite formed as shown in Fig. 3.

(4) **Effect on "de-stabilization" of austenite**

Fokina et al (4) studied the effect of pulsating magnetic fields on the "de-stabilization of austenite" in a 0.5C 22Ni 2Cr steel using a magnetometric method. The austenite was previously stabilized either mechanically by plastic deformation or thermally by ageing at temperatures above the $M_s$. The critical field strength necessary to initiate martensite transformation increases with increasing amounts of plastic deformation as shown in Table 3.

Table 3. Variation of critical field strength with Percentage of deformation (of austenite) in 0.5C 22Ni 2Cr steel (4).

<table>
<thead>
<tr>
<th>Percentage Deformation</th>
<th>Critical field strength K. Gauss</th>
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<tbody>
<tr>
<td>20</td>
<td>105</td>
</tr>
<tr>
<td>35</td>
<td>115</td>
</tr>
<tr>
<td>50</td>
<td>130</td>
</tr>
<tr>
<td>70</td>
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The fact that the field has to exceed a critical limit before further transformation could be induced is similar to the observation in conventional stabilization experiments where once austenite is stabilized, a certain additional undercooling has to occur before transformation is resumed. The amount of additional martensite formed due to an applied field once the transformation is initiated, increases with the strength of the field (Fig. 4).
FIGURE 4  EFFECT OF PULSATING MAGNETIC FIELDS ON THE MARTENSITIC TRANSFORMATION OF AUSTENITE STABILIZED BY PLASTIC DEFORMATION IN 0.5C 22Ni 2Cr STEEL (4).

1. No field at 20°C
2. No field at -196°C
3. 170 K. Gauss
4. 300 K. Gauss
5. 420 K. Gauss
6. 500 K. Gauss
The effect of a magnetic field on austenite which has been thermally stabilized was investigated using a Fe-Ni-Cr alloy (0.05C 13.7Ni 9Cr) which has an \( M_s \) at \(-30^\circ C\). After soaking at \( 1100^\circ C \) the austenite was stabilized at \( 550^\circ C \) for 2 hours and on subsequent cooling the \( M_s \) dropped down to \(-90^\circ C\). When the alloy was cooled in a field of 350 K. Gauss, after being stabilized under the same conditions the \( M_s \) shifted up to \(-60^\circ C \) i.e. a field of 350 K. Gauss reduced the amount of undercooling necessary to resume the martensite transformation by \( 30^\circ C \).

(5) **Summary of the effects of pulsating magnetic fields**

The effects of a pulsating magnetic fields on martensitic transformations can be summarised as follows:

1. Application of a field rises the \( M_s \) at a rate of \( \approx 1/3^\circ \) per K. Gauss
2. The amount of martensite formed below the \( M_s \) also increases with the strength of the field.
3. "De-stabilization" effects can be associated with the \( M_s \) shifts.

While these various effects seem fairly conclusive, it is not clear why an unnecessarily complicated initial structure was used in the majority of these experiments (1,2,3).

### 2.1.3 The effect of constant magnetic fields

Fokina et al (5) found that similar effects could be obtained by a constant magnetic field (generated by a superconducting solenoid) and a pulsating magnetic field of the same strength. Specimens of 0.5C 23Ni 1Cr steel were austenitized and cooled to liquid helium temperature. The amount of martensite formed was \( \approx 8-9\% \). A constant magnetic field of \( 40 \) K. Gauss was then applied at this temperature. The amount of martensite formed increased to \( \approx 20-21\% \). When the experiment was repeated using a pulsating magnetic field of the same strength the additional amount of
martensite formed due to a field was found to be of the same order i.e., about 12%. This result also implies that the effect of magnetic fields cannot be attributed to the mechanical forces generated by the magnetic pulses.

Similar results with static magnetic fields were obtained at the Lebedev Physics Institute (5); Table 6 shows the effect of field strength on the amount of martensite formed in a 0.5C 23Ni 1Cr steel at liquid helium temperature.

Table 6. Effect of field strength on the amount of martensite formed in a 0.5C 23Ni 1Cr steel (5).

<table>
<thead>
<tr>
<th>Field strength (K. Gauss)</th>
<th>Amount of martensite formed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8 - 9</td>
</tr>
<tr>
<td>19.5</td>
<td>13</td>
</tr>
<tr>
<td>30</td>
<td>17</td>
</tr>
<tr>
<td>43.5</td>
<td>20</td>
</tr>
</tbody>
</table>

M.L. Bernsteyn et al (7) followed the effect of a constant magnetic field on the martensite transformation of nickel steel covering a composition range C 0.03-1.1% and Ni 5-16%, using a dilatometer method, and observed that the amount of martensite formed was greater when the transformation took place in a magnetic field. Fig. 5 shows the martensitic transformation curves with and without a field of 4.2 K. Gauss for a 0.6C 12Ni steel. The difference in dilation between the transformation curves in a field and without a field was as much as 15-20%. Bernsteyn et al did not observe any detectable change in the Ms, but this is not surprising in view of the small fields used. As will be shown later (Section 5.2) the expected shift in Ms for 4.2 K. Gauss can be calculated from the equation \( \Delta T = T_0 \cdot \Delta J H \), which yields a value of \( \Delta T \) of about 1.3°C. Bernsteyn et al also studied
<table>
<thead>
<tr>
<th>References</th>
<th>Shift in Ms without an Field (°C)</th>
<th>Field Applied</th>
<th>Alloy Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(9) 5</td>
<td>-3 - 5</td>
<td>24</td>
<td>Fe - 0.5G 1651</td>
</tr>
<tr>
<td>(10) 5.3 - 5</td>
<td>5</td>
<td>19</td>
<td>Fe - 0.66 8.5 %</td>
</tr>
<tr>
<td>(11) 6</td>
<td>10 - 1</td>
<td>18.6</td>
<td>Fe - 0.5G 1941</td>
</tr>
<tr>
<td>(12) 60</td>
<td>0.4 - 40</td>
<td>350</td>
<td>Fe - 0.5G 245</td>
</tr>
<tr>
<td>(3) 85</td>
<td>55 - 10</td>
<td>350</td>
<td>Fe - 0.5G 245</td>
</tr>
<tr>
<td>(3) 80</td>
<td>40 - 0.4</td>
<td>350</td>
<td>Fe - 0.5G 245</td>
</tr>
<tr>
<td>(13) 70</td>
<td>65 - 0.7</td>
<td>350</td>
<td>Fe - 0.5G 245</td>
</tr>
</tbody>
</table>

*In steels, (Shift in Ms produced due to an applied Field)*

Table 2: Effect of Magnetic Fields on Martensitic Transformation
<table>
<thead>
<tr>
<th>Reference</th>
<th>Results</th>
<th>Field Strength</th>
<th>Method of Investigation</th>
<th>Alloy Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6)</td>
<td>reverse transformation retarded</td>
<td>22</td>
<td>Magneite</td>
<td>Fe 37%</td>
</tr>
<tr>
<td>(6)</td>
<td>reverse transformation retarded</td>
<td>22</td>
<td>Magneite</td>
<td>Fe 28%</td>
</tr>
<tr>
<td>(6)</td>
<td>reverse transformation retarded</td>
<td>22</td>
<td>Magneite</td>
<td>Fe 26.3%</td>
</tr>
<tr>
<td>(5)</td>
<td>Amount of martensite increased by 12%</td>
<td>0.4</td>
<td>-</td>
<td>Fe 0.50 &amp; Zn 1.5%</td>
</tr>
<tr>
<td>(5)</td>
<td>Amount of martensite increased by 8%</td>
<td>0.72</td>
<td>-</td>
<td>Fe 0.50 &amp; Zn 2%</td>
</tr>
<tr>
<td>(5)</td>
<td>Amount of martensite decreased by 8%</td>
<td>0.16</td>
<td>-</td>
<td>Fe 0.60 &amp; 16%</td>
</tr>
<tr>
<td>(4)</td>
<td>Retained austenite decreased by 7%</td>
<td>4.5</td>
<td>Diffusometry</td>
<td>Fe 0.50 &amp; 16%</td>
</tr>
<tr>
<td>(4)</td>
<td>Retained austenite decreased by 7%</td>
<td>4.5</td>
<td>Diffusometry</td>
<td>Fe 0.60 &amp; 16%</td>
</tr>
<tr>
<td>(4)</td>
<td>(observed through length change)</td>
<td>4.5</td>
<td>Diffusometry</td>
<td>Fe 0.60 &amp; 16%</td>
</tr>
<tr>
<td>(4)</td>
<td>Amount of martensite increased by 5%</td>
<td>4</td>
<td>Diffusometry</td>
<td>Fe 0.60 &amp; 16%</td>
</tr>
<tr>
<td>(6)</td>
<td>Rate in Ns by 5°</td>
<td>4.5</td>
<td>Diffusometry</td>
<td>Fe 0.60 &amp; 16%</td>
</tr>
<tr>
<td>(5)</td>
<td>Rate in Ns by 3.5°</td>
<td>4</td>
<td>Diffusometry</td>
<td>Fe 0.60 &amp; 16%</td>
</tr>
<tr>
<td>(8)</td>
<td>Rate in Ns by 6°</td>
<td>4</td>
<td>Diffusometry</td>
<td>Fe 0.50 &amp; 19%</td>
</tr>
</tbody>
</table>
FIGURE 5 MARTENSITE TRANSFORMATION CURVES FOR Fe 0.6C 1.2Ni ALLOY WITH A FIELD AND WITHOUT A FIELD.

Cooling Time, min
FIGURE 6  EFFECT OF A MAGNETIC FIELD ON THE AMOUNT OF RETAINED AUSTENITE PRESENT IN 5%Ni OF VARYING CARBON CONTENT. ( alloy Fe-Si-Ni-C)

Austenitized 1200°C above AC3 (Bernsteyn)

1. With a field of 16 K.G.
2. Without a Field
FIGURE 7 EFFECT OF INTERMITTENT APPLYING A FIELD IN THE TRANSFORMATION RANGE AS REVEALED THROUGH LENGTH CHANGES. (Estrin)

Alloy Fe 0.5C 19 Ni
Strength of field applied 18.6 K.G.
the effect of quenching in a magnetic field of 16 K. Gauss on the amount of retained austenite in a Fe,5 Ni alloy of varying carbon contents and the results are shown in Fig. 6. All the alloys were quenched from a relatively high austenitizing temperature ($A_s + 120^\circ$C).

Quenching in a magnetic field reduced the amount of retained austenite from 37% to 27%.

2.1.4 The Effect of the intermittent application of a magnetic field

Estrin (8) followed the effect of a magnetic field on the martensite transformation of 0.5C 19Ni steel ($M_S \approx 10^\circ$C) by a dilatometric method and observed a shift in $M_S$ by 6°C due to an applied field of 18.6 K. Gauss. Malinen and Sadovskiy (9) have found a rise in the $M_S$ of 5°C in a 0.5C 16Ni 2Cr steel due to a field of 24 K. Gauss. They also observed that application of a field in the transformation range produced an additional amount of martensite, the effect being most pronounced near the $M_S$ temperature. This effect of the periodic application of a magnetic field in the transformation range was studied in detail by Estrin (8) who followed the transformation curve of a 0.5C 19Ni steel, by a dilatometric method. When a field is applied (Fig. 7) there is a sudden increase in dilation due to an additional amount of martensite formed. It can be seen that the effect of a field is more pronounced in the initial stages of the transformation (i.e. just below the $M_S$) than in the later stages. Estrin offered a schematic explanation of the effect of an intermittent (or local) application of a magnetic field in the transformation range which is discussed in more detail in Section 4.4.1.

2.1.5 Effects on the reverse transformation ($\alpha' \rightarrow \gamma$)

Malinen and Sadovskiy (9) studied the effect of a magnetic field (22 K. Gauss) on the reverse transformation ($\alpha' \rightarrow \gamma$) in the Fe-Ni alloys (Ni 26.5 - 31%, C - .04 - .06) using a dilatometric method, and found that a magnetic field reduces the extent of $\alpha' \rightarrow \gamma$ transformation for all the three alloys that were investigated. Fig. 8 shows the reverse transformation curves in a field (22 K. Gauss) and without a field for a Fe 28Ni alloy.
2.1.6 Determination of the latent heat of martensite transformation

L.V. Voranchikin and I.G. Fakidov (10) determined the latent heat of martensitic transformation in two steels (Fe 0.4C 2Cr 20Ni and Fe 0.6C 4Cr 8Ni 3Si) by using a calorimetric method.

The temperature peaks obtained when the field was raised above a critical field $H_c$ (Section 2.1.2; below the Ms was correlated with the extra-martensite measured by a magnetic method.

The alloys that were investigated showed burst martensite formation which fortunately provided synchronisation for these otherwise separate measurements. Since a pulsating magnetic field was used, a correction had to be made for the effects of eddy currents on the temperature rise. The latent heat of transformation was determined using the formula

$$ L = \frac{C \Delta t}{%M} \times 100 $$

where

$L$ is the Latent heat of transformation

$C$ the specific heat in Cal/gm/deg for the alloy at the appropriate temperature

$\Delta t$ the rise is due to an additional amount of martensite $%M$, formed. The results are summarised in Table 23 (Section 5.5.5).

Estrin (8) also calculated the latent heat of martensitic transformation $L$ from the observed shift $%T$, in the $Ms$, due to a field $H$ using the equation

$$ L = T_o \Delta J / \Delta T $$

where $\Delta J$ is the difference between the saturation magnetization of the two phases and $T_o$ the equilibrium temperature. For the Fe 0.5C 19Ni alloy which he used, Estrin obtained a shift, $%T = 6^\circ$ in a field of 18.6 K. Gauss (H). Using values of $\Delta J = 280$ Gauss/gm and $T_o \approx Ms + 200 = 460^\circ K$, $L$ was found to be $\approx 7$ cal/gm or 400 calories/gm mole. An analysis of this method will be made in Section 5.5.5.
FIGURE 8  EFFECT OF A MAGNETIC FIELD ON THE EXTENT OF THE \( \alpha \rightarrow \gamma \) TRANSFORMATION IN THE Fe-28Ni ALLOY.

Fig. 10. Schematic analysis of the effect of a field on isothermal martensitic transformation (solid curves indicate the course of the transformation)
FIGURE 9 EFFECT OF PERIODICALLY APPLYING A FIELD ON THE KINETICS OF ISOTHERMAL TYPES OF MARTENSITIC TRANSFORMATION, AS REVEALED THROUGH LENGTH CHANGES. (Estrin)
FIGURE 11 EFFECT OF A PULSATING MAGNETIC FIELDS ON MARTENSITE TRANSFORMATION Fe 0.03C 24Ni 3.6Mn ALLOY AT -196°C. (Fukina et al)

FIGURE 12 THE COMBINED EFFECT OF ELASTIC STRESS AND MAGNETIC FIELD ON MARTENSITIC TRANSFORMATION. (2)
2.1.7 Effect of a magnetic field on isothermal martensitic transformations

All the work discussed so far relates to athermal martensitic reactions; relatively little work has been done on the isothermal type of martensitic transformations. Estrin (8) has studied the effect of periodically applying a field of 18.6 K. Gauss below the Ms on the isothermal martensitic transformation in a Fe - Ni - Mn alloy (0.06C 22.7Ni 3.3Mn) using a dilatometric method. When a field was applied in the transformation range there was no sudden increase in the amount of martensite formed; instead there was an increase in the rate of martensite formation (Fig. 9). On removal of the field no temperature hysteresis occurred but the rate of transformation dropped. Fig. 10 is a schematic illustration showing the effect of periodic application of a field on the transformation rate for such an alloy. Estrin's schematic analysis (Fig. 10) qualitatively explains the effect of a periodic application of a field on isothermal martensitic transformation; a limitation of this analysis is the implication that the transformation rate is always higher in a field than without a field, which may not be true when the proportion of the residual austenite becomes small.

Another alloy which exhibits isothermal transformation characteristics is the Fe 0.03C 23.6Ni 3.6Mn alloy. When cooled from the austenitic state, the transformation starts slowly below room temperature; the transformation rate then increases up to -130°C and then drops. At -196°C hardly any transformation occurs, and only 4-5% martensite is formed in 24 hours. Ye. A. Fokina et al (4) investigated the effect of strong pulsating magnetic fields on the martensitic transformation of this alloy at -196°C. A field of 160 K. Gauss was required to induce transformation at this temperature (Fig. 11).

2.1.8 The origin of magnetic field effects

It can be seen from the results described so far that the effect of a magnetic field on the martensitic transformation is primarily to raise the Ms temperature; a reduction in the amount of retained austenite
follows from the shift of the transformation curve to higher temperatures. The theories proposed to explain this effect fall into two distinct groups (a) those based on magnetostrictive effects and (b) those based on thermodynamic effects.

(a) **Magnetostrictive theories**

Sad&vskii V.D. et al (1) suggested that magnetostrictive stresses produced through the magnetization of a ferromagnetic phase could be mainly responsible for inducing martensite formation. In order to test this hypothesis Fokina and Zavadosky (2) studied the combined effect of a pulsating magnetic field and elastic stress on martensitic transformation in a Fe 0.5C 22Ni 2Cr alloy. Their results showed (Fig. 12) that application of an elastic stress reduced the critical field strength necessary to initiate the transformation by 30%. Encouraged by this result and Fokina and Zavadski (2) put forward 'magnetostrictive theories' on a purely ad hoc basis without suggesting a detailed mechanism. However calculations of the various magnetic energies by Bernsteyn et al (7) later showed that the contributions of magnetostrictive forces are several orders of magnitude lower than the driving force necessary to start the martensitic transformation (see Table 12, Section 2.9.2).

(b) **Thermodynamic theories**

According to the second group of theories (11, 12) the magnetic field influences the range of stability of phases having different saturation magnetizations. In the presence of a magnetic field a ferromagnetic phase is more stable than a paramagnetic phase, because its free energy is lowered by an amount $\Delta J H$ where $\Delta J$ is the difference in the saturation magnetization of the two phases and $H$ the applied field. Meyer and Tagland (11) derived an expression for the shift in the transformation temperature $\Delta T$ produced by an applied magnetic field $H$ according to which

\[
\Delta T = \frac{T_0 \Delta J H}{q} \quad \text{........................................} \quad 2.2
\]

where $\Delta J$ is the difference in the saturation magnetization of the two
FIGURE 13 EFFECT OF MAGNETIC FIELD ON FRACTURE STRESS AND ITS VARIATION WITH CARBON CONTENT (Bernsteyn)

![Graph showing the effect of magnetic field on fracture stress and its variation with carbon content.]

**Figure 13**

**FIGURE 14 (a) and (b)**

**Figure 14(a)**

STEEL ...... 0.4C 1.4Cr 1Ni
TREATMENT .. Quenched 830°C
Tempered 650°C for 1 hr. 30 mins.
Tempered 520°C for 20 hrs.
M - Quenched in a field
O - Quenched without a field

**Figure 14(b)**

STEEL ...... 0.4C 1Cr
TREATMENT .. Quenched 880°C
Tempered 650°C for 1 hr. 30 mins.
Tempered 520°C for 20 hrs.
M - Quenched in a field
O - Quenched without a field

**Figure 14** EFFECT OF QUenchING IN A MAGNETIC FIELD ON IMPACT STRENGTH OF STEELS (Bernsteyn)
phases, \( T_0 \) the temperature of equilibrium of the two phases and \( q \) the heat of transformations at \( T_0 \).

Krivaglaz and Sadovskii (12) also derived a similar relationship and this equation was used by Estrin (8) and other Russian workers to explain the observed shifts in \( M_s \). Equation 2.2 is similar to the well-known Clasius - Clapeyron equation for the change in temperature of transformation under the influence of pressure

\[
T = \frac{\Delta V T_0 P}{q} \quad \text{.................................................. 2.3}
\]

Further implications of these two equations will be discussed in Section 5.7.4.

2.2 Effects of magnetic fields on the mechanical properties of steels

2.2.1 Introduction

This section deals primarily with the use of a magnetic field to alter the mechanical properties of steels as distinct from the effect on transformation characteristics. Much of the earlier work in this field was concerned with the possible practical advantages that might be derived from heat treatment in a magnetic field especially improvements in strength, ductility and impact properties.

2.2.2 Tensile properties

M.L. Bernsteyn (13) investigated the effect of a magnetic field of strength 2 K. Gauss on the mechanical properties of plain carbon steels of various carbon contents. The direction of the field was maintained parallel to the axis of the specimen. A small increase in tensile strength and yield strength was observed due to heat-treatment in a magnetic field. For instance, the tensile strength of a 0.45C steel was increased from 182 to 192 kg/mm\(^2\) while the yield strength increased from 146 to 150 kg/mm\(^2\). Fig. 13 shows how the percentage increase in fracture stress due to heat-treatment in a magnetic field varies with the carbon content for plain carbon steels.
The changes in mechanical properties on magnetic heat-treatment were attributed by Bernsteyn to the following factors:

(1) Slight fragmentation of subgrains owing to magnetostriction.

(2) Considerable refinement of structure due to an oriented arrangement of martensite crystals with their longer axis along the easy direction of magnetization.

There is no metallographic evidence in the literature published so far to show any orientation of martensite plates occurring as a result of transformation in a field. As regards the refinement of martensite structure only Jahn (14) has produced any supporting microstructures. As regards the effect of magnetostriction it is difficult to conceive how magnetostriction with its small energy contribution (see Section 2.9.2) could cause fragmentation of subgrains.

2.2.3 Impact properties

One of the earliest investigations on the effect of magnetic fields on the structure and properties of steels was carried out by Jahn (14) who observed that a constant magnetic field of 20 K. Gauss applied during normalising of a 0.04C steel, refined the microstructure. It was also observed that there was considerable improvement in the impact strength of steels when they were normalised in an alternating (50 c/s) magnetic field of 8 K. Gauss. The impact strength of a 0.05C steel increased by 25%, while for an alloy steel the reported increase was as high as 87%.

Bernsteyn (13) has studied the effect of quenching in a magnetic field on the temper-embrittlement of two steels having compositions 0.4C 1.4Cr and 0.4Cr 1Ni. The steels were quenched in a magnetic field, tempered at 650°C for 1 hr and 30 minutes and then given a temper-embrittling treatment by tempering at 500°C for 20 hours. The impact test results are shown in Figures 14a and 14b. The results indicate that
<table>
<thead>
<tr>
<th>Reference</th>
<th>Tensile Strength Increased by</th>
<th>16 K.C.</th>
<th>Heat Treatment</th>
<th>Alloy Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(7)</td>
<td>17%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(8)</td>
<td>10%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(9)</td>
<td>65%</td>
<td>8 1/16 D.C.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(10)</td>
<td>7%</td>
<td>5 3/8 D.C.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(11)</td>
<td>5%</td>
<td>8 A.C.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(12)</td>
<td>3%</td>
<td>20 D.C.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7: The Effects of Metallurgical Treats on Mechanical Properties of Steel
quenching the steels in a magnetic field lowers the transition temperature and reduces the susceptibility of the steels to temper-brittleness.

Bernsteyn proposed that the orientation of martensite along the domain structure created by the applied field, evens out the effect of the former austenitic grains, so that the susceptibility to temper-brittleness is reduced. Although this hypothesis needs to be viewed with caution since no orientation of martensite along the domain structure has been observed, the effect is sufficiently startling to call for investigation in greater detail.

2.2.4 Bend strength

The effect of quenching and tempering in a magnetic field on two steels - a low alloy steel (1C 1Mn 1Cr and 1.25W) and a tool steel (18W 4Cr 1V) was studied by Chudnovskaya (15) using a constant magnetic field of 5 K. Gauss and an alternating magnetic field of 1.2 K. Gauss at 50 c/s. Hardening of the alloy steel followed by tempering in a constant magnetic field increased the transverse strength by 65%. A normal hardening treatment followed by tempering in an alternating magnetic field resulted in an increase of bend strength by 10 - 15%. Tempering in a magnetic field (both constant and alternating) resulted in an improvement of bend strength for the tool steel.

2.2.5 The performance of tool steels

The effect of a combined thermal mechanical and magnetic treatment during quenching followed by tempering in a magnetic field on the tensile strength of a 18W 4Cr 1V steel is shown in Table 8 (15). The results of stability tests on the high speed drills and cutters after a thermomagnetic treatment are interesting. The mean torsional moment sustained by 1mm drills after a single tempering treatment at 560°C in a magnetic field (after initial quenching without a field) was 1610 kg/mm, whereas the torsional moment of the same drills after conventional triple tempering at 560°C was 1250 kg/mm (15). Similarly the wear resistance coefficient of tool steels improved by 15% due to tempering in a magnetic field.
FIGURE 15 ISOTHERMAL MARTENSITE TRANSFORMATION OF RETAINED AUSTENITE IN 18W 4Cr 1V STEEL.
Preliminary Treatment: Quenched from 1300°C and tempered at 560°C for 1 hr.

M - With a field of 4 K. Gauss
O - Without a field
<table>
<thead>
<tr>
<th>Tensile Strength</th>
<th>Field strength was applied and measured</th>
<th>Temperature</th>
<th>Quenching</th>
<th>Heat Treatment</th>
<th>% Deformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>228-292</td>
<td>I (A.C.)</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>210-244</td>
<td>I (D.C.)</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>200-210</td>
<td>G (D.C.)</td>
<td>-</td>
<td>0</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>197-208</td>
<td>I (D.C.)</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>169-180</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

*Table 8: Tensile test results on 18-4-1 steel after various thermal mechanical treatments.*
L.A. Chudnovskaya et al. (16) investigated the possibility of replacing the accepted technique of triple tempering of high speed steels (18W - 4Cr - 1V) by a single heat-treatment in a magnetic field. A preliminary investigation was made on the effect of tempering in a magnetic field followed by cooling in a field on the transformation characteristics.

Specimens were quenched from 1300°C, kept for four days at room temperature to stabilize the retained austenite and then tempered at 560°C for 1 hour in a magnetic field. They were then cooled to 400°C in a field and transformed isothermally at this temperature also in a field. Fig. 15 shows the isothermal transformation curves of the retained austenite at 40°C with and without a field. It can be seen from Figure (15) that the presence of a field during heat-treatment resulted in the transformation of more retained austenite. The actual performance of the drills was then tested after three different tempering treatments:

1. tempering at 570°C for $\frac{1}{2}$ hour in a constant magnetic field of 4 K. Gauss followed by cooling in a field.

2. tempering at 570°C for $\frac{1}{2}$ hour in an alternating magnetic field of 600 Gauss and then cooling in the same field.

3. triple tempering for 1 hour at 560°C and then cooling immediately.

The drills were tested according to standard specifications and it was found that the performance of drills heat treated in a constant or alternating magnetic field was superior to those that were triple-tempered in a conventional manner.

2.2.6 Ausforming treatments in magnetic fields

Troiano and his co-workers (17) have reported the absence of any additional effects resulting from ausforming treatments carried out in
intense magnetic fields up to 25 K. Gauss. The effect of a magnetic field was primarily to reduce the yield to ultimate tensile strength ratio as compared to ausformed and conventionally treated specimens.

2.2.7 Summary

From the results described so far, it appears that the effect of a magnetic field on the mechanical properties of quenched steels is significant if not startlingly large - particularly in view of the comparatively low fields that were used in most of the investigations. A quantitative assessment is however difficult in view of the large scatter band obtained in the evaluation of tensile test data on quenched steels. Some of the magnetic heat-treatments were combined with prior mechanical treatment (13, 15) which makes any assessment of the effect of a magnetic field alone very difficult.

2.3 The effect of a magnetic field on the kinetics of tempering in steels

2.3.1 Tempering Reactions in steels

There are three distinct stages in the tempering of quenched plain carbon steels containing martensite and retained austenite (18). The first stage involves the decomposition of primary martensite with the precipitation of epsilon carbide ($\epsilon$-carbide) and predominates in the temperature range below $170^\circ$C. This is followed by the transformation of retained austenite into an aggregate of ferrite and carbide. This reaction constitutes the second stage of tempering and takes place in the temperature range $170 - 300^\circ$C. The third stage of tempering results in the formation of ferrite and cementite and takes place at temperatures over $300^\circ$C. It should however be stressed that these stages are not strictly confined to definite ranges and a certain amount of overlap is likely to occur in practice (82).

2.3.2 Effect of a magnetic field on the kinetics of the first stage of tempering

Bernsteyn (7) has studied the effect of quenching in a magnetic field on the subsequent tempering kinetics of the decomposition of
FIGURE 16(a & b) EFFECT OF A MAGNETIC HEAT TREATMENT ON KINETICS OF FIRST STAGE TEMPERING IN A 1.1C 8Ni STEEL. (Bernstejn)

Tempering Temperature 170°C

FIGURE 16(c) EFFECT OF TEMPERING IN A MAGNETIC FIELD ON THE DECOMPOSITION OF RETAINED AUSTENITE AT 300°C IN A 1.1C 8Ni STEEL. (Bernstejn)
martensite during the first stage of tempering. Specimens of 1.1C 8Ni steel were quenched in a constant magnetic field of 16 K. Gauss and then tempered at 175°C without a field. The tempering kinetics was followed by a dilatometric method. It was found that in steels quenched in a magnetic field, but subsequently tempered without a field, there was a delay in the decomposition of martensite as revealed by uniaxial length changes (Fig. 16a, b). Tempering in a magnetic field after quenching under normal conditions (without a field) also delayed the kinetics of the decomposition of martensite.

2.3.3 Second stage tempering

The effect of a magnetic field on the decomposition of retained austenite during the second stage of tempering was also studied using a dilatometric method (7). Specimens of 1.1C 8Ni steels were quenched without a field and then tempered at 300°C in a magnetic field of 4.2 K. Gauss. It was found that tempering in a magnetic field accelerated the decomposition of retained austenite (Fig. 16c). The contribution made to the length changes by the overlap of the decomposition of primary martensite was however not taken into account in analysing the results of Fig. 16c, but it is interesting to note that the overall time for the decomposition of retained austenite was reduced by 35% due to tempering in a magnetic field.

Chudnovskaya et al (16) observed that tempering high speed cutting steel specimens in an alternating magnetic field of 1200 Gauss (50 c.p.s) accelerated the decomposition of retained austenite in the temperature range 550 - 660°C.

No work has been reported so far on the effect of a magnetic field on the formation of ferrite and cementite during the third stage of tempering. However since the temperatures concerned for the third stage of tempering come very close to \( T_c/2 \), the effect of a magnetic field at these temperatures should be reduced in any case (for details refer Section 5.2.2 and 5.3.1).
2.4 Effects of a magnetic field on various other metallurgical processes

2.4.1 Introduction

The effect of magnetic field on the structure and properties of steels during quenching and tempering was reviewed in the last section. In addition to being used as a heat treatment variable, magnetic fields have also been applied in other metallurgical processes such as recrystallization, electrodeposition, solidification and diffusion. The role played by a magnetic field in these processes will now be briefly reviewed in order to place the effects on the heat treatment of steel in perspective.

2.4.2 Recrystallisation and growth processes

It was shown by Smoluchowski and Turner (19, 20) that a magnetic field applied during recrystallisation influence the resulting preferred orientation of grains in a ferromagnetic alloy (Fe - 35% Co), when the recrystallisation temperature is several hundred degrees below the Curie temperature of the alloy. Sayer and Smoluchowski (21) later investigated the recrystallisation texture of the same alloy using a continuous pole figure technique, and observed that the effect of a magnetic field was to increase the amount of recrystallised texture components having \( <100> \) parallel to the field and decrease those having \( <110> \) components parallel to field. An explanation was offered in terms of the high magnetocrystalline anisotropy energy associated with the alloy.

Roberts (23) observed spire or column growths in Mn-Bi alloys induced by a field of 1.5 K. Gauss. Recrystallisation experiments by Boothby et al (24) on Mn-Bi in a field of 8 K. Gauss at temperatures between 270 - 350°C revealed the development of a fibre texture in which the crystals are oriented with the easy direction of magnetization parallel to the field. Grain boundary motion induced by a magnetic field was investigated by Mullens (25) in polycrystalline bismuth, using a strong magnetic field of 77 K. Gauss. Bismuth is strongly diamagnetic and is magnetically anisotropic with large differences in principal susceptibilities.
When annealed in a magnetic field, a strong preferred orientation is developed with the c-axis of the crystal parallel to the field.

It is thus clear that under favourable conditions (i.e. when conditions such as high magnetic anisotropy energy exists in the alloy) the application of a magnetic field can influence the recrystallisation texture and grain growth. It is nevertheless surprising that magneto-crystalline anisotropy energy is large enough to produce such marked effect when it may be only of the order of $10^5 - 10^6$ ergs/c.c. (Section 2.9.2.) Although the activation energy for these processes is very large and several orders higher than the anisotropy energy, the driving forces, being sufficiently small can be influenced by the contribution made by anisotropy energy.

Bacigulpi (30) observed aligned polycrystalline growth due to the application of a magnetic field (900-4000 Gauss) during the growth of iron whiskers at 680°C. He proposed that the aligned growth might be due to the interaction energy resulting from unbalanced spins in iron atoms with the applied field. The precise nature of this interaction energy was however not explained.

### 2.4.3 Magnetic annealing

Magnetic annealing may be defined as the heat-treatment of a material in a magnetic field for the purpose of improving the magnetic properties. The materials which show the largest magnetic annealing effects are the alloys of Fe - Ni - Co and Al - commercially known as Alnico (a permanent magnet alloy) and Perminvor (a soft magnetic alloy). It is not intended to give a detailed review of the structural and property changes induced by magnetic annealing, as excellent reviews are available elsewhere (26,27); the effect however, can be quite striking (Fig.17c).

### 2.4.4 The effect of a magnetic field on the electrodeposition of cobalt

Goddard J. and Wright W.J. (28) investigated the electrodeposition of cobalt from a cobalt sulphate bath on to $\{001\}$ and $\{110\}$ copper
FIGURE 17a MAXIMUM SEGREGATION (CHILL-FACE) RESULTS FOR THE NORMALLY AND FIELD-SOLIDIFIED INGOTS OF THE Al-Cu SYSTEM. (Youdelis)

FIGURE 17b SEGREGATION (CHILL-FACE) VERSUS THE FIELD STRENGTH FOR THE Al-10% Cu ALLOY. (Youdelis)
FIGURE 17c EFFECT OF MAGNETIC ANNEALING ON 65Ni35Fe ALLOY
single crystal surfaces. Electron diffraction patterns from the deposits indicate that for solutions with a pH less than 2.4, face centred cubic $\beta$-Co was obtained growing parallel to the face centred cubic copper substrate. For solutions with a pH greater than 2.9 epitaxial growth of close packed hexagonal $\alpha$-Co was observed. In the pH range 2.4 - 2.9 the deposits consisted of varying proportion of hexagonal and cubic phases. It was found that a strong magnetic field of 17 K. Gauss markedly reduced this range for mixed phase deposition to an almost critical value namely 2.65 $\pm$ .05. With the pH set at this critical value the $\beta$-Co $\rightarrow$ $\alpha$-Co transition could be induced at a definite deposit thickness by varying the applied field. The critical deposit thickness $t_c$ is also a function of the field and is reduced by an increase in field strength. The authors suggested that the variation of the critical transition thickness with the applied field strength might be related to the propagation of defects or imperfections in the deposit, which effectively reduce the 'binding energy' at the surface and allow the growth of the lower energy phase, $\alpha$-Co.

2.4.5 The effect of magnetic fields on cast structures during solidification

W.Y. Youdelis et al (29) investigated the effect of magnetic fields of strengths 13 K. Gauss and 34 K. Gauss on the degree of segregation resulting during solidification of aluminium - copper alloy castings. It was found that the segregation of the chill faces of a unidirectionally solidified ingot increased when a field was applied during solidification. Figures 17a and b show the effect of a magnetic field on the segregation during solidification of an Al-Cu alloy. In a field of 34 K. Gauss the degree of segregation increased approximately by 57%. The segregation effect was found to be independent of the field direction.

The authors propose that since diffusion is slowed down in a magnetic field (Section 2.4.7) there is a non equilibrium concentration change at the solid liquid interface and this has the effect of raising
FIGURE 18  SELF DIFFUSION IN IRON AND ITS RELATION TO THE CURIE TEMPERATURE OF $\alpha$-IRON.
(Borg and Birchenall)
the liquidus curve for the alloy system and thus increasing microsegregation. The increased microsegregation is a manifestation of the fact that the reaction path during solidification is determined by the principle of minimum entropy production, and the decrease in entropy of production occurs largely through diffusional and convective processes of solidification.

2.4.6 Activation Energy of Diffusion in ferromagnetic metals and alloys

Investigations on self- and inter-diffusion in the ferromagnetic metals and alloys have shown that diffusion coefficients below the Curie temperature are smaller than those above. Borg and Burchenall (31) measured the self-diffusion coefficients of \( \alpha \)-iron in the temperature range 980 and 1167°K and found a decrease in the diffusivity of iron by a factor of two at the Curie temperature of iron. With decreasing temperature the diffusivity of iron decreased more rapidly than predicted by the Arrhenius equation in the region of the Curie temperature as shown in Fig. 18. The authors attribute this anomalous decrease in diffusivity to a decrease in the equilibrium concentration of vacant lattice sites as well as to a decrease in mobility. According to this view the vacancy concentration should decrease as the degree of electron spin order increases. Stanley and Wert (32) using an internal friction as well as radioactive tracer technique also found an abnormal decrease in diffusivity of an iron-18% vanadium alloy in the ferromagnetic state. Their results showed that diffusion in the ferromagnetic state was about 100 times slower than would be expected by the extrapolation of data from the paramagnetic region. The authors attribute this retardation of diffusion partly to the increase in the activation energy for diffusion in the ferromagnetic state and partly to the decrease in the frequency factor \( D_0 \) in the diffusion equation \( D = D_0 e^{-Q/RT} \). Hirano et al (34) also showed from their self-diffusion measurements of Co and Ni in cobalt-nickel solid solutions that the activation energy for diffusion is higher in the ferromagnetic state that in the paramagnetic state. For the self-diffusion of iron (33) and for diffusion
FIGURE 19a PROBABILITY PLOTS FOR COUPLES Al-Cu (Youdelis et al)

FIGURE 19b MATANO AREA VERSUS (TIME)\(^{1/2}\) COUPLES Al-Cu
of nickel in iron (34) this difference is of the order of 0.12 eV. According to Girifalco (35) this increase in activation energy is due to an increase in the energy of formation of a vacancy in a magnetically ordered alloy where an additional contribution to the binding energy arises due to the interaction of the spin with the Weiss molecular field.

2.4.7 **Effect of a magnetic field on diffusion in paramagnetic alloys**

While considerable evidence has accumulated in the literature to prove that alignment of electron spins below the Curie temperature influence the diffusion constants in ferromagnetic metals and alloys there is hardly any evidence regarding the effect of an applied magnetic field on diffusion coefficients in ordinary paramagnetic metals and alloys. Only one reference has been published so far on the effect of a magnetic field on the diffusion of aluminium 3 pct. copper alloy. W.Y. Youdelis et al (35) investigated the diffusion in Al - 3 pct. Cu alloys in magnetic fields up to 30 K. Gauss using a microhardness technique. A statistically significant decrease in diffusivity was obtained when the couples were annealed in a field, the direction of the field being perpendicular to the direction of diffusion (Fig. 19). The authors proposed a theory based on plasma - magneto - hydrodynamics. On a simplified model of this theory an alloy can be viewed basically as a two fluid plasma of electrons and ions. A concentration gradient in the alloy results in a free - electron gradient if the electron densities differ for the diffusing components. The free electron gradient is analogous to an electron plasma under a density or pressure gradient. An interaction of the magnetic field with the electron gradient will cause the plasma to drift. For diffusion perpendicular to the magnetic field, the 'Lorentz force' on the electron results in a drift of the diffusion current in the 'Hall direction' and thus reduces the electron flux along the concentration gradient. The ion current along the gradient is correspondingly reduced as the system must fulfill the requirement of electrical neutrality. If D is the normal diffusion constant in the absence of a field, the diffusion constant transverse to a magnetic field $D'$ is given by

$$D' = D / \left(1 + \frac{W_{cc}^2}{V_e^2}\right)$$

where $W_{cc}$ and $V_e$ are the cyclotron frequency and collision frequency respectively.
FIGURE 20 INTERSTITIAL SITES IN THE b.c.c. STRUCTURE AND POSSIBLE JUMPS OF AN ATOM ON A Z-SITE TO NEIGHBOURING SITES.

FIGURE 21 CRITICAL TEMPERATURE FOR ZENER ORDERING VS CARBON CONTENT. $M_s$ AND $M_f$ LINES ARE ALSO SHOWN (Imai)
2.4.8 Directional ordering of interstitials in iron and iron alloys

There are three different kinds of sites for interstitials on the lines joining the two iron atoms, in a b.c.c. lattice, as shown in Fig. 20. These sites can be designated \( x(100) \), \( y(010) \) and \( z(001) \) sites corresponding to the direction of the line defined by the two nearest iron atoms. In the absence of any external constraint, the interstitial atoms will be randomly distributed over the three kinds of available sites. When a magnetic field is applied along one particular direction the occupational probabilities of these sites will be altered. In other words altering the direction of magnetization in the domain alters the local equilibrium configuration of the interstitials. Snoek (37) argued that the interstitial atoms should enter \( z \) sites preferentially if a magnetic field was applied in the \( z \)-direction, because of the positive magnetostriction of \( \gamma \)-iron which should enlarge these sites. Neel (38) pointed out that the interaction energy computed from this model was rather small and hence could not be the only factor determining the position of the interstitials sites. Neel's model for the interaction between the magnetization vector and the interstitials is as follows. The energy of occupied sites \( x, y, \) and \( z \) depends in a simple way on the angle which the magnetization vector \( J \) makes with the \( x, y \) and \( z \) axis. This energy can be expressed as \( \alpha^2 W, \beta^2 W \) and \( \gamma^2 W \) respectively where \( \alpha, \beta, \gamma \) are the direction cosines of the magnetization vector \( J \) with respect to the cube axis, and \( W \) is defined as the interaction energy constant. The physical significance of \( W \) will be discussed later. When a magnetic field is applied, the magnetization vector \( J \) is suddenly changed into some other direction given \( \alpha_1, \beta_1, \gamma_1 \) and this leads to a redistribution of interstitial atoms. For this process the energy required is:

\[
E = W_0 \left( \alpha^2 + \beta^2 + \gamma^2 \right)
\]

where \( W_0 = \frac{C W^2}{3kT} \)

C is the number of interstitial atoms per unit volume
K the Boltzmann constant and T the absolute temperature.
In the expression for $W_0$, the factor $W/kT$ determines the deviation from an isotropic distribution of interstitials and $W$ represents the maximum contribution of every interstitial atom to the stabilization energy. The value of $W$ for C atoms in iron as found by Rathenau is $0.79 \times 10^{-15}$ erg/atom (39).

G. de Vries et al (40) have investigated the after effects of directional ordering of interstitials in a magnetic field by an internal friction technique and observed that with magnetization along the $z$-direction interstitial atoms moved from $z$ sites to the neighbouring $x$ and $y$ sites.

2.4.9 The effect of magnetic fields on the relative proportion of cubic to tetragonal martensites

Since no preferred orientation of martensite crystals has so far been observed the interaction energy coupling the interstitial atoms with the magnetization vector does not seem to influence the choice of the principal martensite axis during nucleation. However there remains the possibility that the interaction energy may affect the relative amounts of cubic to tetragonal martensites formed by the critical ordering temperature $T_c$ (see next paragraph and Fig. 21) and this might be expected to affect the accommodation stresses and hence the habit plane. No detailed crystallographic analysis is available to check this point.

Zener (42) has shown that in iron carbon alloys there exists a critical temperature above which a random distribution of carbon atoms is in equilibrium and below which a preferred distribution is in equilibrium. The critical temperature $T_c$ is related to the carbon content by the equation $T_c \approx 28,000 x_c$ where $x_c$ is the atomic fraction of carbon. The decrease in free energy on ordering of carbon atoms is given by:

$$\Delta F^* = 2.39 \times 10^{-8} x_s V_o \Delta f^* \text{ calories per gram} \quad 2.5$$

where $x_s$ is the sum of the mole fractions of all substitutional elements, $V_o$ is the volume corresponding to a mole of lattice sites and $\Delta f^*$ is
is given by the expression

\[
\Delta f^* = -\frac{1}{2} \left( \frac{2/3}{n_1 z^2 E} + \frac{1}{3} \frac{kT}{n_1} \left[ (2(1-z) \ln (1-z) + (1 + 2z) \ln (1 + 2z) \right] \right)
\]

where 

\[
n_1 = 6.03 \times 10^{23} \frac{x_c}{x_s} V_0 \text{ carbon atoms per c.c.}
\]

\[
\lambda = 1.68 \times 10^{-25} V_0 \text{ strain per carbon atom}
\]

\[
z = \text{Zener's order parameter}
\]

\[
E = 1.30 \times 10^{12} \text{ dynes/cm}^2
\]

Fig. 21 shows how the critical temperature for ordering of carbon atoms \( T_c \), the \( M_s \) temperature, as well as how the probable \( M_f \) temperature vary with the carbon content (44). In alloys with the carbon concentration lower than point A both \( M_s \) and \( M_f \) will lie above \( T_c \) and hence austenite will be completely transformed into supersaturated ferrite (or b.c.c. martensite). At concentrations between A and B, supersaturated ferrite will be formed first and b.c.T martensite will be formed below \( T_c \). In alloys with concentrations greater than that corresponding to B, austenite will be transformed into b.c.T martensite. The position of the line \( T_c \) therefore effectively controls the relative amounts of tetragonal to cubic martensite formed.

Imai et al (44) have also obtained a critical ordering temperature \( T_c \) but by a different analysis and their values differ significantly from those obtained by Zener. There is at present no way of finding out which of the two values is correct, but the absolute values do not affect the principle that a magnetic energy component could alter the proportion of martensite under certain conditions.

2.5 Thermodynamic analysis of martensite transformations in steels

2.5.1 Introduction

In order to be able to assess the theoretical effect of adding magnetic energy to the system it is useful to have a measure of the free
energy differences between austenite and martensite. Hence in this section the thermodynamic analysis of alpha and gamma modifications of pure iron will be considered together with the various refinements that are introduced to take cognizance of the magnetic contributions to the stability of these two allotropes. This is followed by an analysis of the expressions for the free energy changes accompanying the martensitic transformations in iron-base alloys. Nucleation concepts as applied to martensitic transformations, as well as some of empirical equations which deal with the rate of formation of martensite below the $M_s$ will also be considered.

2.5.2 Thermodynamic analysis of $\Delta F^\gamma \rightarrow \alpha$ for pure iron

(1) Allotropy of iron

Iron at atmospheric pressure, exists in the b.c.c. form at low temperatures transforms to the f.c.c. form ($\gamma$ iron) at $910^\circ C$, and reverts back to the b.c.c. form ($\delta$ iron) at a higher temperature ($1400^\circ C$). $\delta$-iron is ferromagnetic with a Curie temperature of $770^\circ C$ while $\gamma$-iron is antiferromagnetic having a Néel temperature around $-193^\circ C$. It has also been suggested that $\gamma$ exists in two electronic modifications, $\gamma_1$ and $\gamma_2$ (45). Iron being a transition metal and strongly ferromagnetic, there are significant contributions from electron and magnetic components to the free energies of the alpha and gamma phases. But since these contributions are difficult to evaluate, precise calculations of free energies of alpha and gamma iron ($\Delta F_\alpha$ and $\Delta F_\gamma$) and prediction of the effect of alloying elements on the relative stability of the two allotropes has remained one of the most formidable tasks in thermodynamics.

(2) Zener's analysis of $\Delta F^\gamma \rightarrow \alpha$ curve for pure iron

Fig. 22 shows the $\Delta F^\gamma \rightarrow \alpha$ curve for iron, as computed by Johansson (46) for the entire temperature range up to the melting point of iron. The curve is linear from 100 to $500^\circ C$ beyond which it acquires an increasing negative curvature which reaches a maximum in the neighbourhood of the Curie temperature, i.e. at $770^\circ C$. In order to explain this curvature Zener (47) proposed that the free energy change in pure iron, $\Delta F^\gamma \rightarrow \alpha$ should be resolved
FIGURE 22. RESOLUTION OF FREE ENERGY DIFFERENCE OF \( \alpha \) AND \( \gamma \) IRON INTO MAGNETIC AND NON-MAGNETIC COMPONENTS.

FIGURE 23. THE TOTAL FREE ENERGY DIFFERENCE OF \( \alpha \) AND \( \gamma \) IRON AS A FUNCTION OF TEMPERATURE TOGETHER WITH ITS MAGNETIC AND NON-MAGNETIC COMPONENTS.
into a magnetic and non-magnetic components. The significance of this resolution can be seen from Fig. 22.

The slope

$$\frac{d \Delta F_{\gamma \rightarrow \alpha}}{dT} = -\Delta s_{\gamma \rightarrow \alpha}$$ ................................. 2.7

and the curvature

$$l = \frac{d^2 \Delta F_{\gamma \rightarrow \alpha}}{dT^2} = -\frac{c^\alpha - c^\gamma}{T}$$ ................................. 2.8

where $c^\alpha$ and $c^\gamma$ are the specific heats per mol of the alpha and gamma phases. Zener suggested that the large negative curvature might be due to an unusually high specific heat of the alpha phase around 770°C since anomalously low specific heats of gamma iron are unlikely to occur at this temperature. This specific heat was in fact identified with the uncoupling of spins in ferromagnetic iron atoms around the Curie temperature. Zener estimated the total entropy change due to magnetic disordering to be $R \ln 3 = 2.2$ cal mol$^{-1}$ deg$^{-1}$ which is actually slightly greater than the observed change in entropy between the phases from 500°C to the melting point. Also since the total heat released at the Curie temperature ($\approx$ 1500-2000 cal/mol) is much greater than the latent heat of $\alpha \rightarrow \gamma$ transition ($\approx$ 200 cal mol$^{-1}$) it is obvious that magnetic disordering should affect the equilibrium state (43). Christian (43) points out that although magnetic disordering does not suppress the transition it raises the critical temperature appreciably. According to this viewpoint it follows from the curve (Fig. 22) that if $\alpha$-iron had a lower Curie temperature, there would be no equilibrium gamma field in pure iron (43).

(3) Rationalisation of gamma loop anomalies

Zener's theory offers an explanation for the apparent anomaly presented by several gamma loop formers like chromium and vanadium which act as alpha stabilizers at higher temperatures (i.e. form gamma loops) but appear to act as gamma stabilizers at lower temperatures (i.e. lower the $M_s$ temperature). A decomposition of $\Delta F_{\gamma \rightarrow \alpha}$ into $\Delta F_{\text{Non Mag}}$ and $\Delta F_{\text{mag}}$ allows that the two parameters could be affected differently by these alloying elements. Zener's
two parameter analysis of $\Delta F^{\gamma \rightarrow \alpha}$ has been extended recently by Aaronson et al (48) to encompass gamma stabilizing elements.

(4) Weiss and Tauer's extension of Zener's analysis

Zener's analysis has been criticized by later workers (Weiss and Tauer (50) and Kaufman et al (51)) as inadequate, since an explicit definition of $\Delta F^{\gamma \rightarrow \alpha}_{\text{Non mag}}$ and $\Delta F^{\gamma \rightarrow \alpha}_{\text{mag}}$ in terms of the physical properties of $\gamma$ and $\alpha$ irons is difficult, and the precise nature of magnetic contribution is not known. Christian (43) considers that the effect of alloying elements is rather complex since changes in Bohr magneton numbers as well as Debye temperatures must be included in the magnetic and non magnetic terms respectively.

Weiss and Tauer (50) proposed that thermodynamic functions such as enthalpy, entropy and free energy of each phase could be resolved into lattice, magnetic and electronic components on the basis of additivity of the respective specific heat components. The free energy function of each of the allotropes of iron can then be written as

$$F(T) = F(T)_{\text{lattice}} + F(T)_{\text{electronic}} + F(T)_{\text{magnetic}}$$

The limiting value of magnetic entropy, according to their analysis approaches $R \ln (2s + 1)$ where $s$ is the number of unpaired spins, while the limiting value of magnetic enthalpy becomes $\gamma RT_C$ where $T_C$ is the Curie temperature. The free energy difference of alpha and gamma forms of iron as functions of temperature, together with their magnetic and non magnetic components is shown in Fig. 23. Weiss and Tauer conclude that b.c.c. $\alpha$-iron is only stabilized because of the magnetic terms.

(5) Double spin states in gamma iron

Kaufman et al (51) on the basis of resistivity and high pressure measurements of f.c.c. iron have postulated that the properties of f.c.c. iron can only be satisfactorily explained if two electronic configurations ($\chi_1$ and $\chi_2$) exist separated by an energy gap of 0.0355 eV. Although it
is difficult to establish their individual properties in pure iron, some idea of these can be obtained from alloy extrapolation and these are shown in Table 9.

Table 9 Approximate values of some of the properties of the two electronic configurations of gamma iron obtained by extrapolation from alloy data (52).

<table>
<thead>
<tr>
<th>States</th>
<th>Crystal Structure</th>
<th>Lattice Parameter A°</th>
<th>Magnetic Structure</th>
<th>Spin per atom</th>
<th>Curie or Néel Temp °K</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ₁ low energy</td>
<td>f.c.c.</td>
<td>3.54</td>
<td>Anti ferromagnetic</td>
<td>0.5</td>
<td>80°</td>
</tr>
<tr>
<td>γ₂ high energy</td>
<td>f.c.c.</td>
<td>3.64</td>
<td>ferromagnetic</td>
<td>2.8</td>
<td>1800°</td>
</tr>
</tbody>
</table>

γ₁ from Fe-Mn, Fe-Ni
γ₂ from Fe-Ni, Fe-Pt, Fe-Pd

Let $E_o$ and $E_1$ be the two energy levels associated with the two spin configurations. Then the fraction of atoms present in the upper level at any temperature $T$ is given by (51)

$$y = \left(1 + \frac{\theta_1}{\theta_0}\right) \exp \left(\frac{\Delta E}{RT}\right)^{-1} \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots
The difference in free energy between alpha and gamma iron according to Kaufman is 1303 cal mol$^{-1}$ at 0°K (53). If b.c.c. iron were not ferromagnetic its free energy would be increased by $\approx 2309$ calories mol$^{-1}$ so that gamma iron would be more stable than nonmagnetic b.c.c. iron by 1000 calories mol$^{-1}$ (53). From further calculations Kaufman concludes that if b.c.c. iron were not ferromagnetic the stable low temperature phase ($< 400°K$) would have a C.P.H. structure (53). High pressure measurements have in fact revealed that at pressures greater than 133 k.b. the high pressure low temperature form of iron is a C.P.H. phase (54) which is not ferromagnetic (at 150 k.b. $a = 4.05 \AA$ and $c = 2.46 \AA$; $c/a$ decreases rapidly with increasing pressure reaching a value of 1.58 at 400 k.b. (54)).

(f) Conclusion

It has been shown that there is a considerable influence of magnetic properties such as the Curie temperature and the number of Bohr magnetons upon the relative stabilities of the various allotropes in iron. Consequently in the free energy expression of each of the allotropes of iron a term due to the intrinsic magnetic properties must be included. The effect of energy contributed by interaction energy with an external magnetic field is considered in Section 5.2.3 where it is shown that the relative stabilities of the phases may be altered by an appreciable amount. The two effects are linked through the magnitude of the saturation magnetization of the phases concerned.

2.5.3 Empirical equations for $\Delta F^{\gamma \rightarrow \alpha}$ in pure iron

In the calculations of the free energy changes accompanying martensite transformations in steels (which will be dealt with in Section 2.5.5) the thermodynamics of the alpha-gamma transformations in pure iron plays an important part. Johansson (46) Zener (42) and Darken and Smith (55) have provided basic data which has been utilised by Fisher (41) to yield the following equation for calculating $\Delta F^{\gamma \rightarrow \alpha}_{Fe}$ below 500°K:

$$\Delta F^{\gamma \rightarrow \alpha}_{Fe} = 1238 - 398T - 12.5 \times 10^{-4} T^2 \text{ cal/mol} \quad \cdots \quad 2.12$$
whereas Kaufman and Cohen (56) have proposed

\[ \Delta F_{Fe}^{\chi \rightarrow \gamma} = 1202 - 2.63 \times 10^{-3} T^2 + 1.54 \times 10^{-6} T^3 \text{ cal/mol} \]

between 200 and 900°K which is the range of interest with respect to martensite. Equations 2.12 and 2.13 do not take precise account of the electronic and magnetic contributions to the free energies of alpha and gamma iron, because the nature of the contributions of these terms to \( \Delta F_{Fe}^{\chi \rightarrow \gamma} \) was not exactly known at that time. Kaufman et al (51) have re-evaluated \( \Delta F_{Fe}^{\chi \rightarrow \gamma} \) by taking into consideration two spin states of gamma iron and other experimental evidence from various sources (51). Their free energy values for \( \Delta F_{Fe}^{\chi \rightarrow \gamma} \) is therefore the most accurate of all those available to date (see Section 2.5.2).

2.5.4 Effect of alloying elements on \( \Delta F_{F}^{\chi \rightarrow \gamma} \)

The addition of a second element to pure iron (such as C, N, Cr, V, Ni, Mn etc.) introduces additional contributions to the free energy equation \( \Delta F_{F}^{\chi \rightarrow \gamma} \), depending on the nature of the element added. These contributions depend upon:

(a) the difference in free energy between f.c.c. and b.c.c. modifications of the element added

(b) the free energy of mixing between solute atoms in the two phases.

From a thermodynamic point of view it is convenient to treat martensite as supersaturated ferrite, and hence the difference in free energy between austenite and martensite for substitutional solid solutions can be taken to be the same as the difference in free energy between austenite and ferrite of the same composition. If however, the element forms interstitial solid solutions in austenite and ferrite then there will be an additional contribution to the free energy expression due to the preferential ordering of carbon atoms along the tetragonal axis of the b.c.T martensite lattice. Zener (42) and Imai et al (44) have evaluated the contribution to the free energy due to preferential ordering of carbon atoms which have already been discussed in Sections 2.4.9 and 2.4.8.
FIGURE 24  LINEAR APPROXIMATION OF FREE ENERGY-TEMPERATURE RELATIONSHIP.
2.5.5 The driving force, \( \Delta F^{\alpha \rightarrow \gamma} \) for martensite formation in steels

Fig. 24 shows a hypothetical free-energy-temperature relationship for austenite \( (\gamma) \) and martensite \( (\alpha') \). Martensite transformation on cooling is not thermodynamically possible until the temperature is below \( T_0 \), which is the point where the two phases \( \gamma \) and \( \alpha' \) have equal free energies (i.e., \( \Delta F^{\alpha' \rightarrow \gamma} = 0 \)). In some alloys the \( M \) temperature is only a little way below the thermodynamic transition temperature \( T_0 \), but in steels and in many other alloys (e.g., Fe-Ni alloys) considerable supercooling \( (T - M \approx 200^\circ C) \) is needed to initiate the transformation. This is because energy has to be made available to overcome the interfacial and elastic restraints associated with the transformation. \( \Delta F^{\alpha' \rightarrow \gamma} \) at \( M \) represents the chemical driving force for the transformation and a knowledge of \( \Delta F^{\alpha' \rightarrow \gamma} \) at \( M \) also provides an important link with the kinetics of transformations. Calculations of \( \Delta F^{\alpha' \rightarrow \gamma} \) however have been possible only for a limited number of systems such Fe-C (41, 57), Fe-Ni (56) and Fe-Cr (58), owing to lack of relevant data for other systems.

For a binary alloy Fe-A where A may be carbon, nickel, chromium or manganese etc., the free energy change accompanying the martensite reaction in steels be written (following Kaufman and Cohen's notation) as:

\[
\Delta F^{\alpha' \rightarrow \gamma} = x_{Fe} \Delta F_{Fe}^{\alpha \rightarrow \gamma} + x_{A} \Delta F_{A}^{\alpha \rightarrow \gamma} + \Delta F_{M}^{\alpha' \rightarrow \gamma} \quad .... 2.14
\]

Analysis of the free energy expression for \( \Delta F^{\alpha' \rightarrow \gamma} \)

The first term in equation 2.14, \( \Delta F_{Fe}^{\alpha \rightarrow \gamma} \) represents the difference in free energy between gamma and alpha phases in pure iron. Some available empirical equations for evaluating \( \Delta F_{Fe}^{\alpha \rightarrow \gamma} \) have been discussed in Section (2.5.2). Since the term \( \Delta F_{Fe}^{\alpha \rightarrow \gamma} \) is much larger than the other terms of equation (2.14) it is necessary to evaluate it as accurately as possible.

The second term in the expression \( \Delta F_{A}^{\alpha \rightarrow \gamma} \) is the difference in free energy between the f.c.c. and b.c.c. modifications of the pure element A.
It is negative for f.c.c. elements and positive for b.c.c. elements. In case of elements which do not have stable f.c.c. or b.c.c. allotropes the sign of $\Delta F_{\text{M}}^{\gamma \rightarrow \text{M}}$ can not be inferred but values do exist in principle (59). $\Delta F_{\gamma}^{\text{M}}$, the difference in free energy of mixing solute atoms in martensite and austenite is difficult to estimate. It can be derived either by extrapolation from activity measurements of solute in the gamma and alpha phases of iron (41), or by calculation from an assumed thermodynamic model for the solid solutions of gamma and alpha iron (56) (58).

2.5.6 Empirical calculations of $\Delta F_{\gamma}^{\rightarrow \gamma}$

a) Fisher's analysis

Fisher (41) estimated the free energy change accompanying the austenite martensite transformation in steels by using Johansson's data for pure iron (46), and extrapolating the high temperature properties of solutes in iron-carbon solutions to the supersaturated range. The following approximations were made:

1) the term $x \Delta F_{\gamma}^{\rightarrow \gamma}$ was taken to be negligible

2) the free energy of mixing term $\Delta F_{\text{M}}^{\gamma \rightarrow \gamma}$ was made equal to $RT \ln \frac{f_{\gamma}^{\text{M}}}{f_{\gamma}^{\gamma}}$, and $f_{\gamma}^{\gamma}$ being the activity coefficients of the component $A$ in the austenite and martensite phases of the same composition.

The activity coefficients $f_{\gamma}^{\text{M}}$ and $f_{\gamma}^{\gamma}$ were evaluated using Smith's data (60) on the heats of solution of graphite in gamma and alpha iron and Mehl and Well's data (61) for the equilibrium boundaries of iron-carbon diagram. With these approximations the expression 2.14 for $\Delta F_{\gamma}^{\rightarrow \gamma}$ can be written as:

$$\Delta F_{\gamma}^{\rightarrow \gamma} = x_{Fe} \Delta F_{Fe}^{\rightarrow \gamma} + \frac{10,500}{3.4257 \gamma} + \sum_{A} \chi_{A} \frac{RT \ln \left( \frac{f_{\gamma}^{\text{M}}}{f_{\gamma}^{\gamma}} \right)}{f_{A}^{\gamma}} - \Delta F^* \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots 2.15$$
Fig. 25. Changes in chemical free energy attending the austenite-martensite reaction in iron-carbon alloys as a function of carbon content (Cohen et al).
where \( x_{Fe}, x_c, \) and \( x_A \) are the atomic fractions of iron carbon and the element A respectively.

### 2.5.7 Difference between free energies \( \Delta F^{x\rightarrow y} \) and \( \Delta F^x \)

In the expression for \( \Delta F^{x\rightarrow y} \) (equation 2.15) Fisher introduced a parameter \( \Delta F^* \), following the concept of Zener ordering (42) to take into account the free energy change due to preferential ordering of carbon atoms when b.c.T martensite is formed. The expression for \( \Delta F^* \) is given in Section 2.4.9.

Imai et al (44) in their statistical thermodynamic treatment of free energy changes accompanying the transformation of austenite to martensite also introduced an order parameter (to the expression \( \Delta F^{x\rightarrow y} \)) to take into account the preferential distribution of carbon atoms along the tetragonal axis of the b.c.T martensite.

### 2.5.8 Free energy changes in alloys

#### a) Fe-C alloys

Cohen et al (57) have derived an expression for the free energy changes in iron-carbon alloys using extrapolated solute activities from high temperature measurements; their results agree with those of Fisher (41). From their results the slope of the linear portion of the free energy curves for Fe-C alloys (Fig. 25) \( \frac{\partial \Delta F^{x\rightarrow y}}{\partial T} \propto -1.4 \text{ cal mol}^{-1} \text{ deg}^{-1} \); therefore \( \Delta F^{x\rightarrow y} \) at \( M_s = 1.4 (T_o - M_s) \) which according to their derivation is independent of carbon content (it is assumed the \( M_s \) for most Fe-C alloys lies in the linear portion of the curve).

#### b) Fe-Cr and Fe-Ni alloys

Kaufman and Cohen (56) and Kaufman (58) have assumed a regular solution model for the alpha and gamma solid solutions in their calculations for \( \Delta F^{x\rightarrow y} \) for Fe-Ni and Fe-Cr alloys.

Taking the Fe-Cr system as an illustration, Kaufman (58) applied the regular solution approximation and evaluated \( \Delta F^{M^{x\rightarrow y}} \) which can be
expressed in the form:
\[ \Delta F_{M}^{\alpha \to \gamma} = x_{Fe} x_{Cr} (-2800 + 0.75T) \] .................. 2.16

\[ x_{Fe} \text{ and } x_{Cr} \text{ being the atomic fractions of iron and chromium respectively.} \]

Svechnikov and Lesnik (62) derived the following value for \( \Delta F_{Cr}^{\alpha \to \gamma} \) from a consideration of the Fe-Cr equilibrium diagram:
\[ \Delta F_{Cr}^{\alpha \to \gamma} = 460 + 1.0T \] .................. 2.17

By combining 2.16 and 2.17 Kaufman obtained the following free energy change, \( \Delta F^{\alpha \to \gamma} \) for martensite reaction in Fe-Cr system:
\[ \Delta F^{\alpha \to \gamma} = x_{Fe} \Delta F_{Fe}^{\alpha \to \gamma} + x_{Cr} (460 + 1.0T) + x_{Fe} x_{Cr} (-2800 + 0.75T) \] .................. 2.18

Brook, Entwistle and Ibrahim (74) have combined equations 2.18 and 2.15 to evaluate \( \Delta F^{\alpha \to \gamma} \) for Fe-Cr-C system which is of the form:
\[ \Delta F^{\alpha \to \gamma} = x_{Fe} \Delta F_{Fe}^{\alpha \to \gamma} + x_{Cr} (460 + 1.0T) + x_{Cr} x_{Fe} (-2800 + 0.75T) + x_{C} (-10,500 + 3.425T) - \Delta F^{*} \] .......... 2.19

It is obvious that a considerable number of approximations are built up into the free energy expression such as equation 2.19. There is at present very little experimental data to test the validity of these assumptions and approximations.

2.6 Kinetics of martensite transformations

2.6.1 Nucleation of martensite

a) Introduction

The overall kinetics of martensite transformations are dependent mainly on the nucleation process, since each plate grows rapidly to its
limiting size, once the transformation is initiated. Hence it is necessary to consider the salient features of nucleation concepts. Not much development has taken place in this field since the operational nucleation theory was proposed by Knapp and Dehlinger (63), and expanded by Kaufman and Cohen (59), Christian (64) and Kaufman (65).

b) **Operational nucleation theory**

If the martensite embryo is taken to be a thin oblate spheroid, the total free energy change when a small martensite plate of radius and thickness $c$ is formed (volume $= \frac{4}{3} \pi r^2 c$ and surface area $= 2 \pi r c^2$) can be written as:

$$\Delta W = \frac{4}{3} \pi r^2 c \Delta f + 2 \pi r c^2 \sigma_s + \frac{4}{3} \pi r c^2 A \frac{\delta}{\gamma} \text{cal/particle}$$

Where $\Delta f$ is the change in chemical energy per unit volume, $\sigma_s$ the surface energy per unit area and $A \frac{\delta}{\gamma}$ the strain energy per unit volume.

Since the free energy of nucleation $\Delta W^*$ (corresponding to $d (\Delta W) = 0$) is too large ($10^8$ - $10^9$ cal/mol) to be reached by thermal fluctuation it is necessary to assume pre-existing embryos in the austenite and then consider whether some process other than the formation of a super critical nucleus controls the rate of propogation of martensite plates.

According to Frank's analysis (66) the austenite-martensite interface for a $\frac{1}{2}225$ habit plane consists of long circumferential dislocation loops spaced on every sixth close-packed plane, and the embryo grows by expansion of dislocation loops.

Knapp and Dehlinger (63) extended Frank's model by postulating that the embryo will spontaneously grow into full size plates as soon as the chemical driving force exceeds the required interfacial and strain energies. In otherwords the initiation of martensite transformation is determined by the condition $\Delta W < 0$ rather than by the saddle point in the free energy barrier where $d (\Delta W) \leq 0$. 


\[ \Delta W \text{ ... Over all Free Energy} \]

\[ W_i \text{ ... Energy of Equivalent Circumferential Loop} \]

\[ \Delta W_e \text{ ... Energy increment for each thermally activated growth step} \]
Kaufman and Cohen (59) realised that Knapp and Dehlinger condition for nucleation, namely $\Delta W < 0$ was purely intuitive by choice and there was no theoretical basis for assuming either the creation or expansion of dislocation loops to be possible when the overall free energy change is negative i.e. when $\Delta W < 0$. To bring the operational concept to a more realistic plane, Kaufman and Cohen postulated that for an embryo to grow spontaneously the difference between the chemical free energy and the strain energy must be sufficiently large to move interface dislocations, overcoming their line tension and shear resistance. Fig. 26 shows a schematic analysis of the various nucleation conditions described above (59 and 67).

**Summary**

Since free energy of classical nucleation is large, pre-existing nucleation sites are postulated in the austenite above $T_o$. However, the operational nucleation theory does not clearly explain the origin of such martensite embryos and has nothing to say concerning the nature of the forces that are operative in limiting the size of such embryos. Another possible limitation of the operational theory lies in the absence of details concerning the triggering mechanism.

2.6.2 The $M_s$ temperature and factors which influence the $M_s$

A considerable amount of experimental data has been accumulated since a detailed account of martensite kinetics was published by Kaufman and Cohen (59), particularly regarding the factors that influence the start of the martensite transformation temperature i.e. the $M_s$, as well as the progress of the transformation below the $M_s$. The information concerning the $M_s$ will be summarised in this section while the relationships that have been proposed for the rate of martensite formed below the $M_s$ will be discussed in Section 2.6.3.

1) Definition of the $M_s$ temperature

The temperature at which martensite begins to form spontaneously on cooling in a time independent manner (athermal transformation) is called
the $M_s$ temperature (68). This temperature is however affected by a number of factors which will now be considered (it is assumed that other transformations products are not present).

2) **Factors which influence the $M_s$**

1. Thin foils and thin films exhibit $M_s$ temperatures which are much higher than those of bulk materials (68).

2. Transformation at free surfaces occurs at temperatures higher than those of bulk materials (68).

3. Austenitizing temperature-treatments influence the $M_s$ temperature.

4. Decreasing the grain or particle size lowers the $M_s$.

5. Prior plastic deformation above $M_s$ temperature can either suppress or raise the $M_s$ temperature.

6. The application of hydrostatic pressure depresses the $M_s$ temperature (69).

7. Neutron irradiation usually lowers the $M_s$ temperature (70).

8. The application of a magnetic field raises the $M_s$ temperature in ferrous alloys (see Section 4.2.2).

The same factors that influence the $M_s$ temperature also influence in a similar manner the amount of transformation which occurs below the $M_s$.

2.6.3 **Rate of martensite formation below the $M_s$**

Current treatment of the kinetics of martensitic transformation has been largely confined to the start of the transformation i.e.
FIGURE 27 RATE OF MARTENSITE FORMATION BELOW THE $M_s$ (Koistenen and Marburger)

FIGURE 28 CORRELATION BETWEEN THE SLOPE OF MARTENSITIC TRANSFORMATION CURVES AND $\frac{\theta \Delta F}{\Delta T}$ AT $M_s$ FOR NICKEL AND CHROMIUM STEELS (Brook et al).
1 Nickel Steels 2 Chromium Steels
Austenite (1100°C)  
Quenched to Room Temperature

First Stage of Tempering (20-200°C)
Retained Austenite  
Martensite

Second Stage of Tempering (200-300°C)
Retained Austenite  
ε-Iron Carbide  
Low-Carbon Martensite

Third Stage of Tempering (> 300°C)
Ferrite  
ε-Iron Carbide  
ε-Iron Carbide  
Low-Carbon Martensite

*Cementite formed from the reaction of ε-Iron Carbide with Ferrite and/or Low-Carbon Martensite.

Figure 29 Phase changes taking place in the tempering of a high carbon steel. (101).
prediction of the $M_s$, rather than the progress after the transformation has been initiated. However, a few empirical equations have been suggested for the variation of volume fraction transformed with temperature for athermal martensites. Koistinen and Marburger (72) obtained accurate data on pure iron-carbon alloys with an X-ray diffractometer and found that the results fitted a curve

$$1-V = \exp (-0.011 (M_s - T))$$  \hspace{1cm} 2.21

where $V$ is the volume fraction which has become martensite at the temperature $T$. As shown in Fig. 27, this curve also gives a reasonably good fit with experimental data for plain carbon steels, including some for which Harris and Cohen (73) proposed a more complex relation. It will be seen, that according to the equation 2.21 complete transformation is never attained, i.e. that there is no true $M_f$ temperature.

It is also implied in Fig. 27 that athermal transformation curves of steels should have similar shape. Further implications of this will be dealt with in Section 5.3.3.

Brook, Entwistle and Ibrahim (74) examined the martensite transformation curves for a number of Fe-Ni- and Fe-Cr-alloys; combining experimental rates of reactions with calculated $\Delta F^{\alpha\gamma}$ from equation 2.19 they showed that $\frac{\sigma}{\delta T}$ is directly proportional to the slope of the transformation curve (in the linear portion) although the constant of proportionality is different in the two alloy systems (Fig. 28). Further implications of this will be dealt in Section 5.3.3.

2.7 The mechanism and kinetics of first stage tempering in steels

2.7.1 Introduction

The schematic sequence of tempering reactions in high carbon steels can be represented in Fig. 29. The first stage of tempering in plain carbon and low alloy steels corresponds to the precipitation of epsilon-carbide ($\varepsilon$-carbide) and the formation of low carbon martensite at the expense of the primary martensite present in the quenched alloy. The reaction primary
martensite $\rightarrow$ low carbon martensite + $\varepsilon$-carbide can be split into the following sequences (75).

1. Segregation of carbon atoms to defects - such as dislocations, twin boundaries (and possibly domain boundaries).

2. Formation of $\varepsilon$-carbide platelets coherent with the matrix.

3. Transformation of tetragonal martensite to cubic martensite.

Tempering of martensite in the early stages can be looked upon as a process of precipitation from a supersaturated solid solution. Transmission electron micrographs reveal a fine structure within the martensite, which can be a dense dislocation network or a fine stack of twins (76, 77) and this is related to the inhomogeneous shear part of the deformation in the crystallographic theories of martensite (78). Hence the morphology and fine structure of martensite resulting from a shear transformation seriously influences the tempering sequence in the early stages.

2.7.2 Morphology of precipitation of $\varepsilon$-carbide

The crystallography and morphology of $\varepsilon$-carbide precipitation during tempering in ferrous alloys has been investigated by several workers (80, 81, 82). Pitch and Shrader (79) investigated the precipitation of $\varepsilon$-carbide in Fe-0.42C steel and found that $\varepsilon$-carbide precipitated on $\{100\}$ planes in a flat network with fine bands which grow with $[11\bar{2}0]_c$ in two $<110>$ directions of ferrite. Hale and Mclean (80) confirmed that $\varepsilon$-carbide precipitates on $\{100\}$ plane from their tempering investigations of an Fe 0.05C alloy at 100°C. Kelly and Nutting (77) made a detailed study of the tempering of 1 pet C steel at 200°C using transmission electron microscopy and observed carbides lying along the twins and also perpendicular to twin plane. Although the carbides did not give satisfactory diffraction patterns they were suggested to be of $\varepsilon$-carbide. M.G.H. Wells (2) observed, that $\varepsilon$-carbide generally
grows along narrow plates or laths usually in more than one direction, in a characteristic criss-cross manner.

Turkalo (83) observed similar carbide configurations in the tempering of 0.49C 1.9Mn steel; in addition, the presence of a continuous carbide film at the austenite-martensite interface was also observed. Further implications of this observation will be dealt in Section (7.2.4).

It is thus clear that the transformation substructure of martensite influence the morphology of precipitation of ε-carbide during tempering. It should also be stressed that initial stages of tempering may have already occurred before any semblance of a precipitate is revealed in an electron micrograph and that first stage tempering may have been initiated during the quenching treatment itself (auto-tempering).

2.7.3 Interaction of defects with carbon atoms

Wilson has shown (84) that if a medium carbon martensite (0.47 - 0.74C) is sufficiently cold worked, the normal precipitation of ε-carbide in the first stage of tempering is suppressed. Kurdjumov (75) has proposed that most of the carbon will segregate to dislocations so that less of carbon atoms will be available for precipitation. However description of the situation in terms of competition for the solute between the dislocations and the nuclei of ε-carbide is difficult to accept unless convincing evidence is provided to prove that dislocation sites are not themselves preferred sites for the nucleation of ε-carbide. Thomas and Leak (85) have pointed out that if a dislocation is able to absorb a variable number of solute atoms, a spectrum of interaction energies will be involved. Only for sites near the core of a dislocation, where the interaction energy is at a maximum, will the energy binding the carbon atom in the dislocation be greater than that in iron-carbide. In the presence of a carbide precipitate the size of a stable atmosphere (the number of c atoms per atom plane) will be limited and will depend on the energy binding the carbon atom in the precipitate. However in a general sense the distribution of total carbon content between dislocations and
particles of a precipitate will clearly depend on dislocation density. It is also not clear to what extent cold work can increase the dislocation density of a martensitic structure which already has a high dislocation density in itself ($10^{12}$ lines/cm$^2$).

Damask et al (86, 87) have shown that when a quenched iron 0.01%-carbon specimen is irradiated at low temperatures, subsequent internal friction measurements show that carbon atoms rapidly disappear from solution in the temperature range 40-50°C. Electron metallographic studies did not reveal the formation of any metastable carbide precipitate at 160°C. In the un-irradiated alloys similar measurements indicated that carbon disappeared from solution at about 160°C, and electron metallographic confirmed the presence of a metastable precipitate. This suggests that in irradiated specimens carbon atoms may be trapped at point defects - presumably vacancies produced during irradiation. The binding energy of carbon atoms to these defects was measured by calorimetry and was found to be 0.41 ev/atom, while the energy released per carbon atom in forming the metastable carbide was estimated to be 0.27 ev/atom. It is clear that the distribution of carbon is sensitive to the precise distribution of various energy sites.

Two further aspects may be considered in some detail namely (1) the tempering mechanism of low carbon martensites and (2) the precise significance of activation energy during the first stage of tempering.

2.7.4 Tempering mechanism in low carbon martensite

Kurdjumov and Lysaak (88) studied the tempering of an iron carbon alloy containing 1.4C, using X-ray methods and pointed out that martensite during tempering does not lose its tetrogonality gradually; instead a new martensite is formed with a tetrogonality corresponding to 0.25C. If primary martensite decomposes into an aggregate of $\gamma$-carbide and low carbon martensite with a carbon content of say 0.25C, and if these two phases are in metastable equilibrium then a steel containing less than 0.25C should exhibit no first stage tempering at all.
This suggestion was tested by King and Glover (89) who in their resistometric investigation of tempering of a 0.19C steel, observed only a small change in the resistivity during the first stage. This small change in resistivity was attributed to the migration of carbon atoms to dislocations rather than to the precipitation of $\epsilon$-carbide. An equally plausible explanation has been given by Hillert (90) who points out that in low carbon steels most of the martensite is formed at a higher temperature and as such may be considerably tempered before room temperature is reached.

**Composition of low carbon martensite formed during tempering.**

The early theories of tempering (91) were based on the assumption that the carbon content of low carbon martensite formed in equilibrium with $\epsilon$-carbide is of a fixed composition, independent of the carbon content of primary martensite. The tempering results of low carbon martensites do not however substantiate this hypothesis. Modin (92) has observed $\epsilon$-carbide in a tempered 0.18%C steel, and has also been reported (18) that a low carbon martensite having a tetragonality corresponding to 0.1 to 0.2%C does occur on tempering a low carbon nickel steel (0.32C-19Ni). Further the results of Alsetter (74) on the X-ray diffraction studies of carbides formed during tempering indicate that $\epsilon$-carbon may form independently of low carbon martensite. Alsetter suggests that the converse of this statement should be investigated, namely whether low carbon martensite can form discontinuously in the absence of $\epsilon$-carbide. This should not be the case if coherency is necessary to stabilize low carbon martensite so that as soon as coherence is lost the martensite will lose carbon to form $\epsilon$-carbide and ferrite.

2.7.5 **The activation energy of first stage tempering**

The second problem of interest concerns the precise significance of the activation energy for the first stage of tempering. Robert, Averbach and Cohen (91) found that the rate equation for the kinetics of the first stage of tempering for steels (0.6C-1.4C) could be expressed as:

$$-\ln(1-f) = K t^n$$
where \( f \) is the fraction transformed, \( K \) the rate constant, \( t = \) time and \( n = \) exponent of time. The experimental value of \( n = 0.3 \) obtained by Averbach and Cohen (95) differs significantly from the lowest possible theoretical value of \( n = 0.5 \) predicted by Zener (42) for diffusion controlled growth of a precipitate. Cohen et al (95, 91, 96) obtained activation energy values for the first stage of tempering of 8000, 16000, 27000 cal mol\(^{-1}\) based on \( n \) values of 0.3, 0.5 and 1 respectively.

2.7.6 The relation of activation energies for first stage tempering and the diffusion of carbon in martensite

If diffusion of carbon in martensite is the only temperature dependent factor involved in the tempering sequence obtained, and if all other processes are related to it then the activation energy for the first stage tempering should correspond to the diffusion of carbon in martensite.

King and Glover (89) from their resistometric study found that the activation energy of first stage of tempering (\( Q_0 \)) varies with the carbon content (\( c \)) according to the equation:

\[
Q_c = Q_F + 8500c
\]

where \( Q_F \) represents the activation energy for diffusion of carbon in ferrite. Hillert (97) has made a theoretical evaluation of the diffusion coefficient of carbon in martensite and concludes that the first stage of tempering in the early stages is too rapid to be explained by an ordinary diffusion process with

\[
D = D_F \exp\left(-8500c/RT\right)
\]

which is easily derived from equation 2.23.

It has been pointed out in this connection that it is always possible to define an activation energy for a process on a purely formal basis, without postulating any physical model concerning the mechanism of the process. A derived activation energy may not therefore always have a clear physical significance and the value of comparing it directly with the activation energy for some atomic process like diffusion may be highly questionable in some cases (97). Birchenall and Mead (98), have discussed
the kinetics of grahtization in cast iron, and shown that it is erroneous to identify the plot of the growth or dissolution rate $v_g$ versus reciprocal of temperature with activation energies determined by diffusion measurements in chemically similar systems.

2.7.7 **Dilatometric study of tempering kinetics**

The kinetics of the first stage tempering has been studied in detail by many methods such as dilatometric (91), resistometric (89), calorimetric (99) and X-ray (88) techniques. Since excellent reviews on the morphology and structural changes taking place during tempering are available elsewhere (81) they will not be repeated. But it is worthwhile considering the meaning of property changes associated with dilatometric and magnetic methods since they are the experimental techniques used in the present work to study the tempering reactions.

The decomposition of primary martensite into low carbon martensite and $\varepsilon$-carbide is accompanied by a contraction in volume while the transformation of retained austenite into an aggregate of ferrite and carbide is associated with an expansion.

Robert et al (91) studied the tempering kinetics of plain carbon steels (C 0.29 – 1.43%) and observed that the contraction at the end of the first stage of tempering is proportional to the carbon content of steel while the rate of tempering (as observed by the slope of the dilation curves) increased with the tempering temperature. Assuming that the composition of low carbon martensite does not vary with the carbon content of primary martensite, the total length change per unit length at the end of the first stage, can according to Robert et al, be expressed as:

$$L = 2930 \times 10^{-6} (C - 0.25)$$

where $L$ is the total length change per unit length and $C$ the carbon content of primary martensite.
FIGURE 30  DECOMPOSITION OF MARTENSITE AND RETAINED AUSTENITE AT 170°C (Mentser)

FIGURE 32  HARDNESS VARIATIONS OF AUSTENITE AND MARTENSITE IN A 1.7 per cent CARBON STEEL WITH TEMPERING TEMPERATURE (Hanemann)
Some doubts have been expressed about the use of length changes for kinetic measurements, since it is suspected that the relief of microstresses can also produce a change in length. This possibility was investigated by Robert et al (91) who determined the specific volume and length changes on specimens of 1.4C and 1.7C steels. It was found that the difference between the specific volume and the corresponding length changes were within 5%. The extent of linear contraction can therefore be taken as a criterion for the extent of tempering.

2.7.8 Magnetic analysis of tempering reactions

The magnetic analysis of phase changes produced during the tempering of steels has been investigated in detail by Crangle and Sucksmith (100) and Mentser (101). The decomposition of martensite during the first stage of tempering is associated with a decrease in magnetization while the transformation of retained austenite during the second stage of tempering is accompanied by an increase in magnetization. Figure 30 shows the extent of changes in magnetization produced due to the decomposition of martensite and retained austenite on tempering a high carbon steel (1.62C) at 170°C.

The results of Bernsteyn et al (Section 2.3.2 and 2.3.3) indicate that a magnetic field when applied during tempering affects the kinetics of tempering reactions. Hence magnetization measurements in situ are likely to be affected by the field used to measure magnetization. If however the tempering kinetics are not followed in situ then the magnetization changes measured has to be synchronised with the extent of tempering that has occurred.

2.8 Hardness and its relation to the structure and mechanical properties of steels

2.8.1 Introduction

Indentation hardness is a measure of the resistance of the metal to plastic deformation and it is expressed formally as the ratio of load to surface area which in fact has the same dimensions (M L^{-1} T^{-2}) as pressure (102). The two mechanical properties most closely linked with
indentation hardness are (i) tensile strength (ii) strain hardening capacity. Several empirical equations have been proposed connecting hardness with these two properties. Most of the previous work done on the effect of a magnetic heat treatment is associated mainly with its effect on tensile strength of steels while the present investigation (described in Section 3.3) largely concerns the effect of quenching in a magnetic field on hardness. Some of the equations connecting hardness and tensile strength will be discussed in the next Section so that the two properties can be correlated.

2.8.2 Relation between hardness and tensile strength of steel

Brinell, in 1902 proposed an empirical relationship between the Brinell Hardness \( H_B \) of steel and the ultimate tensile strength \( \sigma_B \) of the form \( \sigma_B = K_H H_B \) where \( K_H \) is a constant of proportionality (0.21 - 0.23 tons/in\(^2\)). It is found, however that Vickers diamond pyramid hardness gives a more consistent correlation with the tensile strength of steel because

1) the mode of indentation flow is similar for all conditions of hardness in any one material and is comparable in different materials

2) hardness values for the material have a direct simple relationship with the mode of plastic flow

3) higher modulus of the Vickers indentor makes the indentor less sensitive to the deformation of the indentor when testing hard materials.

To convert a diamond pyramid hardness into approximate tensile strength in steel in p.s.i. the hardness number is multiplied by a factor \( K \) which is about 500.

\[
\text{V.P.N.} = K \times T.S \text{ (p.s.i.)} \quad \text{................................. 2.24}
\]
Tabor (102) has shown that there is a simple theoretical basis for such relationships if the triaxial nature of deformation under an indentor is taken into account. Brittle materials like quenched steel show a good deal of scatter in the value of K and the relation 2.24 does not apply to them. This is understandable in view of the fact that for brittle materials the tensile strength observed characterises fracture, rather than resistance to deformation or plastic flow (102).

2.8.3 Use of hardness and microhardness tests to study the structure of quenched and tempered steels.

Hardness tests have been widely used in the investigations of various metallurgical processes such as recrystallization, precipitation hardening and tempering because tensile and impact tests made on brittle structures, such as ferrous martensites (there are some exceptions, where ferrous martensites are soft) give a large scatter band and hence are not so reliable in any investigation of heat treatment effects. The lower sensitivity to premature fracture in hardness tests is a more useful property in an assessment of a heat treatment effect where only small changes are expected as in the case when studying the effect of magnetic fields on the mechanical properties of quenched steels.

2.8.4 Causes for Hardness of martensite in steel

The overall measured hardness is normally the result of a number of overlapping hardening mechanisms; the factors which are likely to contribute to the strength (the terms strength and hardness are used as synonyms) of martensite are (103):

1) Carbon (or nitrogen) in solid solution

2) ageing during the quench  ) Precipitation or segregation of carbon or nitrogen

3) ageing after the quench

4) dislocation substructure

5) internal twinning substructure
Fig 31: Schematic representation of hardness changes (at 19°C).

On ageing a 0.82% C - 16.7% Ni martensite artificially after the quench: $\Delta H_1 (= 345 \text{ HV})$ is the contribution to hardness due to 0.82% C in solution, $\Delta H_2 (= 170 \text{ HV})$ is the contribution to the hardness of aged martensite due to the carbon still in solid solution; $\Delta H_A (= 310)$ is the contribution to the hardness of aged martensite due directly to the precipitation or segregation of carbon (Kelly and Nutting).
The effect of other factors such as grain size, elements in substitutional solid solution are very small. The strength of martensite is a combination of these factors, and although the various individual effects which are responsible for the high strength of martensite are established there is a good deal of controversy regarding the relative role played by each of these hardening effects in producing the resultant high strength \((103)\).

Fig. (31) shows a schematic representation of hardness changes (at-196°C) on ageing a \(0.82\% C - 16.7\% Ni\) martensite artificially after the quench.

\(\Delta H c_1\) \((= 345 \, HV)\) is the contribution to hardness attributed due to \(0.82\% C\) in solution, \(\Delta H c_2\) \((= 170 \, HV)\) is the contribution to the hardness of aged martensite due to carbon still in solid solution; \(\Delta H A\) \((= 310 \, HV)\) is the contribution to the hardness of the aged martensite due directly to precipitation or segregation of carbon. The hardness of quenched martensite in this case therefore appears to be a combination of (a) the interstitial solid solution of carbon in martensite and (b) precipitation or segregation of carbon during auto-tempering.

### 2.8.5 Hardness changes associated with tempered steels

The tempering characteristics of a \(1.7\% C\) steel have been investigated by Haneman \((104)\) with help of micro hardness tests using a Vickers indenter with loads up to 20 gms. Fig. 32 shows the hardness variations of austenite and martensite with tempering temperature. The hardness of martensite increases on tempering in the temperature range 100 - 150°C, and this is attributed to the coherency hardening associated with the precipitation of \(\varepsilon\)-carbide coherent with the matrix. Haneman could not explain, however, the increase in hardness of austenitic areas on tempering. This problem was reinvestigated by Stark and Lement \((105)\) using a high purity Fe-\(1.7\% C\) alloy, who found that some of the austenite areas showed a light etching constituent after being tempered at \(450^\circ F\). This constituent was considered to be surface martensite formed at new surfaces created either by mechanical or electrolytic etching.
FIGURE 53  VARIOUS DEVICES FOR PRODUCING MAGNETIC FIELDS

TYPES OF MAGNETS

ELECTROMAGNET

AIR CORE ELECTROMAGNET

IRON CORE ELECTROMAGNET

PERMANENT MAGNETS

CONSTANT FIELD MAGNETS

PULSATING MAGNETS

BITTER TYPE MAGNETS

SUPER CONDUCTING MAGNETS
<table>
<thead>
<tr>
<th>Type</th>
<th>Frequency (kHz)</th>
<th>Current (A)</th>
<th>Gap (mm)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron-cored Magnet</td>
<td>3000-5000</td>
<td>0</td>
<td>2</td>
<td>None</td>
</tr>
<tr>
<td>Copper Wire Magnet</td>
<td>2000-3000</td>
<td>10-15</td>
<td>2</td>
<td>None</td>
</tr>
<tr>
<td>Copper Wire Magnet</td>
<td>2000-3000</td>
<td>10-15</td>
<td>2</td>
<td>None</td>
</tr>
<tr>
<td>Copper Wire Magnet</td>
<td>2000-3000</td>
<td>10-15</td>
<td>2</td>
<td>None</td>
</tr>
<tr>
<td>Copper Wire Magnet</td>
<td>2000-3000</td>
<td>10-15</td>
<td>2</td>
<td>None</td>
</tr>
</tbody>
</table>

Table 1: Typical Characteristics of the Various Electromagnets
2.9 Production of magnetic fields and types of magnetic energy

2.9.1 Production of magnetic fields

There are two general classes into which devices for producing magnetic fields may be divided (i) Permanent magnets (ii) Electromagnetic. Fig. 33 gives the general classification of the devices for producing magnetic fields. Table 10 gives the typical characteristics of the various electromagnets, with the size of the working gap and the maximum fields attainable at present with each type of electromagnet. The choice of a magnet will be set largely by the size of the field desired and financial considerations; whatever the type of magnet finally chosen, the interactions with ferromagnetic materials will be the same and the rest of this Section (2.9) is largely concerned with this aspect.

2.9.2 Types of magnetic energy

(1) Introduction

The magnetic behaviour of a ferromagnetic material may be summarised by two observations: (i) it is possible to attain magnetic saturation by the application of a very weak field to the specimen and (ii) it is possible for the same specimen to have zero overall magnetization in the absence of any field. The first observation can be explained by postulating that in a ferromagnetic material the elementary magnetic moments (electron spins) are subjected to an internal molecular field which tends to align them so that effective magnetic saturation occurs even in the absence of an external field. The physical origin of the internal molecular field was shown by Heisenberg (71) to be the result of a quantum mechanical exchange interaction between the electron spins. In order to explain the second observation, the concept of 'domains' is introduced. A ferromagnetic material is divided into small regions called domains each of which is magnetized to saturation along a certain direction. In the unmagnetized state the directions of the magnetization vectors are so distributed as to give a zero resultant over any macroscopic volume.
(2) Magnetic interaction energy

The free energy available from the interaction of the magnetization vector $\mathbf{J}$ with an applied field $\mathbf{H}$ is given by (106)

$$\Delta E_{\text{mag}} = -\mathbf{J} \cdot \mathbf{H} \quad \cdots \quad 2.25$$

For fields beyond saturation $\mathbf{J}$ and $\mathbf{H}$ will be parallel so that 2.25 becomes

$$\Delta E_{\text{mag}} = -J H$$

For iron $J \approx 1700$ gauss/cm$^3$

Table 11 (a) Interaction energy for iron.

<table>
<thead>
<tr>
<th>$H$ K. Gauss</th>
<th>$E_{\text{mag}}$ ergs/cm$^3$</th>
<th>$E_{\text{mag}}$ cal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>$2.8 \times 10^7$</td>
<td>4.5</td>
</tr>
<tr>
<td>100</td>
<td>$17 \times 10^7$</td>
<td>28</td>
</tr>
</tbody>
</table>

Meyer and Tagland (11) and Krivaglaz and Sadovskiy (12) have both assumed a value of interaction energy equal to $JH$ in their derivations for the shift in the transformation temperature due to an applied field. According to Graham (107) the maximum interaction energy available is of the order of $2JH$ but there is very little theoretical or experimental support in literature for this value. In an ensemble of magnetized particles the field of each particle will act on the other particles, and the interaction energy then becomes $JH/2$ (108). In the case of a system with a gradually increasing number of martensite plates the interaction energy can therefore be expected to decrease at some point (Section 4.2.2) although the previous work on the effect of magnetic fields on steel transformations does not seem to have considered this possibility.
FIGURE 34 Magnetization for single crystals of iron in the principal crystallographic directions.

FIGURE 35 Schematic representation of magnetization, linear and volume magnetostriiction of iron as a function of magnetic field strength.
(3) **Magnetocrystalline anisotropy energy**

Experiments on single crystals have shown that the magnetization vector $J$ in the absence of any external constraints, tends to lie along certain crystallographic directions. The effect is known as Crystalline anisotropy. In iron the preferred direction is along the cube edges $\langle 100 \rangle$; in nickel it is along cube diagonals $\langle 111 \rangle$ and in close packed hexagonal cobalt the hexagonal axis $\langle 0001 \rangle$ is the preferred direction. If, by applying a field, the magnetization vector $J$, is turned away from the preferred direction towards the direction of the field, work must be done against magneto-crystalline forces which tend to keep $J$ along the preferred directions, and the energy difference is stored in the system. The existence of crystalline anisotropy is revealed in the magnetization curves of single crystal specimens (Fig. 32). For iron and nickel with cubic symmetries, the magnetocrystalline anisotropy energy is expressed as:

$$E_K = K_0 + K_1 (\alpha_1^2 + \alpha_2^2 + \alpha_3^2) +$$

$$\frac{K_2}{2} \alpha_1^2 \alpha_2^2 \alpha_3^2 \text{ ergs/cm}^3$$

where $K_0$, $K_1$, and $K_2$ are constants and $\alpha_1$, $\alpha_2$, and $\alpha_3$ are the direction cosines of the magnetization with the cube axis. $K_0$ can be ignored if one is comparing the difference between two orientations.

For iron $K_1 = 4.3 \times 10^5$ ergs/cm$^3$ $K_2 = 2 \times 10^5$ ergs/cm$^5$ and therefore $E_K \approx 6 \times 10^5$ ergs/cm$^3$.

The contributions to the total free energy from magnetocrystalline anisotropy energy is thus small in iron, nickel and their alloys.

(4) **Magnetostriuctive energy**

The term magnetostriiction is used to describe any dimensional change of the material which is associated with its magnetization. In a ferromagnetic material, spontaneous distortion of the crystal lattice
accompanies spontaneous magnetization, and this interaction of magnetization with the state of strain in the lattice leads to magnetostrictive energy. Fig. 35 shows the changes in length in polycrystalline iron accompanying magnetization. In small fields which correspond to domain boundary displacements there is an expansion and this is followed in higher fields by a gradual contraction. In fields beyond saturation there is again an expansion. This expansion is a volume effect and is known as volume magnetostriction. This is of the order of $10^{-6}$/kG., and is associated with an increase in spontaneous magnetization. Table 11(b) gives the order of the saturation magnetostriction for iron and nickel.

Table 11 (b) Saturation magnetostriction values for iron and nickel ($\times 10^{-6}$)

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{(100)}$</th>
<th>$\lambda_{(111)}$</th>
<th>(Isotopic saturation magnetostriction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>19.5</td>
<td>-18.8</td>
<td>-7</td>
</tr>
<tr>
<td>Ni</td>
<td>-46</td>
<td>-25</td>
<td>-34</td>
</tr>
</tbody>
</table>

The magnetostrictive energy can be expressed as

$$E_\lambda = \frac{y}{2} \left[ \lambda_{100} + 3 (\lambda_{111} - \lambda_{100}) (\alpha_1^2 + \alpha_2^2 + \alpha_3^2) + \alpha_3^2 \alpha_1^2 \right] \frac{1}{2}$$

where $y$ is the young's modulus

$\lambda = $ appropriate magnetostriction constant

Taking $y = 30 \times 10^{11}$ dynes/cm$^2$ (for iron and steel) and substituting for $\lambda$ from Table 11(b).

$$E_\lambda = 10^3 \text{ ergs/cm}^3.$$
The magnetostrictive energy thus falls several orders of magnitude smaller than the interaction energy.

(5) Shape anisotropy energy

Shape has an important effect in a magnetic material, which appears as a directional anisotropy term. An ellipsoidal particle having a high \( \ell/d \) ratio (ratio of major axis to minor axis) can be magnetized more easily along its major axis than along its minor axis, because of the difference in the number of free poles which appear at the ends of magnetized specimen. The field produced by the free poles, the demagnetizing field, tends to reduce the magnetization in the material and the magnitude of this field will increase if the poles are more closely spaced i.e. if \( \ell/d \) ratio is small. The demagnetizing field \( H_D \), is proportional to the magnetization \( J \) and can be expressed as:

\[
H_D = -NJ
\]

where \( N \) is the demagnetizing coefficient and depends on the shape of the specimen. For an elongated particle the shape anisotropy energy is given by:

\[
F_D = \frac{1}{2} J^2 (N_a - N_b)
\]

where \( N_a \) and \( N_b \) are the demagnetizing coefficients along the major and minor axes respectively. The value of \( F_D \) then depends on \( N_a - N_b \) i.e. the extent of shape anisotropy. For an ellipsoidal particle with an \( \ell/d \) ratio of 20 (which is a typical ratio for a martensite embryo) a reasonable estimate of \( N_a - N_b \) is 5. Taking \( J = 1700 \) Gauss/cm\(^3\) for iron \( F_D \approx 6 \times 10^6 \) ergs/cm\(^3\).

For very elongated particles the shape anisotropy could be an important factor in producing orientation dependent effects. The order of magnitude of various magnetic energies for iron are given in Table 12.
Table 12 Order of magnitude of various magnetic energies for iron.
\( J = 1700 \text{ gauss/cm}^2; \ H = 1.6 \times 10^4 \text{ gauss}; \ l/d = 20. \)

<table>
<thead>
<tr>
<th>Interaction energy ( \text{ergs/cm}^3 )</th>
<th>Crystalline anisotropy energy ( \text{ergs/cm}^3 )</th>
<th>Magnetostrictive energy ( \text{ergs/cm}^3 )</th>
<th>Shape anisotropy energy ( \text{ergs/cm}^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2.8 \times 10^7 )</td>
<td>( 6 \times 10^5 )</td>
<td>( 10^3 )</td>
<td>( 6 \times 10^6 )</td>
</tr>
</tbody>
</table>
SECTION 3 Experimental Techniques

The various experimental techniques used to investigate the effect of magnetic fields on transformations in steels during quenching and tempering are described in this section. Some of the preliminary experimental methods used are also included so as to justify the modifications and refinements subsequently made.

3.1 The effect of a magnetic field on martensite formation

3.1.1 General procedure

Previous workers (1-10) have used indirect means of establishing the change in the amount of martensite formed, dilatometric and saturation magnetization being the favoured methods. This is perfectly adequate for tracing a shift in the $M_s$ temperature but requires careful interpretation if studies are to be made on the progress of martensite transformation below the $M_s$. Accordingly it was thought worthwhile to study the effect of a magnetic field on the martensite transformation by using the Greninger-Troiano technique (110) which allows a direct metallographic estimation of the amount of martensite formed as the transformation proceeds below the $M_s$.

Specimens 4 mm in diameter and 8 mm in length were homogenised in a vacuum $< 2 \times 10^{-5}$ torr at $880^\circ$C for 15 hours and then austenitized at $1100^\circ$C for 30 minutes in a nitrogen atmosphere. The magnetic-heat treatments were performed by air-cooling the specimens to various temperatures below the $M_s$ between the poles of a 4" Newport electromagnet arranged to give a field of 16 K. Gauss. Cooling curves were recorded on a Leeds-Northrup Azar recorder, and as soon as a predetermined temperature below the $M_s$ was reached, the specimen was reheated to $190^\circ$C for 75 secs (alloy 1) and $600^\circ$C for 20 secs (alloy 2) (see Table 13 and 14 for details) to temper any martensite present and then quenched in water. The volume fraction of martensite formed during the initial quench was calculated using a Swift point-counter and a count of 800 points per specimen. The individual items in the overall procedure will now be
FIGURE 36 SPECIMEN HOLDING JIG

C---- Cage      S.T. Stainless Steel Tube      G---Gas Inlet
G --- Guide (Stop) P---Clamp       T. Thermocouple     S---Specimen
discussed in greater detail.

3.1.2. Materials

The compositions of the alloys used are given in the table below:

Table 13 Composition of alloys

<table>
<thead>
<tr>
<th>Chemical Composition %</th>
<th>A.S.T.M. Grain Size No</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Alloy 1</td>
<td>0.65</td>
</tr>
<tr>
<td>Alloy 2</td>
<td>0.3</td>
</tr>
</tbody>
</table>

3.1.3 Method of quenching and specimen-holding jig

Preliminary investigations showed that the effect of the magnetic field (upto 16 K. Gauss) was the same whether the field was applied along the axis of the specimen or at right angles to the axis. Vertical quenching was eventually favoured because it offered the following advantages: (1) simplicity of design and construction of the specimen-holding jig (2) rapid transfer of the specimen from the furnace to the gap between the poles of the magnet aided by a guided gravitational fall (3) better reproducibility in the location of the specimen between the poles of the magnet.

The specimen-holding device is shown in Fig. (36). A thin-walled stainless-steel tube 36" in length and 1/4" dia. was taken and cuts were made at one end along the length 90° apart. The four steps that formed were bulged slightly convex in the middle to form a cage (c) to house the specimen. A 28" gauge chromel/alumel thermocouple, spot welded onto the specimen, supported the specimen in the cage. The thermocouple passed through the bore of the stainless steel tube and was connected to
Fig 37 ELECTRO MAGNET
Figure 38 Temperature Gradient Along the Furnace

Height from the Bottom of the Furnace (inches)

Temperature °C
FIGURE 39 GENERAL VIEW OF THE APPARATUS FOR MAGNETIC HEAT TREATMENT.
FIGURE 40 TEMPERATURE INDUCED MAGNETIC VOLTAGES IN THERMOCOUPLE WIRES (\(\mu V\))

(a) magnetovoltage independent of direction of field
(b) equivalent thermocouple
(c) magnetovoltage dependent on direction of field
(d) equivalent Nernst effect.

\[ \Delta E = K \frac{\Delta T}{\Delta T} \]
FIGURE 41(a) FIELD DIRECTION INDEPENDENT MAGNETIC VOLTAGE IN ALUMEL WIRE (IDF) (111).

FIGURE 41(b) RELATIVE VALUES OF DDF MAGNETOVOLTAGE FOR CHROMEL AND ALUMEL WIRES AS FUNCTION OF A POSITIVE TEMPERATURE GRADIENT (111).
a Leeds and Northrup Azar recorder. The stainless steel tube, with the specimen in the cage was held in the furnace (with the specimen at the centre of the furnace) by a clamp (p), during austenitising. When the clamp was released a guide (G) attached to the tube at the top directed the cage to drop vertically. The height of the drop was adjusted by a stop such that the specimens was positively located at the centre of the gap between the poles of the magnet at the end of the fall.

3.1.4 Magnetic field

The main features in the design and construction of the Newport magnet are shown in Fig. 37. The yoke BC is a forging of dead mild steel (magnetically as soft as possible). The pole pieces AA' and DD' are also made of dead mild steel or soft iron. Plane pole tips or conical pole tips made of a high permeability alloy (such as Mu-metal) are fixed to the pole pieces at A' and D' by axial steel bolts. The distance between the pole tips (i.e. the gap) could be varied by a screw adjustment mechanism S and S'. The magnet is excited by a current supplied to the coils x and y from a 10 K.W. rectifier. Provision was made for reducing the current gradually before switching off by incorporating two high duty rheostats in the magnetic circuit.

A considerable amount of energy is stored in the magnetic circuit and if the circuit is broken off suddenly, the arcs which can be formed due to sudden interruption of the circuit can be dangerous. The rheostats were therefore always used except in experiments where it was necessary to have a sudden change of field.

3.1.5 Austenitising furnace and austenitising conditions

A Kanthal-wound vertical furnace was used for austenitising the specimens. A relatively high austenitizing temperature was chosen to obtain a large grain size and a coarse martensite structure. A high temperature also seemed preferable from consideration of work of Bernsteyn et al (7) which showed that the effect of magnetic field on martensitic transformation was more pronounced if the austenitising temperature of
the specimens was relatively high. The temperature of the furnace was controlled by an Ether Transitrol controller and a mercury switch. The controller operates from a chromel/alumel thermocouple placed in the small air gap between the outer and inner furnace tube, close to the furnace windings. To improve the temperature control, a resistance \( R/3 \) (\( R \) being the resistance of the furnace winding) was connected in parallel with the mercury switch. This gave a better temperature control as the current to the furnace windings was never cut off to zero but fluctuated from a value \( i \) to \( 3/4 \, i \) (\( i \) being the current flowing through the furnace winding with the mercury switch on). The power input to the furnace was regulated from a Variac transformer. Before the furnace was used the operating characteristics were established; the temperature gradient along the central zone of the furnace is shown in Fig. 38. At 1100°C the overall temperature gradient, 1 inch from the centre was ± 8°C. This was considered adequate for austenitising.

The temperature of the specimen was recorded by a 28\(^{\text{th}}\) gauge chromel/alumel thermocouple, spotwelded onto the specimen at the centre. The distance between the spotwelds of individual wires was \( \approx 1 \text{mm} \) and the position of the spotwelds was maintained the same in all experiments.

3.1.6 Magnetic heat-treatment

After austenitising, the magnetic heat treatments were performed by cooling the specimens in air to various temperatures below the \( M_s \) between the poles of the electromagnet. The arrangement for the heat-treatment with the furnace, electromagnet and the specimen holding device is shown in Fig. 39. The cooling curves were recorded on a Leeds and Northrup Azar recorder with suppressed zero facilities. A full scale deflection of 2mV or 5mV was used depending on the sensitivity required.

3.1.7 Limitations in the use of thermocouple in magnetic fields

When a thermocouple is placed in a magnetic field two types of magnetovoltage are produced - one independent on the direction of the field (IDF) and the other dependent on the direction of the field (DDF).
Fig. 40 a and b show the source of IDF magnetovoltage. A thermocouple wire, along which a longitudinal temperature gradient exists, develops a magnetovoltage, when placed in a magnetic field (111). The magnitude of the voltage does not depend so much on the temperature gradient in the wire, as on the temperature difference between the hottest and the coldest parts of the wire in the field. Figure 41a shows the variation of IDF voltage with temperature difference in a field of 9 K. Gauss. It is seen from the Figure that the magnitude of the voltage is only of the order of 0.12 - 0.30 \( \mu V \) per deg, which is negligible compared to the thermoelectric power of a chromel/alumel thermocouple which is 40 \( \mu V \) per deg °C.

When a temperature gradient exists along the diameter of the wire and when a magnetic field is applied at right angles to the directions of the temperature gradient and to the axis of the wire (i.e. the plane of the diagram 40 c and d) a magnetovoltage is induced at the ends of the wire proportional to the applied field and to the temperature gradient according to the equation:

\[
\Delta E = K \frac{\Delta T}{\Delta Y} HY
\]

where \( \Delta E \) is the induced DDF voltage, \( \frac{\Delta T}{\Delta Y} \) the temperature gradient along the diameter of the wire, \( Y \) the diameter of the wire and \( H \) the applied field. Fig. 41b shows the relative magnitudes of DDF voltage for chromel and alumel, in a field of 9 K. Gauss for a positive temperature gradient. For alumel, (for which the effect is maximum) the magnitude of DDF voltage at a field of 9 K. Gauss would be 12 \( \mu V \) corresponding to a temperature gradient of about 12°C, between the two ends of the wire. This corresponds to an error of about \( 1/4 - 1/5 \)°C. Even with a field of 16 K. Gauss the recorded temperature of the specimen would therefore only be affected by \( < 1/2 \)°C.

It is thus seen that in low fields the induced magnetovoltages are of much smaller magnitude, compared to the thermoelectric voltages.
FIGURE 42  ISOTHERMAL TRANSFORMATION DIAGRAM
FOR Fe 1C 1.4 Cr. ALLOY
FIGURE 43  ISOTHERMAL TRANSFORMATION DIAGRAM FOR
Fe 0.32 C  2.4 Ni  0.7 Cr  0.5 Mo Steel
(Similar in composition to alloy2)
3.1.8 Up-quenching conditions

After austenitising the specimens were cooled to various temperatures below the $M_s$. They were returned to the austenitising furnace and held in a predetermined temperature zone for a short time $T$ (Table 14) to temper any martensite present and then quenched in water. The optimum conditions were obtained by experiments based on $T$-$T$-$T$ curves for the two steels (Figures 42, 43).

<table>
<thead>
<tr>
<th>Table 14</th>
<th>Up-quenching conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp $T^\circ C$</td>
</tr>
<tr>
<td>Alloy 1</td>
<td>190</td>
</tr>
<tr>
<td>Alloy 2</td>
<td>600</td>
</tr>
</tbody>
</table>

Stevens and Haynes (112) have pointed out that tempering times during up-quenching must be sufficiently short to avoid the formation of lower bainite which on micro-examination would be indistinguishable from martensite. The formation of lower bainite is also known to be accelerated by the presence of martensite. In the case of alloy 1 (Fe 1C 1.5Cr) the incubation time for the formation of lower bainite is quite long (Fig. 42) due to the high carbon content; hence up-quenching conditions are not very critical. However in the case of alloy 2 the bainite-incubation time is quite short; so the up-quenching conditions were thoroughly investigated before arriving at the optimum conditions. In some specimens traces of bainite were detected, but these were subsequently found to have formed not during up-quenching, but during air-cooling from $500^\circ C$ to $M_s$. In order to minimise such bainite formation, the cooling rate below $500^\circ C$ was accelerated by using a cold blast of nitrogen.
3.1.9 Point counting

The volume fraction of martensite formed was estimated using a Swift point counter and a count of 800 points per specimen. Magnifications of 150 and 450 were used for alloy 1, while for alloy 2, the counting was done using a magnification of 900. The standard deviation was calculated (113) to be .008 at 10% martensite and .013 at 50% martensite. The accuracy of this technique decreases as the percentage of martensite increases, because samples containing more than 50% martensite contain considerable areas at the junction of tempered and untempered martensite which cannot be easily classified as tempered or untempered.

3.2 The effect on intermittent (periodic) application of a field in the transformation range

The effect of periodically (or locally) applying and removing a field below the $M_s$ was investigated for alloy 1 and alloy 2 by a study of the associated cooling curves. The same experimental arrangement as that used to obtain the martensite transformation curves (Section 3.1) was used for this investigation. The cooling curves were recorded on a Leeds-Northrup speedomax recorder, using zero suppression facilities to increase the sensitivity of the instrument in the temperature of martensite transformation.

The results and implications of the study of the cooling curves are discussed in Section 4.4.

3.2.1 Effect of continuous and local application of a magnetic field below the $M_s$

In order to correlate the additional amount of martensite formed at any temperature $T$ below the $M_s$ with the field applied continuously in the transformation range with the extra-martensite formed when a field is applied locally at that temperature, a simple experiment using the Greninger-Troiano technique (110) was performed.

One of the specimens of alloy 1 (Fe 1C 1.5Cr) was austenitised at $1100^\circ$C and cooled to a predetermined temperature below the $M_s$ ($85^\circ$C).
As soon as the temperature was reached, a field of 16 K Gauss was applied for a short period. The specimen was then quickly withdrawn into the furnace, tempered under standard conditions (190°C, 75 secs) and then quenched. The amount of martensite formed was estimated by point-counting. The results are given in Section 4.4.2 and the implications of the results in evaluating the heat of transformation are dealt with in Section 5.5.

3.3 Effect of magnetic-heat treatment on the hardness of quenched steels

3.3.1 Introduction

Having studied the effect of a magnetic field on martensitic transformation of two steels, it was decided to investigate the influence of this effect on the mechanical properties. Preliminary tensile tests using a Hounsefield tensometer on martensites, quenched in a field and without a field gave a large scatter band due to the notch sensitivity of the extremely brittle martensitic structure. Hence hardness measurements were used as a guide to mechanical property changes (Section 2.8).

3.3.2 Materials

Four different steels were chosen for investigation and their compositions are given in Table 15. The specimens were vacuum annealed at 880°C for 15 hours and then austenitised and quenched both with and without a field.

3.3.3 Magnetic heat-treatment

Two types of magnetic heat-treatments were given -

1) Axial quenching in a field of 6.2 K Gauss - the axis of the specimen being parallel to the direction of the field.

2) Transverse quenching in a field of 16 K Gauss - the axis of the specimen being perpendicular to the direction of the field.
FIGURE 44  SPECIMEN HOLDING JIG FOR AXIAL QUENCHING.
Fig. 45. Schematic arrangement for Axial Quenching in a field

F: furnace  S: specimen holding jig  T: stainless steel tube
I: Gas Inlet  G: Guide  M: Magnet

(Note: Water inlet W not shown in the diagram)
3.3.4 Specimen holding jig for axial quenching

In order to locate the specimen axially in a magnetic field, a jig made of a heat-resisting steel was constructed (Fig. 44) incorporating the following features in its design:

1) minimum mass - to cut down the heat transferred from the jig to the specimen during quenching

2) sufficient rigidity so that the jig holding the specimen is not displaced by the magnetic field

3) simplicity of design - to minimise distortion due to quenching stresses.

The specimen was held in the jig by catches at each end (C & C') which slide across the specimen. A thin-walled stainless steel tube ½" O.D., was welded onto the centre of the jig, as shown in Fig. 44. A 28" gauge chromel/alumel thermocouple was spot welded onto the specimen so that the entire cross-section of the specimen formed the hot junction of the thermocouple. The distance between the welds was maintained constant in all experiments. The thermocouple was threaded through the base of the stainless steel tube and connected to a Leeds and Northrup speedomax recorder. Cooling curves were recorded in each experiment to check that the quenching was satisfactory.

3.3.5 Preliminary experiments

Preliminary experiments were conducted by coating the specimen with a heat-resistant coating 'Berketet' and also by nickel plating the surface before austenitising. These specimens were then quenched axially in a field of 6.2 K. Gauss and hardness measurements were made using a standard Vickers testing machine. The results (which are given in Section 6.1.1) indicated an increase in hardness on magnetic heat treatment.

Having ascertained that there was a reasonable increase in hardness, it was decided to conduct further magnetic heat-treatment in an inert atmosphere.
3.3.6 Quenching arrangement for magnetic heat treatment in an inert atmosphere

The schematic arrangement for axial quenching in a field of 6.2 K. Gauss is shown in Fig. 45. In order to transfer the specimen and the jig quickly and effectively from the furnace to the centre of the magnet, a guide G was fixed to the stainless steel tube. The guide moved freely over a pair of brass rails which ran inside the copper tube. The distance between the centre of the guide G and the specimen was adjusted to be equal to the distance between the centre of the poles of the magnet and the end of the copper tube. The tube W (which has an elliptical cross-section) was connected to the water inlet. To quench the specimen, the stainless steel tube was withdrawn from the furnace (by gently pulling away) until the rider moving along the brass rails stopped at the end of the copper tube. With the rider in this position the specimen located itself in between the poles of the magnet. The whole quenching assembly was slightly inclined to prevent any water from entering the furnace.

3.3.7 Transverse quenching

For axial quenching, it was necessary to work with relatively large air gaps between the poles of the magnet and hence the field strengths obtained had to be restricted to 6 - 7 K. Gauss. By switching over to transverse quenching - where the axis of the specimen was perpendicular to the direction of the field, it was possible to reduce the air-gap between the poles of the magnet to about 2 cms; hence a higher field of the order of 16 K. Gauss was available for magnetic - heat-treatment.

The general arrangement for transverse quenching in a field of 16 K. Gauss is described in Section 3.1.

3.3.8 Hardness measurements

Hardness measurements were made on quenched specimens using a standard Vickers hardness testing machine and 30 K. Gauss load. 8 hardness readings were taken on each specimen.
The V-P-N hardness value, with a 30 K. Gauss load gives only the average hardness (or the overall hardness) of the specimen since the size of the indentation is so large that it invariably covers more than one phase. In order to get more detailed information of the hardness of the individual phases, microhardness tests were made using a G-K-N microhardness tester with a 10 gm load. Another advantage of microhardness tests is that a large number of hardness values be obtained from a single specimen (150 per specimen compared with about 8 macro-indentations).

3.4 The effect of quenching in a magnetic field on the kinetics of the first stage of tempering

3.4.1 Procedure

Two alloys, a 1.4C steel and Fe 1C 1.5Cr alloy (alloy 1 of section) were chosen for investigation. Specimens 0.8" in length and 0.25" dia (Fig. 46) were machined from as-received rods and homogenised in a vacuum better than 2 x 10^-5 mm of Hg at 880°C for 15 hrs. They were then austenitised at 1100°C, quenched in a field and without a field and then tempered to various temperatures between 80-150°C without a field. The tempering kinetics was followed by a dilatometric method. Magnetic measurements were also made on the tempered specimens, using a differential Hall-probe technique. From the dilation curves the overall activation energy for the first stage of tempering could be calculated.

Details regarding the method of quenching, strength and direction of the applied field and tempering temperatures are given in Table 16.

3.4.2 Quenching procedure for 1.4%C steel

The specimens were austenitised at 1100°C for \( \frac{1}{2} \) hour in a nitrogen atmosphere and then quenched in a flowing stream of water between the poles of an electromagnet with the axis of the specimens being parallel to a field of 6.2 K. Gauss. The details of the quenching arrangement are described in Section 3.3.4.
FIGURE 46 DILATOMETER SPECIMEN
GAUGE LENGTH 0.8"
DIAMETER ¼"

FIGURE 47 DILATOMETER ASSEMBLY
3.4.3 **Tempering**

The quenched specimens were tempered at 80°, 100°, 120° and 140°C in a bath of silicone oil. Occasionally specimens which cracked during quenching were rejected and repeated runs were made. About an hour elapsed between quenching and tempering for each specimen.

1) **Tempering baths**

Two tempering baths were used: (1) silicone oil (for 1.4C steel) and (2) woods metal bath for (Fe 1C 1.5Cr alloy). The same methods of temperature control was used as for the austenitising furnace with additional provision for stirring in the case of the silicone oil bath. The temperature fluctuation, in case of the metal bath, was within ± 1°C where as for the oil bath it was ± 2°C.

2) **Liquid nitrogen treatment before tempering**

A quenched high carbon steel contains martensite and retained austenite and the presence of retained austenite could affect the tempering kinetics. It was therefore considered worthwhile to study the tempering kinetics, starting with a fully martensitic structure. Accordingly, some of the specimens were quenched in a field of 6.2 K. Gauss and without a field and immediately transferred to a bath of liquid nitrogen to transform as much of the untransformed austenite present at room temperature as possible. These liquid-nitrogen treated specimens were then tempered at 140°C.

3.4.4 **Dilatometry**

A dilatometer was constructed to follow the tempering kinetics of the first stage of tempering; the essential features are shown in Fig. 47. The dilatometer consists of two silica tubes 15" in length and 4 mm internal diameter, which are held vertically by a Nilo-Collar cemented to the tubes at the upper end by araldite. The lower ends of the tube were sealed with a thick-walled silica tube (1" in length) having a 3 mm bore at the centre to support the specimen at one end. A fused silica tube 15" in length and 3 mm I.D. was ground optically flat and located centrally in between the
two silica tubes, one end making contact with the specimen and the other end actuating a transducer through a niloc® push rod. A relatively long tube was used to reduce the effect of heat convected upwards from the tempering bath, which would otherwise cause expansion of the push rod and the measuring device.

3.4.5 Transducer, multimeter and recorder unit

A differential inductance linear displacement transducer coupled with a Pendeford multimeter c 21 Mark 2 was used to measure the dilation of the specimen. The transducer selected was of type F 13 A (Bolton Paul Aircraft Ltd.) which measures relative displacements up to 0.025". The transducer consist essentially of a movable armature and two small coils which are connected to form two arms of a bridge network (energised by 5 V at 1 k c/s). Movement of the armature varies the inductance of two coils differentially which unbalances the bridge, producing an output signal at 1 k c/s, proportional in phase and magnitude to the displacement of the armature from its central position. The output signal after passing through an attenuator system is amplified and converted to D.C. by means of a phase sensitive detector. The D.C. signal can be read on the indicated meter, calibrated to a full scale deflection of .001" or can be recorded on a Leeds and Northrup speedomax recorder. Correlation between the multimeter readings and the chart scale on the potentiometer was obtained using a helipot potentiometer between the output from the multimeter and the input to the recorder. This arrangement enables length changes to an accuracy of $\pm 10^{-6}$ inch to be detected.

In order to reduce the specimen vibration during the introduction of the specimen to the tempering bath, the dilatometer assembly was fixed and the tempering bath was lifted by pulleys and counterweights.

3.4.6 Electron metallography

Since dilatometric, magnetic and hardness measurements were made using the same specimen, it was decided to use the same specimen (i.e. bulk specimen, Fig. 46) and look for any structural details using am
electron metallography (details such as precipitation of carbide at the austenite-martensite interface). Attempts to obtain thin foils using a combination spark cutting machine (to cut thin discs) and P.T.F.E. technique (for electro polishing) proved unsuccessful, because of several inherent limitations associated with the technique such as attack on the edges, and non uniform thinning. Consequently a carbon extraction replica technique was used instead and the replicas examined in an Akashi transcope microscope.

3.4.7 Tempering retained austenite

After studying the tempering kinetics of the decomposition of primary martensite, the specimens were re-tempered at a higher temperature (240°C) to find out whether quenching in a magnetic field had any effect on the decomposition of retained austenite. In addition it was thought that an estimate of the relative amounts of retained austenite present in the steels quenched in a field and without a field could be made from any dilation attributable to the decomposition of retained austenite.

3.4.8 Tempering kinetics of the Fe 1C 1.5Cr alloy

Having studied the tempering kinetics of 1.4C steel in detail it was considered worthwhile to check the tempering kinetics of another high carbon steel, altering certain variables such as the strength of the field.

Dilatometric specimens of alloy 1 (Fe 1C 1.5Cr) were quenched in a jet of water in a field of 16 K. Gauss, the direction of field being perpendicular to the axis of the specimen. The quenched specimens were immediately transferred to a metal bath and tempering kinetics followed by a dilatometric method. Only two tempering temperatures were used (130 and 150°C) as it was not intended to study the kinetics in detail. The experiments were repeated using fully martensitic specimens, obtained by prior cooling the water-quenched specimens in liquid nitrogen.
FIGURE 49  CALCULATION OF FLUX DENSITY B.

FIGURE 48  PRINCIPLE OF THE HALL EFFECT.

FIGURE 53  METHOD FOR INCREASING THE ACCURACY IN THE DETERMINATION OF B.
FIGURE 54 VARIATION OF MAGNETIC FIELD IN THE GAP BETWEEN THE POLES OF THE MAGNET.

FIGURE 52 A PLOT OF $B$ FOR A MAGNET.
3.5 The differential Hall probe method of magnetic analysis

3.5.1 Procedure

The tempered specimens were fixed in a saturation magnetization jig and their saturation magnetizations were compared relative to that of a standard using a differential Hall probe and a Gaussmeter, Bell 120 (Fig. 51).

3.5.2 Principle of the Hall-probe technique

A Hall-probe consists of a sensing element which is a small thin crystal of a semiconductor such as indium arsenide.

Consider a Hall probe a c b and d (Fig. 48) through which a steady current \( i \) flows in the direction a b. If now, the probe is placed in a magnetic field of flux density \( \vec{B} \) perpendicular to \( \vec{i} \), some of the charge carriers will be deflected in the direction \( \vec{B} \times \vec{i} \) (i.e. at right angles to \( \vec{B} \) and \( \vec{i} \)) resulting in a Hall voltage \( E_H \) developing across the faces c d, the magnitude of \( E_H \) is given by:

\[
E_H = \frac{R B i}{t} \quad \text{2.29}
\]

where \( R \) is called the Hall coefficient and \( t \) the thickness of the probe.

From equation 2.29 it follows, if a steady current \( i \) passes through the probe, the Hall voltage \( E_H \) developed will be directly proportional to the magnetic flux density, \( \vec{B} \) linking with the probe (\( \vec{B} \) being at right angles to \( \vec{i} \)).

3.5.3 Calculation of magnetic induction \( B \)

When a ferromagnetic specimen is placed in a magnetic field \( H \), the flux density inside the specimen is increased by an amount given by:

\[
B = H + 4 \pi I \quad \text{2.30}
\]

where \( B \) is the magnetic induction or flux density, \( H \) the applied field and
I the magnetic moment or intensity of magnetization per unit volume.

(The symbol \( J \) is used in Section 5.2 to refer to saturation magnetization/ mol).

The magnetic induction at a point \( x \), just inside the material is given by (114):

\[
B = 2\pi I \sin \alpha \quad \text{.................................. 2.30a}
\]

\[
B = \frac{2\pi I}{\sqrt{a^2 + l^2}} \quad \text{.................................. 2.30b}
\]

\[
B = 2\pi I - I S / l^2 \quad \text{.................................. 2.30c}
\]

where \( S \) is the cross sectional area \( (l) \) the length and \( (a) \) the diameter of the specimen.

The magnitude of \( B \) at a point \( x \) just outside the material is the same as that just inside, since the normal component of \( B \) must be continuous (115). By using a specimen, whose length is very much greater compared to the diameter \( (l > 2a) \) the flux density just outside the specimen could be written as:

\[
B = H + 2\pi I \quad \text{.................................. 2.31}
\]

If a Hall probe is placed at the ends of the specimen, such that all the field emerging out of the specimen links with the probe then from the field measured by the probe the overall saturation magnetization of the various constituents in the specimen could be calculated, provided the magnetizing field \( (H) \) is sufficiently strong to saturate the specimen. The amount of ferromagnetic content in the specimen can then be calculated, knowing the saturation magnetization of a standard containing 100 pet of the same ferromagnetic phase. In order to increase the sensitivity, and to eliminate the possible effects of non uniformity of the field around the specimen, it is preferable to use a differential technique. Here the saturation magnetization of the specimen is compared with that of the standard and the difference measured.
FIGURE A6 SPECIMEN USED FOR MAGNETIC MEASUREMENTS.
(SAME AS DILATOMETER SPECIMENS)

FIGURE 50(a) SATURATION MAGNETIZATION JIG.
FIGURE 50b SATURATION MAGNETIZATION JIG.
FIGURE 51 APPARATUS FOR DIFFERENTIAL HALL PROBE METHOD OF MAGNETIC ANALYSIS.
As the magnetic measurements are concerned with tempered martensitic structures in the current investigation, it was decided to choose a standard, having as fully a martensitic structure as possible. This was obtained by using one of the specimens of the same material (having the same dimensions and shape) austenitized (under the same conditions), quenched in water and cooled to liquid nitrogen temperature.

3.5.4 Design and construction of the Jig

The design of the saturation magnetization jig for locating the specimen and the standard, together with the differential probes is shown in Figs. 50 a and b. The specimen M, and the standard are located symmetrically with respect to the line joining the centres of the poles of the electromagnet, in the holder S and held rigidly in position by screws $S_1$, $S_2$, and $S_3$. The Hall probes $P_1$ and $P_2$ are fixed at one end such that all the flux emerging out of the specimen and the standard link with the probes. As pointed out in Section 3.5.2 this is one of the stringent requirements since the principle of this technique is to measure the field in the space immediately outside the specimen in conditions which justify the assumption that value of field so obtained applies also inside the specimen. The positions of the probes, the specimen and the standard, with respect to the line joining the centres of the poles of the magnet, are maintained the same in all experiments. The magnetization jig is fixed rigidly in between the poles of the magnet by means of a brass bolt B.

3.5.5 Accuracy of measurement

Possible sources of errors can be listed as follows:

1) lines of induction emerging out of the specimen may not be parallel to each other

2) non-reproducibility in the location of the specimen with respect to the probe

3) non-uniformity of the field in the gap.
4) errors associated with the conversion of Hall probe readings to saturation magnetization if the magnetizing fields are not strong enough to saturate.

1) Fig. 52 illustrates the directions of the lines of flux emerging out of a ferromagnetic material. The lines of flux will not be parallel at the ends; hence the probe must be confined to a region around the centre of the specimen to ensure that the lines of force are parallel. Another way of satisfying this requirement would be to make a small groove in the specimen Fig. 53 and place the probe in the groove. Since the probe is surrounded on either side by a ferromagnetic material, not only will the lines of \( \mathbf{B} \) be parallel but the condition that \( \mathbf{H} \) be perpendicular to \( \mathbf{I} \) will also be fulfilled.

2) The error due to non-reproducibility in the location of the specimen could be easily eliminated by fixing the specimen and the standard in the saturation magnetization jig such that their ends are gently touching the probes.

3) The third error namely non-uniformity in the field is largely eliminated by using the differential method of measurement. Fig. 54 shows the variation of the field across the gap for plane pole tips. By using standards of known ferromagnetic contents (covering the range of ferromagnetic contents likely to be measured in the experiments) and applying the given field a calibration curve can be obtained. Even without the calibration the results can be used to estimate the relative content of ferromagnetic constituents but not absolute values.

The problem of obtaining standards of known ferromagnetic contents is not so easy to tackle. Greninger and Troiano up-quenched-specimens—unfortunately are not suitable as both tempered and untempered martensites
have more or less the same ferromagnetic constituents.

The differential Hall probe readings have therefore been used in a relative sense although it should be noted that the relation between magnetic and dilation results (Section 6.2.8), suggests that the figures may be quantitative.

3.5.6 Evaluation of tempering kinetics by magnetic analysis

Let $I_M$ be the saturation magnetization of a sample of a fully martensitic structure. Let $I_{M+E}$ be the overall saturation magnetization of the ferromagnetic phases (of the same sample) at the end of the first stage of tempering. If $I$ be the saturation magnetization of a sample partially tempered during the first stage, then the extent of decomposition of martensite $x$ is given by:

$$x = \frac{I_M - I}{I_{M+E} - I}$$

$x$ will be directly proportional to the amount of tempering during the first stage.
SECTION 4  RESULTS - EFFECT OF A MAGNETIC FIELD ON MARTENSITE FORMATION

4.1 Introduction

The results presented in this section fall into two groups,

1) Martensite transformation curves for alloys 1 and 2 with and without a field.

2) The effect of periodically applying and removing a field below the \( M_S \) on the associated cooling curves.

4.2 Determination of the \( M_S \) temperature

As already mentioned in Sections 3.1 and 3.2 a relatively high austenitising temperature was chosen to obtain a large grain size in order to give readily countable coarse martensite plates in the subsequent Greninger-Troiano treatment. Some difficulty was however experienced in determining a criterion for the precise location of the \( M_S \). The investigations of Wells (116) and Brook et al (74) have shown that a high austenitising temperature produces an initial non-linear portion in the transformation curves and the general shape of the martensite transformation curves is not well established although several attempts have been made (72, 112). It is thus not clear whether a gradual beginning is a general feature of all transformation curves (117).

In view of the uncertainties and errors involved in establishing the exact beginning of transformation, it was decided to extrapolate the experimentally determined portion of the curve to zero percent transformation and define the \( M_S \) as the point of intersection of this curve with the temperature axis.

4.3 Martensite transformation curves

Figs. 55 and 56 show the martensitic transformation curves with and without a field for the two alloys. The transformation was not followed beyond 55-60% martensite because the accuracy of the technique decreases as the percentage of martensite increases (Section 3.1.9).
FIGURE 55  MARTENSITE TRANSFORMATION CURVES FOR Fe-1Cr ALLOY
(austenitised at 1100°C)

○ with a field of 16 K. Gauss
○ without a field
FIGURE 56
MARTENSITE TRANSFORMATION CURVES FOR
Fe 0.3C 2.8Ni 0.6Cr 0.6Mo ALLOY
(austenised from 1100°C)

○ with a field of
16 kGauss

- without a field

Percent Martensite

Temperature
FIGURE 57: THE INCREASED PERCENTAGE OF MARTENSITE PRODUCED BY A MAGNETIC FIELD OF 16 K. GAUSS PLOTTED AS A FUNCTION OF TEMPERATURE BELOW THE $M_s$.

Graph showing the percentage of martensite as a function of $(M_s - T)$ degrees for different compositions:

- Fe 1% C 1.5Cr
- Fe 0.3C 2.5Ni 0.6Cr 0.6Mo
FIGURE 59(a) MARTENSITIC TRANSFORMATION CURVES FOR Fe 30Ni ALLOY WITH A FIELD AND WITHOUT A FIELD (Fokina).

FIGURE 60 MARTENSITIC TRANSFORMATION CURVES FOR Fe 0.6C 8Ni 4Cr 3Si ALLOY WITH A FIELD AND WITHOUT A FIELD.
ALLOY Fe-30Ni
FIELD 350 K. Gauss

FIGURE 59(b) PERCENTAGE OF EXTRA-MARTENSITE PRODUCED IN A MAGNETIC FIELD AS A FUNCTION OF TEMPERATURE DROP BELOW THE $M_s$. 
FIGURE 61 TYPICAL CHANGES IN TEMPERATURE RESULTING FROM THE APPLICATION AND REMOVAL OF A MAGNETIC FIELD DURING THE TRANSFORMATION OF AN Fe 8%Cr ALLOY.
FIGURE 62 EFFECT OF INTERMITTENT APPLICATION OF A FIELD IN THE TRANSFORMATION RANGE FOR Fe 0.3C 2.3Ni 0.6Cr 0.6Mo ALLOY.
Figure 63: Schematic Explanation of the Effect of Local Application of a Field in the Transformation Range (Estrin).
(Solid curve indicates the course of the transformation.)
FIGURE 64  SCHEMATIC EXPLANATION OF THE REMOVAL OF FIELD IN THE TRANSFORMATION RANGE. (Estrin)
(Solid curve indicates the curve of the transformation).
a) Cooled to 95°C in a field (16 K. Gauss). x 150
Etchant Nital

b) Cooled to 95°C without a field. x 150
Etchant Nital

FIGURE 58 a and b  MICROSTRUCTURES OF Fe 1C 1.5Cr ALLOY TRANSFORMED IN A FIELD AND WITHOUT A FIELD. (After up-quenching treatment).
c) Cooled to 85°C in a field (16. K. Gauss).  x150
Etchant Nital

d) Cooled to 85°C without a field.  x 150
Etchant Nital

FIGURE 58 c and d  MICROSTRUCTURES OF Fe 1C 1.5Cr ALLOY TRANSFORMED IN A FIELD AND WITHOUT A FIELD.
4.3.1 General features of the transformation curves

1) There is a shift in the $M_s$ temperatures when the transformation takes place in a magnetic field. In a field of 16 K. Gauss the shift in the $M_s$ for alloy 1 (Fe 1C 1.5Cr) is 5°C and for the alloy 2 (Fe 0.3C 2.8Ni 0.6Cr 0.6Mo) is 4.5°C.

2) The transformation curve is also shifted to higher temperatures and as a result a greater amount of martensite is formed at any temperature below the $M_s$ when a field is superimposed. This is clearly revealed in the microstructures of the Fe 1C 1.5Cr alloy, cooled to 95°C,85°C and then tempered. (Fig. 58).

3) The percentage of extra-martensite varies in a characteristic manner as the total percentage of martensite increases falling from a value of 8-9% just below the $M_s$ to a value of 4-5% at lower temperatures (i.e. at about 25-30% martensite) for both the alloys studied (Fig. 57 and Table 17).

The transformation curves for alloys 1 and 2 may be compared with the curves for Fe 30Ni (12) and Fe 0.6C 8Ni 4Cr 3Si (10) (Figs. 59a and 60). In the case of the Fe 30Ni alloy, a field of 350 K. Gauss produces an $M_s$ shift of 5°C, whereas in the other alloy the shift in a field of 19 K. Gauss is 3 - 3.5°C.

Fig. 59b shows how the percentage of extra-martensite produced in the Fe 30Ni alloy due to a field (350 K. Gauss) also varies as the transformation proceeds in a similar way to alloy 1 and alloy 2. A satisfactory explanation can be given for this behaviour in terms of the reduction in magnetic energy from $J_H$ to $J_H/2$ in a system of mutually interacting particles (Section 5.24). For the more complex alloy, Fe 0.6C 8Ni 4Cr 3Si, the transformation curves with and without a field diverge (Fig. 60); so other factors must be operating. However, little is known of the free energy characteristics of this alloy (Section 2.5).
4.4 Effect of a periodic application of the field in the transformation range

The effect of periodically applying and removing a field of 16 K. Gauss below the $M_s$ was investigated by a study of the associated cooling curves (Figs. 61 and 62). On application of a field (point A in Fig. 61) there is an increase in temperature of $\sim 3^\circ C$ which can be associated with the additional amount of martensite formed (Section 4.3.1). On removal of a field cooling proceeds without further transformation for a short time, the transformation only being resumed after a specific reduction in temperature has occurred. Further, it can be seen (Figs. 61 and 62) that the effect of a field is more pronounced when applied immediately below the $M_s$ than at a much lower temperature.

4.4.1 Correlation of the effect of periodic field with the $M_s$ shift

Figs. 63 and 64 give a schematic explanation of the effect following the treatment of Estrin (8) who found an identical pattern of behaviour. $M$ and $O$ (Figs 63 and 64) refer to the transformation curves in a field and without a field. The course of the transformation is indicated by solid curves. Fig. 63 illustrates the effect of applying a magnetic field while Fig. 64 illustrates the effect of removing the field. On application of a field at point A Fig. 63, the course of transformation changes from curve $O$ to $M$; hence the point A jumps from A to D and an additional amount of martensite is formed corresponding to the increment AD. On removal of a field at B the course of the transformation changes from curve $M$ to $O$; hence cooling proceeds without any further transformation till the point C is reached. The quantitative evaluation and significance of the results are discussed further in Section 5.5.

4.4.2 Comparison of the effect of a continuous and local application of a field on the extra-martensite formed below the $M_s$

The results of the effect of continuous and local application of a field (16 K. Gauss) on the percentage of martensite formed below the $M_s$ (at $85^\circ C$) for the Fe 1C 1.5Cr alloy are given in Table 18.
Table 18 Effect of continuous and local application of a magnetic field on percentage martensite at 85°C.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe 1C 1.5Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage martensite without a field</td>
<td>27</td>
</tr>
<tr>
<td>Percentage martensite with the field</td>
<td>36</td>
</tr>
<tr>
<td>applied continuously during cooling</td>
<td></td>
</tr>
<tr>
<td>Percentage martensite with the field</td>
<td>33</td>
</tr>
<tr>
<td>applied locally at 85°C</td>
<td></td>
</tr>
</tbody>
</table>

The implications of these results in the evaluation of heat of martensitic transformation in the alloy (Fe 1C 1.5Cr) are considered in Section 5.5.
SECTION 5 DISCUSSION OF THE EFFECT OF A MAGNETIC FIELD ON MARTENSITE FORMATION

5.1 Introduction

Current understanding of the kinetics of martensitic transformation is surprisingly limited considering the amount of work that has been performed. Most theories deal only with the onset of the transformation, i.e., prediction of the $M_s$, rather than the progress after the transformation has been initiated. There is as yet no satisfactory method for predicting the slope of the transformation curve in the linear region (117). The discussion will accordingly deal with the start of the transformation and its progress separately and then relate both aspects with a particular thermodynamic characteristic of the phases in question.

It will also be shown that other property changes such as recalescence effects and hardness changes, follow directly from the effect of a magnetic field on the amount of martensite present (hardness results will be discussed in Section 7.1).

5.2 Explanation of the shift in the $M_s$ due to an applied field

Fig. 65 illustrates a simple thermodynamic model whereby it is possible to estimate the shift in the $M_s$ temperature due to an applied field.

5.2.1 Assumptions

1) As in most of the previous thermodynamic theories, classical equilibrium conditions are applied to martensitic transformation, which is a diffusionless non-equilibrium solid-state transformation. Thermodynamic equilibrium conditions are assumed so that the standard expressions for free energy can be used.

2) No clear distinction is made between the free energies of ferrite and martensite in the current analysis.
Both Fisher \(^{(41)}\) and Imai et al \(^{(44)}\) introduced an extra term \((\Delta F^*)\) into the free energy expression for the austenite to martensite transformation (\(\Delta F^{\gamma \rightarrow \alpha'}\)) which takes into account the preferential ordering of carbon atoms when b.c.T martensite is formed. This difference in free energy between \(\gamma \rightarrow \alpha\) and \(\gamma \rightarrow \alpha'\) is important but there is at present no way of determining which of the above two assumptions is correct. Fortunately it will be shown that the effect of a magnetic field is largely a function of the saturation magnetization of the phases concerned and this quantity does not seem to be materially affected by a preferential distribution of carbon atoms. Consequently the \(\Delta F^*\) is not critical for the purpose of explaining the \(M_s\) shift although it is highly relevant for the prediction of the \(M_s\) temperature per 5e.

3) Only the interaction energy term due to a field is taken into account (Section 2.9.2); the contributions made by other terms such as magnetocrystalline anisotropy energy are not taken into account. The magnetocrystalline anisotropy energy and magnetostrictive energy fall at least two orders of magnitude lower than that due to magnetic interaction energy (Table 12 Section 2.9.2). The shape anisotropy energy could be of considerable magnitude (i.e. of the order of 25% of the interaction energy for a martensite embryo having a length to thickness ratio of 20). However the model to be proposed in this Section is phenomenological, so the contribution due to shape anisotropy energy is not taken into account as this would entail specific assumptions regarding the size and shape of the embryos. In any case the shape anisotropy energy terms would not be to its full extent except in those martensite plates directly at right angles to the field.

4) A linear variation of the free-energy-temperature curves for austenite (\(\gamma\)) and martensite (\(\alpha'\)) is assumed in Fig. 65 although the actual free energy curves are known to be markedly non-linear \((51)\).

5) It is assumed that the interfacial and elastic constraints are unaffected by a magnetic field (this would be discussed in detail in Section 5.7.3).
5.2.2 Derivation of magnetic free energy terms

To start the formation of martensite the alloy has to be undercooled from $T_o$ (the equilibrium $\gamma \rightarrow \alpha'$ temperature) to the $M_s$ because energy has to be made available to overcome the interfacial and elastic restraints associated with the transformation. The free energy released when one mol of austenite transforms to martensite i.e. $\Delta F^{\gamma \rightarrow \alpha'}$, represents the chemical driving force of the transformation. When the transformation takes place in a magnetic field $H$, the free energy of each phase is reduced by an amount $J_x H$ where $J_x$ is the saturation magnetization of each phase (106). In the region of the $M_s$ temperature a given volume of the specimen can exist either as austenite or martensite, so that the difference in free energy $\Delta E_{mag}$ of a given volume element in the two crystal structures is:

$$\Delta E_{mag} = H \left[ J_{\alpha'} - J_f \right] \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 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\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots
FIGURE 65  LINEAR APPROXIMATION MODEL FOR $F_{\alpha}$ AND $F_{\gamma}$
FIGURE 66 VARIATION OF SATURATION MAGNETIZATION WITH TEMPERATURE FOR IRON (Bozorth).

\[ I_0 = \text{Saturation magnetization at } 0^\circ A \]
\[ T_C = \text{Curie Temperature} \]
generate a value of chemical free energy equal to \( \Delta F' \) will be reduced correspondingly; consequently the \( M_s \) will be shifted to higher temperatures.

The rise in \( M_s \), \( \Delta T \) can be calculated as follows:

Fig. 65 shows that triangles MNO and MTO are similar

\[ \frac{\Delta E_{\text{mag}}}{\Delta F'} = \frac{\Delta T_1 \sec \theta}{(T_0 - M_s) \sec \theta} \]

or \( \Delta T_1 = \frac{\Delta E_{\text{mag}}}{(T_0 - M_s) \Delta F'} \) \( 2.35 \)

If the heat of transformation \( q \) is known, this presents an alternative method for evaluating the shift in the \( M_s \):

Referring to Fig. 65 and comparing the similar triangles \( \triangle T_0^1 x \) and \( \triangle PQT_0 \):

\[ \frac{\Delta E_{\text{mag}}}{q} = \frac{\Delta T_2}{T_0} \]

or \( \Delta T_2 = \frac{\Delta E_{\text{mag}} T_0}{q} \) \( 2.36 \)

This relationship was first derived by Meyer and Tagland (11) for the magnetic transformation in Manganese-Arsenide. It is this equation that has been used by Krivaglaz and Sadovskii (12), Estrin (8) and other Russian workers (10) to calculate the shift in \( M_s \) due to an applied field.

A comparison of the \( M_s \) shift as observed by various experimental methods (direct as well as indirect) with the values calculated using equations 2.35 and 2.36 is given in Tables 19 and 20 and also in Fig. 67.

5.2.4 Variation of extra-martensite formed with the degree of transformation

Fig. 57 shows how the percentage of extra-martensite formed in a field changes in a characteristic manner as the total percentage of martensite increases, falling from a value of 8-9% just below the \( M_s \) to a
Table 19 Calculation of the $M_0$ shift using the relation $\Delta T_0 = \frac{\Delta E_{mag} T_0}{q}$

<table>
<thead>
<tr>
<th>Alloy Composition</th>
<th>Reference</th>
<th>Saturation * magnetization J Gauss/mol</th>
<th>Magnetic Field (H) (K. Gauss)</th>
<th>$\Delta E_{mag}$ (JH cal/mol)</th>
<th>$T_0$ °K</th>
<th>Heat of Trans: Calor:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe 1c 1.5Cr</td>
<td>-</td>
<td>12,070</td>
<td>16</td>
<td>4.6</td>
<td>640</td>
<td></td>
</tr>
<tr>
<td>Fe 0.3c 2.8Ni</td>
<td>-</td>
<td>11,640</td>
<td>16</td>
<td>4.5</td>
<td>830</td>
<td></td>
</tr>
<tr>
<td>0.6Cr 0.6Mo</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe 30Ni</td>
<td>(12)</td>
<td>10,350</td>
<td>350</td>
<td>87</td>
<td>420</td>
<td></td>
</tr>
<tr>
<td>Fe 0.5c 18.7Ni</td>
<td>(8)</td>
<td>11,110</td>
<td>18.7</td>
<td>5.1</td>
<td>480</td>
<td></td>
</tr>
<tr>
<td>Fe 0.58C 3Si</td>
<td>(10)</td>
<td>10,350</td>
<td>19</td>
<td>4.8</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>3.8Cr 8Ni 1.1Mo</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Saturation magnetization. Values were taken from reference (108)

** Values for $T_0$ and $q$ were either taken from reference (59) or were calculated from reference (59)
Table 20 Comparison of the observed $M_s$ shift and theoretical values calculated by different methods

| Alloy Composition | Magnetic Field $H$ (K. Gauss) | $\Delta E_{Mag}$ (JH Cal/mol) | $(T_o - M_s)^*$ | $|\Delta F^{y \rightarrow x}|_{M_s}^{**}$ | $\Delta T_1 = \frac{\Delta E_{Mag}}{\Delta F}$ |
|-------------------|-----------------------------|-----------------------------|----------------|--------------------------------|---------------------------------|
| Fe 1c 1.5Cr       | 16                          | 4.6                         | 260            | 265                            | 4.5                             |
| Fe 0.3C 2.8Ni: 0.6Mo 0.6Cr | 16                          | 4.5                         | 240            | 265                            | 4.05                            |
| Fe 30Ni          | 350                         | 87                          | 200            | 330                            | 52                              |
| Fe 0.48C 18.7Ni   | 18.7                        | 5.1                         | 220            | 220                            | 5.1                             |
| Fe 0.58C 3Si 3.8Cr 8Ni 1.1Mo | 19                          | 4.8                         | 220            | 360                            | 2.9                             |

* and ** Values for $(T_o - M_s)$ and $|\Delta F^{y \rightarrow x}|_{M_s}$ were calculated with data taken from references. Improved fit of $\Delta T$, for Fe -30Ni has to be re-examined in the light of the data.
FIGURE 67 COMPARISON OF \( M_s \) SHIFTS AS OBSERVED BY DIRECT AND INDIRECT MEANS, WITH VALUES CALCULATED FROM HEATS OF TRANSFORMATION AND STRAIN ENERGY VALUES.
value of 4-5% at lower temperatures for both alloys. It is significant that the terminal value is almost exactly \( \frac{3}{4} \) the initial effect and this suggests an explanation related to the magnetic interaction energy. The derivations of equations 2.35 and 2.36 assumes that this energy to be \( JH \) which is true for isolated ferromagnetic particles and therefore applies at the \( M_s \). However when there is an assembly of particles with an overlap of magnetic fields and mutual interaction of the closely spaced particles, the contribution of interaction energy drops from \( JH \) to \( JH/2 \) so that where as equation 2.34 applies for a system of isolated martensite plates (just below the \( M_s \)) the magnetic energy increment must gradually decrease to half this value as interaction between martensite plates increases.

5.3 Utilization of the \( M_s \) shift to yield information about \( \Delta S \rightarrow \alpha' \) for various iron alloys

5.3.1 Introduction

If the relationship outlined in the previous section is accepted then the experimentally determined shift in \( M_s \) temperature, \( \Delta T \) can be combined with a knowledge of the product \( JH \), the magnetic energy (i.e. \( \Delta E_{\text{mag}} \)) to get the slope of the free energy curve \( \frac{\partial \Delta F}{\partial T} \) at \( M_s \) at the \( M_s \) temperature. Referring to Fig. 65 if an increment of magnetic energy, \( \Delta E_{\text{mag}} \) produces a shift in \( M_s \), \( \Delta T \) then:

\[
\frac{\partial}{\partial T} \Delta F^{\alpha' \rightarrow \gamma} = \frac{\Delta E_{\text{mag}}}{\Delta T} \quad \text{..........................} \quad 2.37
\]

But \[
\frac{\partial}{\partial T} \Delta F^{\alpha' \rightarrow \gamma} = \frac{\Delta S^{\gamma \rightarrow \alpha'}}{\Delta T} \quad \text{..........................} \quad 2.38
\]

From 2.37 and 2.38 it follows that:

\[
\frac{\Delta E_{\text{mag}}}{\Delta T} = \frac{JH}{\Delta T} = \Delta S^{\gamma \rightarrow \alpha'} \quad \text{..........................} \quad 2.39
\]
Figure 68 Variation of $\Delta S^{\gamma\rightarrow\delta}$ with Temperature

- Fe Ni (5-30%) alloys (56)
- Fe C (0.1-0.9%) 8Cr alloys (74)
- Fe C (0.1-1%) 4Cr alloys (120)
- Pure iron (the temperature on the x-axis refer to $T_0$) (51)
Value recalculated taking into account, see section 5.3.2.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Reference</th>
<th>0°C</th>
<th>1°C</th>
<th>2°C</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>this work</td>
<td>0.65</td>
<td>6</td>
<td>5.4</td>
<td>5.1</td>
<td>5°C</td>
</tr>
<tr>
<td>(8)</td>
<td>0.85</td>
<td>6</td>
<td>5.4</td>
<td>4.7</td>
<td>2.8%</td>
</tr>
<tr>
<td>this work</td>
<td>1°C</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
<td>2.8%</td>
</tr>
<tr>
<td>this work</td>
<td>1°C</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
<td>2.8%</td>
</tr>
<tr>
<td>this work</td>
<td>1°C</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
<td>2.8%</td>
</tr>
<tr>
<td>this work</td>
<td>1°C</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
<td>2.8%</td>
</tr>
</tbody>
</table>

Table 21: The Variation of Aμ μ / A μ μ μ μ, as determined from experimental values of (D μ / D μ μ μ μ) (μ)
5.3.2 Variation of $\Delta S^{\gamma \rightarrow \alpha}$ with temperature for iron alloys

Table 21 shows the available experimental $\Delta S^{\gamma \rightarrow \alpha}$ values as determined from $M_s$ shifts due to an applied magnetic field; these may be compared with the values from Fig. 68 where the variation of $\Delta S^{\gamma \rightarrow \alpha}$ is plotted for iron (51) and several iron alloys. There has been no systematic work specifically aimed at such a correlation, but it is clear that the experimentally determined values are very similar to those plotted in Fig. 68. By choosing alloys so as to cover a wide range of $M_s$ temperatures it is possible to experimentally determine the $\Delta S^{\gamma \rightarrow \alpha}$ temperature curve, from the observed shifts in the $M_s$ due to an applied field. It should however be noted that this method of evaluation of $\Delta S^{\gamma \rightarrow \alpha}$ is suitable only for those alloys whose $M_s$ is $< T_c/2$ where $T_c$ is the Curie temperature of the ferromagnetic phase (for temperatures $> T_c/2$, the marked variation of $J$ with temperature makes any precise evaluation of $\Delta E_{mag}$ not possible).

The case of the Fe-30%Ni alloy (Table 22) is interesting because the value of $\Delta S^{\gamma \rightarrow \alpha}$ obtained from the relation $J H/\Delta T$ is significantly higher than for other alloys. Table 22 shows that the $\gamma$ phase for this alloy becomes ferromagnetic very close to this composition and in the case of this alloy it is necessary to use equation 2.33 instead of 2.34 to take this into account. It then follows that:

$$\Delta S^{\gamma \rightarrow \alpha} = \frac{H (J_\gamma - J_\alpha)}{\Delta T} \quad 2.40$$

The value of $\Delta S^{\gamma \rightarrow \alpha}$ based on equation 2.40 is very close to the calculated values for similar alloys in Fig. 68.

It is pertinent to note the marked variation of $\Delta S^{\gamma \rightarrow \alpha}$ with temperature and composition. The earlier work of Cohen, Machlin and Paranjpe (57) led to a value of $\Delta S^{\gamma \rightarrow \alpha} = 1.4$ for various carbon steels irrespective of temperature and this value has been used by Aaronson (48) in a recent computerised analysis of the $\gamma \rightarrow \alpha$ transformation in steels and iron alloys. It should however be noted that a figure of 1.4 represents only a good average value and a marked variation of $\Delta S^{\gamma \rightarrow \alpha}$ does occur.
FIGURE 69  CORRELATION BETWEEN THE RATE OF MARTENSITE FORMATION AND THE ENTROPY OF TRANSFORMATION.

\[ \text{Martensite formed per degree} \]

\[ \text{Rate of Transformation} \]

\[ \text{Entropy of Transformation} \] cals/mol/deg.
with temperature and composition. The experimentally determined \(\Delta S^{\gamma\to\alpha}\) values (Table 21) in fact vary from 0.9 to 1.4.

### 5.3.3 Correlation of the rate of martensite formation with \(\Delta S^{\gamma\to\alpha}\)

The martensite transformation of many steels where the transformation is athermal is usually characterised by a linear region (between 5-50\%). Brook, Entwisle and Ibrahim (74) have shown that the slope of the linear region of this transformation curve (which gives the rate at which martensite forms) is directly proportional the rate of change of free energy with temperature; in other words there is a fundamental correlation between the increment of transformation and the entropy of transformation. This can be expressed as:

\[
\frac{d}{dT} (\% \text{Martensite}) = \left| \frac{d\Delta F^{\gamma\to\alpha}}{dT} \right| = \Delta S^{\gamma\to\alpha} \quad \ldots \ldots \quad 2.41
\]

In the absence of experimental data for \(\Delta S^{\gamma\to\alpha}\) their entropy values were calculated for the steels concerned (Section 2.6.3) by combining the available theoretical approximations for the free energy of iron-carbon, iron-nickel and iron-chromium alloys (74).

This relationship (Equation 2.41) was tested in connection with the present work since the data presented in Figs. 55 and 56 not only yields experimental values of the rate of free energy change with temperature from the \(M_s\) shift, but also provides the rate of martensite formation. The resulting linear correlation including some Russian data (10) is shown in Fig. 69.

Koistenen and Marburger (72) have proposed an alternative and more complex empirical relationship for the kinetics of the martensite formation of the form:

\[
1 - V = \exp\left(-A (M_s - T)\right) \quad (\text{Equation 2.21 of Section 2.6.3})
\]
where $V$ is the volume fraction which has become martensite at a temperature $T$ below the $M_s$ and $A$ is a constant ($-1.10 \times 10^{-2}$) suggested to be independent of carbon content in Fe-C alloys. With $A$ independent of carbon content, this equation implies that the percentage of martensite formed during a given temperature interval ($M_s - T$) is independent of the $M_s$ temperature. However Radcliffe and Schatz (69) who studied the formation of martensite at high pressures found that their results only fitted the Koistenen-Marburger relationship with $A$ values which were markedly dependent on carbon content. Koistenen-Marburger's assumption that $A$ (Equation 2.21) is independent of carbon content can be traced back to Cohen et al (57) who assumed $\Delta S^{\gamma \rightarrow \alpha}$ for Fe-C alloys to be constant and independent of carbon content, which is clearly contradicted by the calculated values of $\Delta S^{\gamma \rightarrow \alpha}$ shown in Fig. 68.

The rate of formation of martensite is of considerable importance in relation to the stresses developed during transformation and from this point of view it is clearly desirable to obtain more experimental $\Delta S^{\gamma \rightarrow \alpha}$ values to clarify the situation.

5.4 The effect of applying a magnetic field below the $M_s$

5.4.1 Analysis of the recrystallization effects

It has already been indicated that the cooling curve results (Section 4.4) can be correlated satisfactorily with a shift in the transformation curve (Section 4.4.1). In his schematic treatment, Estrin (8) assumed that when a field is applied, at a temperature $T$, (below the $M_s$) the transformation point shifts from $A$ to $D$ Fig. 63. The experimental results of the associated cooling curves show there is a rise in temperature of about $3^\circ C$ (for alloy 1) and this obviously relates to the release of latent heat associated with the formation of the extra-martensite. However the fact that heat is evolved means that strictly an isothermal interpretation of the magnetic field effect (as postulated by Estrin (8)) is not entirely true and the actual amount of extra-martensite formed is related to a change such as is illustrated by $A D'$ in Fig. 70. The
FIGURE 70  SCHEMATIC EXPLANATION FOR 'REDUCED MARTENSITE' ($\Delta M_L$) DUE TO LOCAL APPLICATION OF A FIELD.
investigations on the effect of a continuous and local application of a magnetic field on the percentage of martensite formed (Section 4.4.2 and Table 18) substantiate this analysis. The additional amount of martensite formed at 85°C when a field is applied continuously is 9% while the same field applied locally at 85°C gives only 6% of extra martensite. Hence a rise of 3°C observed when a field is applied locally at 100°C should be associated not with the extra-amount of martensite formed corresponding to MN but with a reduced amount of martensite MN' corresponding to the analysis in Fig. 70.

Although the degree of recalescence and changes in the percentage of martensite produced are in reasonably good agreement, it is not possible to predict directly which particular combination of martensite and recalescence will take place within the permissible limits set by \( A \) \( \Delta D \) and \( AA' \). According to the laws of irreversible thermodynamics (116), when a perturbation is introduced into a system in quasi-equilibrium; 1) the system will react to the perturbation by setting up a flux in the direction which will tend to reduce the perturbation and 2) the entropy production due to the flux so produced should be minimum for the given conditions. So the dynamic reaction path will be partly determined by the relative entropy changes produced due to a) formation of an additional amount of martensite b) a rise in temperature and finding out the combination of the two processes which has a minimum rate of entropy production.

5.4.2 Effect of removing the magnetic field during transformation

The effect of the removal of the field during transformation is more straightforward. As there will be no sudden heat evolution in this case, the only effect will be a reduction in the driving force for the transformation. Under normal circumstances further transformation will cease until a drop on temperature brings the driving force back to the value corresponding to the point where the field was removed (Fig. 64). The case of thermoelastic martensite should be quite interesting because removal of a field could give the reaction path BC' (Fig. 64).
5.5 Heat of transformation for the martensitic reaction for Fe 1C 1.5 Cr alloy

5.5.1 Introduction

Having established that the raise in temperature in the cooling curve is associated with a particular amount of additional martensite formed on application of a field (Section 5.4.1 and 4.3.1) an estimate of the heat of evolution due to martensitic reaction can now be made for the 1%C 1.5%Cr alloy*. Although the heat is instantaneously evolved within the specimen as the extra-martensite forms, the cooling curve shows that the specimen attains a maximum temperature only after a certain time lag and this is about 2 secs for this alloy (at 100°C). The exact reasons for this time lag are rather difficult to analyse; there will be a component associated with the delay in the response characteristics of the thermocouple and the recording instrument; however as the recording is continuous this should not affect the magnitude of the measured heat evolution although it might produce an error in the absolute value of the temperature at which the pulse appears to be applied. The effect of a magnetic field on the thermo e.m.f. generated has been shown to be small (111) and can therefore be neglected. If allowance is now made for the amount of heat lost to the surroundings by considering the general cooling rate the corrected rise in temperature can be attributed entirely to the extra-martensite formed when the field is applied.

5.5.2 Calculation of the amount of martensite formed at 100°C

The exact increment of the extra martensite, % ∆M_L when the field is applied locally at 100°C was not experimentally determined. So the experimentally determined data at 85°C was used to evaluate % ∆M_L at 100°C as follows:

Comparing similar triangles A DD' and MNN' in Fig. 70

\[
\frac{AD}{MN} = \frac{AD'}{MN'} = 2.42
\]

* Similar calculations were not made for alloy 2 because no measurements were made of the extra martensite formed on application of a field locally below the M, and there are no values in the literature with which to compare the result.
Substituting experimentally determined values of 7%, 6% and 7% for AD, AD* and MN respectively in equation 2.42.

\[ MN' = \% \triangle M_L \simeq 5\% \]

5.5.3 Heat balance and evaluation of heat of martensite reaction

Let the heat evolved within the specimen be denoted by \( H_E \) while the heat gained by the specimen and the heat lost to the surroundings be denoted by \( H_M \) and \( H_L \) respectively, then:

\[ H_E = H_M + H_L \]

The heat evolved within the specimen (\( H_E \)) is given by:

\[ H_E = \frac{M \times L \times 100}{A \times \% \triangle M_L} \]

where \( M \) = mass of the specimen
\( A \) = average atomic weight for the alloy (taken as 56 for the purpose of calculation)
\( L \) = latent heat of the transformation per mol (i.e. per gm atom)

The heat gained by the specimen (\( H_M \)) and manifested through a rise in temperature is given by:

\[ H_M = M \times C \times \triangle \theta \]

where \( C \) = specific heat for the alloy at 100°C (taken as 0.11 c.g.s. units) and \( \triangle \theta \) the rise in temperature

Lastly the heat lost to the surroundings (\( H_L \)) is given by:

\[ H_L = M \times C \times t \times \left( \frac{\partial \theta}{\partial t} \right)_{\theta} \]
where \( t \) = time taken to reach the maximum temperature and \( \frac{\partial \Theta}{\partial t} \) =
rate of cooling at 100°C and is assumed to be constant in the temperature interval \( \Theta \) and \( \Theta + \Delta \Theta \).

Combining the equations for \( H_E \), \( H_M \) and \( H_L \) and simplifying

an equation for \( L \) is obtained of the form:

\[
L = AC (\Delta \Theta + \left( \frac{\partial \Theta}{\partial t} \right) t) \frac{100}{\% \Delta M_L} \tag{2.47}
\]

The experimentally determined values for \( \Delta \Theta \), \( t \) and \( \frac{\partial \Theta}{\partial t} \) in equation 2.47 are:

\[
\begin{align*}
\Delta \Theta &= 3^\circ \\
t &= 2 \text{ secs.} \\
\left( \frac{\partial \Theta}{\partial t} \right) &= 1^\circ/\text{sec.} \\
\% \Delta M_L &= 5\%
\end{align*}
\]

The values for \( A \) and \( C \) were taken as 56.0 and 0.11 cal/mol/deg.

Substituting these values in equation 2.47

\[
L = \frac{\Delta H}{\% \Delta M_L \cdot 100} = q = 600 \pm 100 \text{ cals/mol}^* 
\]

5.5.4 Comparison of the determination of \( L \) with other methods

Estrin (8) and Voranchikin and Pakidov (10) have utilised the effects of a magnetic field on martensitic transformations to evaluate the latent heat of transformation.

Estrin used the equation \( L = \frac{\Delta E_{\text{mag}}}{T_o} \) (Section 5.2.3) to evaluate \( L \) (for Fe 0.6C 19Ni alloy) by using the experimentally observed \( M_s \) shifts due to a field of 18.6 K. Gauss. This method of evaluation of \( L 
\]

* Several approximations are built up in equation 2.47 such as uncertainties in evaluating \( H_E \), and \% \( \Delta M_L \). In view of these approximations the error involved in the calculation of \( L \) is estimated to be of the order of \( \pm 100 \) calories/mol.
is justified only if the free energy curves $F_\alpha$ and $F_\gamma$ are linear; otherwise the heat of transformation at $T_o$ (or the value equated to $Q_o$ at $T = 0^\circ\text{K}$) will be different from that actually evolved at the $M_s$ (Fig. 72).

Voranchikin and Fakidov (10) evaluated the latent heat of martensitic transformations in two steels (0.4C 2Cr 20Ni and 0.6C 4Cr 8Ni 3Si) by measuring the temperature rise due to the additional amount of martensite formed, when a pulsating magnetic field is applied below the $M_s$. Since a pulsating magnetic field was used, a correction had to be made for the temperature rise to subtract the effects due to eddy currents. The results of their investigation are shown in Table 23. The accuracy of these results in comparison with those obtained for alloy 1 (Section 5.5.3) is difficult to evaluate since details of the calculations are not given by these authors. The temperature peaks (obtained when the field was raised above a critical field $H_c$ (Section 2.1) was correlated with the percentage of additional martensite formed and this was measured by a magnetic method (Section 2.1.6). It is a method only suitable for the particular alloys investigated. These alloys show a burst martensite formation, which synchronises the otherwise separate measurements.

There is very little that can be said in the way of really comparing such diverse methods. More work is clearly necessary to improve the accuracy of all three methods. However the order of the magnitude of the value of $L$ in the present calculations is reasonably consistent with other information available for the alloy concerned as is shown in the next Section.
5.6 Free energy changes at the $M_s$ for Fe-Cr-C alloys

5.6.1 Calculation of $\Delta F^{\gamma \rightarrow \alpha'}$ at the $M_s$ for the Fe-C alloy from experimental data

The heat of transformation, $L$ or $\Delta H^{\gamma \rightarrow \alpha'}$ obtained from a study of the associated cooling curves in the previous section can be combined with the entropy of transformation, $\Delta S^{\gamma \rightarrow \alpha'}$ obtained from $M_s$ shifts in Section 5.3 to obtain a value for $\Delta F^{\gamma \rightarrow \alpha'}$ at the $M_s$ temperature.

$$\Delta F^{\gamma \rightarrow \alpha'} = \Delta H^{\gamma \rightarrow \alpha'} - T \Delta S^{\gamma \rightarrow \alpha'} \quad \text{................. 2.48}$$

1) For the purpose of calculating $\Delta F^{\gamma \rightarrow \alpha'}$ at 380°K and the value of $\Delta H^{\gamma \rightarrow \alpha'}$ at 380°K is assumed to be the same as the value at 373°K (i.e. the $M_s$ temperature).

2) The JH/ $\Delta T$ data of Table 21 (Section 5.3.2) gives $\Delta S^{\gamma \rightarrow \alpha'}$ at the $M_s = 0.9 \text{ cal/mol/deg.}$

Therefore

$$\left| \Delta F^{\gamma \rightarrow \alpha'} \right|_{M_s} = \left| \Delta H^{\gamma \rightarrow \alpha'} \right|_{M_s} - T \left| \Delta S^{\gamma \rightarrow \alpha'} \right|_{M_s}$$

$$= 260 \text{ cal/mol.}$$

5.6.2 Theoretical calculation of $\Delta F^{\gamma \rightarrow \alpha'}$ for Fe-Cr-C alloys

There is at present very little experimental data available on the free energy changes accompanying austenite-martensite transformations in steels. Fisher (41), Cohen et al (57), Kaufman and Cohen (56) and Kaufman (58) have derived several semi-empirical equations for evaluating $\Delta F^{\gamma \rightarrow \alpha'}$ in Fe-C, Fe-Ni and Fe-Cr alloys. The Fe-Cr-C system can be considered for illustration. The free energy change accompanying the austenite-martensite reaction can be written following Brook et al (74) as:

$$\Delta F^{\alpha \rightarrow \gamma} = x_{Fe} \Delta F_{Fe}^{\alpha \rightarrow \gamma} + x_{Cr} \left( 460 + 1.0T \right) + x_{Cr} x_{Fe}$$

$$(-2800 + 0.75T) + x_{C} \left( -10,500 + 3.425T \right) - \Delta F* \quad .. 2.19$$

(Section 2.5.8)
FIGURE 7.1 COMPUTED VALUES OF DRIVING FORCE $\Delta F^{\psi \rightarrow Y}$ AT $M_s$ FOR Fe-Cr-C ALLOYS.
Table 25 Computed values of $\Delta F^{\gamma\rightarrow\alpha}$ at $M_\gamma$ for Fe-Cr-C alloys.

| Chromium atomic % | Carbon atomic % | $M_\gamma$ $^\circ$K | $|\Delta F^{\gamma\rightarrow\alpha}|$ |
|-------------------|----------------|---------------------|------------------|
| 1.61              | 1.43           | 633                 | 344              |
|                   | 1.9            | 583                 | 410              |
|                   | 3.25           | 508                 | 384              |
|                   | 4.75           | 383                 | 384.6            |

| Chromium atomic % | Carbon atomic % | $M_\gamma$ $^\circ$K | $|\Delta F^{\gamma\rightarrow\alpha}|$ |
|-------------------|----------------|---------------------|------------------|
| 4.29              | 1.43           | 634                 | 340              |
|                   | 1.9            | 542                 | 415              |
|                   | 3.25           | 493                 | 349              |
|                   | 4.75           | 371                 | 334              |
Table 25 (contd.)

<table>
<thead>
<tr>
<th>Chromium atomic %</th>
<th>Carbon atomic %</th>
<th>$M_s^{°K}$</th>
<th>$\Delta F^{Y \rightarrow \alpha}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.58</td>
<td>1.43</td>
<td>532</td>
<td>396</td>
</tr>
<tr>
<td></td>
<td>1.9</td>
<td>430</td>
<td>465</td>
</tr>
<tr>
<td></td>
<td>3.25</td>
<td>362</td>
<td>399</td>
</tr>
<tr>
<td></td>
<td>4.75</td>
<td>343</td>
<td>264</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chromium atomic %</th>
<th>Carbon atomic %</th>
<th>$M_s^{°K}$</th>
<th>$\Delta F^{Y \rightarrow \alpha}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.3</td>
<td>1.43</td>
<td>481</td>
<td>374</td>
</tr>
<tr>
<td></td>
<td>1.9</td>
<td>377</td>
<td>425</td>
</tr>
<tr>
<td></td>
<td>3.25</td>
<td>330</td>
<td>328</td>
</tr>
<tr>
<td></td>
<td>4.75</td>
<td>319</td>
<td>184</td>
</tr>
</tbody>
</table>
where \( \Delta F_{Fe}^{\gamma \rightarrow \alpha'} = 1202 - 2.63 \times 10^{-3} T^2 + 1.5 \times 10^{-6} T^3 \) cal/mol.

It was decided to omit the \( \Delta F^* \) term, which takes into account the change in free energy accompanying the ordering of carbon atoms along the tetragonal axis of the b.c.T martensite from this expression for the purposes of the calculations which follow, because no reliable data can be established for \( \Delta F^* \) (Section 2.4.9).

Equation 2.19 was fed into a Elliott 503 digital computer and values of \( \Delta F^{\gamma \rightarrow \alpha'} \) were calculated corresponding to the \( M_s \) values for various carbon (0.3 - 1%) and chromium (1.5 - 12.5%) contents. The \( M_s \) values were taken mostly from the data given by Brook et al (74) and Stevens and Haynes (112); the results are summarised in Fig. 71 and are tabulated in Table 25.

### 5.6.3 Comparison of \( \Delta F^{\gamma \rightarrow \alpha'} \) values

The experimentally determined value of \( \left| \Delta F^{\gamma \rightarrow \alpha'} \right|_{M_s} \) may now be compared with the calculated values of \( \left| \Delta F^{\gamma \rightarrow \alpha'} \right|_{M_s} \) and various other approximations (Table 24).

| Alloy          | \( \left| \Delta F^{\gamma \rightarrow \alpha'} \right|_{M_s} \) cal/mol | Source obtained                  |
|---------------|-------------------------------------------------|----------------------------------|
| Fe 1C 1.5Cr   | 260                                             | Present Work                     |
| Fe 1C 1.5Cr   | 384*                                            | Present Work                     |
| Fe 1C         | 265                                             | Kaufman, Radcliffe and Cohen (119) |
| Fe 1.13C 1.8Cr| 516                                             | Fishe, Holloman and Turnbull (124) |

* The term \( \Delta F^* \) due to Zener ordering was omitted from equation hence the value represents \( \Delta F^{\gamma \rightarrow \alpha'} \) and not \( \Delta F^{\gamma \rightarrow \alpha'} \).
The value of 260 cals/mol is very close to the value of 265 cals/mol assumed as the strain energy for this alloy as deduced by Kaufman et al (119) (equation 2.35 and Table 19 Section 5.2.3).

The computer-calculated value of 384 cal/mol refers to $\Delta F^\gamma > \alpha$ and not to $\Delta F^\gamma = \alpha$ since the term $\Delta F^*$ was omitted from equation 2.19 in the computer calculations. From these two free energy values an estimate of $F^*$ can be made and this comes out to be $\approx 120$ cals/mol. Since there is no data on $\Delta F^*$ available in literature for this alloy, it is not possible to assess the accuracy of this estimate. However Imai et al (44) have calculated $\Delta F^*$ values for various Fe-C alloys and their values are compared with the estimated $\Delta F^*$ value in Table 21a.

Table 21a Comparison of $\Delta F^*$ values with the values obtained by Imai et al (44).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$\Delta F^*$ cal/mol</th>
<th>Source obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe 1C 1.5Cr</td>
<td>120</td>
<td>Present Work</td>
</tr>
<tr>
<td>Fe 1C</td>
<td>20</td>
<td>Imai et al</td>
</tr>
<tr>
<td>Fe 1.5C</td>
<td>50</td>
<td>Imai et al</td>
</tr>
<tr>
<td>Fe 2C</td>
<td>120</td>
<td>Imai et al</td>
</tr>
</tbody>
</table>

The value of 516 calories per mol calculated by Fisher et al (120) appears rather high. This is however not surprising in view of the lack of accurate thermodynamic data available at that time.

5.7 General deduction concerning free energy changes in iron alloys

5.7.1 Effect of non-linear free energy curves

In the derivation of $M_\alpha$ shifts due to an applied field (Section 5.2.3), a linear approximation model was assumed for the free energy curves $F^\gamma$ and $F^\alpha$, although it is well known that these curves are
FIGURE 72(a) EFFECT OF NON-LINEAR FREE ENERGY CURVES ON THE RELATIONS BETWEEN $\Delta S$ AND $q$.
FIGURE 72(b) THE UTILISATION OF $\Delta F^\text{ad} \rightarrow ^\text{eq}$ FOR THE PREDICTION OF $\Delta T$ IN THE CASE OF NON-LINEAR FREE ENERGY CURVES.
FIGURE 73 THE EFFECT OF TEMPERATURE (OR COMPOSITION) ON THE DRIVING FORCE AT M FOR IRON-CARBON AND IRON-NICKEL ALLOYS (Kaufman and Cohen).
markedly non-linear \( (51) \). It is therefore necessary to examine the effect of non-linear free energy curves on the relationship outlined in equations \( (2.35 \& 2.36) \), and also on the heat of transformation values evaluated in Section \( (5.5) \).

Fig. 72 shows that the determination of the slope of the free energy curve \( (\Delta S_{\gamma \rightarrow \alpha}^{-1}) \) at the \( M_s \) from \( \frac{\Delta H}{\Delta T} \) should give the true value even with non-linear free energy curves if \( \Delta T \) is not too large. However there will be some difference in the predictive capacity of the two methods of evaluating \( \Delta T \) with non-linear curves:

\[
\text{From equation } 2.39 \quad \Delta S_{\gamma \rightarrow \alpha}^{-1} \quad M_s = \frac{\Delta F_{\gamma \rightarrow \alpha}}{T_0 - M_s} \quad \ldots \ldots \ldots 2.49
\]

\[
\text{and from equation } 2.37 \quad \Delta S_{\gamma \rightarrow \alpha}^{-1} \quad M_s = \frac{q_0}{T_0} \quad \ldots \ldots \ldots 2.50
\]

It can be seen from Fig. 72 that the prediction of \( M_s \) shift from the latent heat of transformation at \( T_0 \) is likely to become increasingly inaccurate with increasing non-linearity. Equation 2.49 should however lead to a closer agreement with the experimental shift, since it is likely to be geometrically closer to the real slope of monotonic free energy curves at the \( M_s \). Table 19 and 20 show a comparison of the predicted \( M_s \) shifts obtained by the two methods. An improved correlation based on available \( \Delta F_{\gamma \rightarrow \alpha} \) data at the \( M_s \) is however linked to the accuracy with which formulations of free energy expressions predict the free energy at the \( M_s \) temperature. The measured \( M_s \) shift therefore can act as a confirmation of a particular free energy expression for the system.

5.7.2 Re-assessment of the value for the driving force \( (\Delta F_{\gamma \rightarrow \alpha}) \) in Fe-C alloys

Fig. 73 shows the variation of driving force at the \( M_s \) as a function of carbon and nickel contents in iron-base alloys. The idea that \( (\Delta F_{\gamma \rightarrow \alpha}) \) in iron-carbon alloys is 290 calories per mol and independent of carbon content historically owes its origin to Zener \( (42) \) and to Cohen et al \( (57) \), who arrived at this result after making the best possible calculations from the existing data available at that time.
Kaufman, Radcliffe and Cohen (119) arrived at a value of 265 cal per mol by taking more precise account of the thermodynamics of interstitial solid solution than had been adopted previously. However if one considers all the composition and temperature dependent factors such as elastic constants, crystallography and nucleation on which strain energy and other non-chemical energies depend, there is no reason to expect that $\Delta F^{\gamma'\rightarrow\gamma}$ should be constant. Recent calculations by Imai et al. (44) based on statistical thermodynamics indicate a considerable variation of $\Delta F^{\gamma'\rightarrow\gamma}$ with interstitial content in Fe-C and Fe-N alloys. In the light of these data, the idea of a constant driving force at $M_s$ for Fe-C alloys may have to be abandoned. The free energy data obtained from magnetic field effects should be useful in clarifying this.

5.7.3 Possible effects of magnetic fields on the non-chemical factors restraining the transformation

The amount of supercooling ($T_o - M_s$) necessary to start a martensitic reaction is small when the shape deformation is small (43), so it is clear that the normal $M_s$ temperature is also largely determined by non-chemical terms. The non-chemical terms include contributions from interfacial energy strain energies and energy needed to create and expand dislocations. Adding a whole list of such terms defines a modified thermodynamic transition temperature ($T_o$) (43). It is therefore worth considering an approximate evaluation of some of these non-chemical energies to see if there is any likely effect of a magnetic field on these energy terms, as distinct from effect in the chemical driving force. It should however be pointed out that any evaluation of the order of magnitude of these is tied up with certain specific assumptions such as a model for austenite-martensite interface, the shape and size of the embryos, and specified critical conditions for triggering off martensite plates.

a) Interfacial energy ($\sigma$)

Knapp and Dehlinger (63), using Frank's model for the austenite-martensite interface (66), calculated the interfacial energy by treating the screw dislocation interface as a low angle boundary and applying Reed-
Shockley equation (59):

\[ \sigma = \frac{G b \Omega_m}{4 (1 - \nu)} \left(1 - \ln \frac{\Omega_m}{\Omega} \right) \text{erg/cm}^3 \quad \text{...... 2.51} \]

where \( \Omega = b/d \), \( b \) being the Burger's Vector, \( d \) the spacing between dislocations, \( \nu \) = poisson's ratio (0.3), and \( G \) = shear modulus \((8 \times 10^{11} \text{ dynes/cm}^2)\). By substituting \( b = a/2\sqrt{2} = 1.27 \AA \) and \( d = 17.8 \AA \) and \( \Omega_m = 0.47 \text{ radians} \) (121) in equation 2.51 \( \sigma \) comes out to be of the order \( \approx 250 \text{ ergs/cm}^2 \). The effect of a magnetic field on the shear modulus is negligible (108); so unless the magnetic field changes the nature of the austenite-martensite interface, its effect on \( \sigma \) should be very small. On the other hand, if the surface energy of the interface, is related to the difference in energy between the two phases rather than the properties of the interface dislocations, then there is a possibility that appreciable magnetic exchange forces might come into play.

b) **Magnetic effects on the strain energy**

The strain energy associated with unit volume of a martensite nucleus could be expressed as (43):

\[ E = \frac{2 \mu S^2}{3 c/\Omega} \quad \text{.......................... 2.52} \]

where \( \mu \) is the shear modulus, \( S \) is the shear associated with the shape deformation, which is of the order of \( 1/\sqrt{32} \) (66) and \( c \) and \( \Omega \) are respectively the semi thickness and radius of a lenticular disc. The value of \( c/\Omega \) quoted for a martensite nucleus is \( 1/2 \gamma \) (59). In the presence of a magnetic field this ratio could in principle become smaller, because the nucleus will assume a shape so as to make \( c/\Omega \) as small as possible, in order to reduce shape anisotropy (Section 2.9.2); it must be assumed for the purposes of discussion that the martensitic nucleus is ferromagnetic. Substituting \( \mu = 8 \times 10^{11} \text{ dynes/cm}^2 \) \( S = 1/\sqrt{32} \) and taking \( c/\Omega = \frac{1}{20} \), the strain energy in the expression 2.52 becomes:

\[ E \approx 8 \times 10^8 \text{ ergs/cm}^2 \quad \text{.......................... 2.53} \]
The maximum contribution from the shape anisotropy energy for a ferromagnetic martensitic nucleus of $c/v_0 = \frac{1}{20}$ is (Section 2.9.2) of the order of $6 \times 10^6$ ergs/cm$^3$. Hence it seems that the shape anisotropy energy is too small to affect the strain energy.

c) The energy needed to create and expand dislocation loops

Although there is some qualitative evidence to show that a magnetic field induces dislocation motion in a ferromagnetic material (125) a quantitative estimate of the magnetoelastic interaction is not precisely known. The total energy of interaction with dislocations is unlikely to be larger than that with the lattice unless dislocations are associated with a magnetic moment.

Summary

It therefore seems that the effect of a magnetic field on the various non-chemical (restraining) energies can be considered to be small. However, a knowledge of $\Delta S^{\gamma - \gamma'}$ obtained from the effects of a magnetic field on martensitic transformations can be utilised in re-evaluating the total non-chemical energies (such as strain energy and interfacial energy) assuming a model for 'operational nucleation'.

5.7.4 Comparison of $\Delta S^{\gamma - \gamma'}$ values derived by magnetic and pressure experiments

The application of hydrostatic pressure depresses the $M_s$, because in the presence of such an external constraint, the phase which has the lowest specific volume is more stable; this is analogous to the situation where in the presence of a magnetic field, a ferromagnetic phase has a greater stability than a paramagnetic phase. It is interesting to compare the relative magnitudes of the shift in the $M_s$ produced by adding energy to the system in these ways, because pressure experiments are experimentally much more difficult, and there seem to be other factors which favour magnetic fields as an easier way of extracting thermodynamic information out of the system.
Application of a hydrostatic pressure depresses the $M_s$ by an amount $\Delta T^*$ according to the equation:

$$\Delta T^* = \frac{P (V_\alpha - V_\gamma)}{\Delta S^\gamma - \Delta S^\alpha} \quad \text{..........................} 2.54$$

or

$$\Delta S^\gamma - \Delta S^\alpha = \frac{P (V_\alpha - V_\gamma)}{\Delta T^*} \quad \text{..........................} 2.55$$

where $P (V_\alpha - V_\gamma)$ is the change in free energy and $\Delta S^\gamma - \Delta S^\alpha$ the difference in entropies between the $\gamma$ and $\alpha'$ phases. Equation 2.54 may be compared with the value of $\Delta S^\gamma - \Delta S^\alpha$ from magnetic field experiments.

$$\Delta S^\gamma - \Delta S^\alpha = \frac{H (J_\alpha - J_\gamma)}{\Delta T} \quad \text{..........................} 2.56$$

It is worth considering the relative advantages and disadvantages of these two methods since it has been emphasized that there is a marked lack of experimental data for the variation of free energy with temperature.

Table (26) shows the magnitude of the hydrostatic pressure and magnetic fields required to produce similar shifts in the $M_s$ temperature. From an experimental point of view, there is a great deal to be said for using a magnetic field instead of hydrostatic pressure, especially with the increasing availability of super-conducting magnets. One major advantage is the relative freedom of access to the specimen, which allows much greater ease with which the specimen can be manipulated and the ease with which heat treatment variables can be altered. Leaving aside the ease and flexibility with which the two variables can be applied, the next factor which has to be considered is the relative availabilities of accurate values of $(J)$ and $(V)$ and their variation with temperature for the phases concerned. It is generally considered easier to measure the saturation magnetization and its variation with temperature, than to measure volume changes. Furthermore, in the majority of steels, the required magnetic properties are essentially those of the $\alpha'$ phase only, whereas volume changes are a complex resultant of changes in both $\alpha'$ and $\gamma$ phases. Another factor which has to be considered is the pressure dependence of $(\Delta V)_{\gamma\alpha'}$ as against any dependence $(\Delta J)_{\alpha'}$ upon magnetic field. The pressure...
dependence of \( (\Delta V) \) is surprisingly large \( (51) \). The dependence of \( (\Delta J) \) on a magnetic field is negligible up to saturation, and for fields beyond saturation there is a small increase which can be easily measured.

Hence both from experimental and theoretical points of view there is a good deal to be said for using a magnetic field (rather than high pressures) in the study of the thermodynamic characteristics of iron base alloys.
SECTION 6 FURTHER RESULTS AND OBSERVATIONS

6.1 The effect of magnetic heat treatment on the hardness of quenched steels

6.1.1 Hardness histograms

An increase in hardness of 20-30 V.P.N. was observed for specimens quenched in a magnetic field (Table 27). This increase tends to be masked by variations within the specimen and a scatter from specimen to specimen, hence it was decided that the best method of representing both the effect of a magnetic heat treatment and the normal scatter associated with the quenching was to draw histograms of the hardness data. (Figs. 74-76).

The microhardness data for a Fe 1C 1.5Cr alloy and 1.4C steel are plotted in Figs. 77 and 78.

Details regarding the compositions of the steels, the strength of the field and the direction of the field used in magnetic heat treatment are given in Table 28a.

6.1.2 General features of macrohardness histograms

The histograms reveal two main features:

1) Specimens heat treated in a magnetic field show an increase in hardness of 20-30 V.P.N.

2) Specimens quenched in a magnetic field reveal a greater uniformity of hardness - the hardness readings show a less scatter within the specimen and also from specimen to specimen.

These are quite evident from Figs. 74, 75 and 76 although for specimens of the Fe 0.3C 2.8Ni 0.6Cr 0.6Mo alloy, quenched in a field and without a field, there is a considerable overlap, and the hardness increase due to quenching in a field is less distinct (Fig. 75)

6.1.3 General features of microhardness histograms

The increase in hardness in specimens quenched in a magnetic field is revealed much more significantly from the microhardness data; however the scatter band is also increased. This can be partly attributed
<table>
<thead>
<tr>
<th>Field Applied</th>
<th>Percent Increase in Hardness</th>
<th>Percent Increase in Overall Hardness</th>
<th>0°C</th>
<th>4°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transverse</td>
<td>0%</td>
<td>16%</td>
<td>1°C</td>
<td>4°C</td>
</tr>
<tr>
<td></td>
<td>25%</td>
<td>6.2%</td>
<td>1°C</td>
<td>4°C</td>
</tr>
<tr>
<td></td>
<td>10%</td>
<td>6.2%</td>
<td>0°C 0.6%</td>
<td>4°C</td>
</tr>
<tr>
<td></td>
<td>30%</td>
<td>6.2%</td>
<td>0°C 2%</td>
<td>4°C</td>
</tr>
<tr>
<td></td>
<td>60%</td>
<td>6.2%</td>
<td>0°C</td>
<td>4°C</td>
</tr>
</tbody>
</table>

Table 27: Effect of a martensite heat treatment on machinability of quenched steels.
<table>
<thead>
<tr>
<th>Property Studied</th>
<th>Transverse</th>
<th>Axial</th>
<th>Transverse</th>
<th>Axial</th>
<th>Transverse</th>
<th>Axial</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microhardness</td>
<td>16</td>
<td>6.2</td>
<td>0.60</td>
<td>6.2</td>
<td>0.60</td>
<td>6.2</td>
</tr>
<tr>
<td>Microhardness</td>
<td>16</td>
<td>6.2</td>
<td>0.60</td>
<td>6.2</td>
<td>0.60</td>
<td>6.2</td>
</tr>
<tr>
<td>Macrophotography</td>
<td>16</td>
<td>6.2</td>
<td>0.60</td>
<td>6.2</td>
<td>0.60</td>
<td>6.2</td>
</tr>
<tr>
<td>Macrophotography</td>
<td>16</td>
<td>6.2</td>
<td>0.60</td>
<td>6.2</td>
<td>0.60</td>
<td>6.2</td>
</tr>
</tbody>
</table>

Table 26a. Experimental Procedure and compositions of steels investigated for the effect of magnetic heat-treatment on hardness.
**FIGURE 74a** HISTOGRAM OF HARDNESS DATA

- **M** - Quenched in a field of 6 K. Gauss
- **O** - Quenched without a field

**STEEL** ............... 0.4\%C steel (Berkefilet coating)

**TREATMENT** ........... Quenched from 860°C

**No. OF SETS OF** ...... 12

**SPECIMENS TESTED** ...... 12
M - Quenched in a field 6.2 K. Gauss
0 - Quenched without a field

STEEL ............ 0.4C (nickel plated)
TREATMENT ......... Quenched from 860°
No. OF SETS OF ) 10
SPECIMENS TESTED )
FIGURE 75  HISTOGRAM OF HARDNESS DATA FOR QUENCHED 0.3C 2.8Ni 0.6Cr 0.6Mo STEELS.

Austenitizing temperature 860°C

Quenched without a field
X Quenched with a field of 6.2 K. Gauss
FIGURE 76  HISTOGRAM OF HARDNESS DATA FOR 1.4 C STEEL
M - Quenched in a field (16 k.Gauss)
O - Quenched without a field

MICROHARDNESS VALUES

STEEL ................ 1.4C
TREATMENT ............ Quenched from 1100°C
No. OF SETS OF ) 10
SPECIMENS TESTED ) 10
STEEL  1 C 1.5 Cr

TREATMENT  AIR COOLED FROM 1100°C

FIGURE 78  HISTOGRAM OF MICRO HARDNESS DATA
to the marked sensitivity of microhardness test to impact and vibration during loading as well as surface preparation; but there is also the fact that one is now dealing with individual phases which differ more extensively in their intrinsic hardness levels.

The hardness of retained austenite is generally taken to be \( \approx 250 \) V.H.N.\((10^4)\), but this assumes that the area indented is at least three times the area of the impression. The histograms are derived from random hardness traverses which did not specifically aim at placing the indentor inside the particular phase areas, which in any case were too small to achieve suitably small impressions without reducing the load to such an extent that the accuracy of measurement would be impaired.

The lowest hardness peak therefore reflects a combination of areas of austenite and adjacent austenite/martensite interfaces. It is however interesting to note the downward shift of this hardness peak in the case of magnetically heat treated specimens in keeping with the expected reduction in retained austenite.

The double peaks associated with martensite are discussed more fully in Section 7.1.3. These peaks seem to be displaced horizontally rather than vertically much in line with the macrohardness results. However it must be remembered that the effect of a magnetic field has a much smaller relative effect on the total amount of martensite than the total amount of retained austenite (80:75 and 20:25 respectively) so that one might only expect a marked upward shift in martensite peaks with a larger number of impressions.

6.2 The effect of quenching in a magnetic field on the kinetics of the first stage of tempering

6.2.1 Length changes on tempering of 1.4C steel

Fig. 80 shows the length changes on tempering a 1.4C steel quenched in a field of 6.2 K. Gauss and the changes when the steel was quenched without a field. The experimental procedure is summarised in Table 28b.
FIGURE 80  KINETICS OF FIRST STAGE TEMPERING OF 1.4C STEEL QUENCHED IN A MAGNETIC FIELD (6.2 K. Gauss) AND WITHOUT A FIELD.

1.4C STEEL .... Quenched from 1100°C

M₁ M₂ M₃ M₄ ... Quenched in a field of 6.2 K. Gauss and tempered without a field at 80°, 100°, 120° and 140° respectively.

O₁ O₂ O₃ O₄ ... Quenched without a field and tempered at 80°, 100°, 120° and 140° respectively.
Fig. 81  Length changes on tempering after prior quenching in liquid nitrogen

Steel: 1.46

Treatment: austenitised from 1100°C
Quenched to liquid nitrogen
and tempered at 460°C

- Quenched in a field (1.2 kGauss)
- Quenched without a field

CONTRACTION (\%\%) x 10^6

TIME (Minutes)

250
0
500
750
1000
1250
20
40
60
80
100
FIGURE 82: LENGTH DUE TO THE DECOMPOSITION OF RETAINED AUSTENITE IN 1.4 C STEEL

(PRELIMINARY TREATMENT: QUENCHED AND TEMPERED 740°C 1 HOUR)

- M: Quenched initially in a field
- 0: Quenched without a field

TIME IN MINUTES

DILATION x 10^-6

-100 -0 100 200 300
FIGURE 83 DECOMPOSITION OF RETAINED AUSTENITE DURING THE SECOND STAGE TEMPERING.

1.4C STEEL
Preliminary treatment: Quenched from 1100°C and tempered at 200°C for 1 hr.

M - Quenched in a field (6.2 K. Gauss)
O - Quenched without a field
FIGURE 8.3a CORRECTED DILATION CURVES SHOWING THE DECOMPOSITION OF RETAINED AUSTENITE DURING SECOND STAGE TEMPERING (CORRECTION FOR FIRST STAGE TEMPERING)

INITIALLY QUENCHED IN A FIELD 6.2 K.G.
QUENCHED WITHOUT A FIELD
a) Quenched initially in a field (6.2 K. Gauss) and then tempered at 140°C for 1 hr.  
Carbon extraction replica x 4000.

b) Quenched without a field and tempered at 140°C for 1 hr.  
Carbon extraction replica x 4000.

FIGURE 79 a and b 1.4C STEEL TEMPERED AT 140°C FOR 1 HR.  
AFTER QUENCHING IN A FIELD AND WITHOUT A FIELD.
c) Quenched initially in a field (6.2 K. Gauss) and tempered at 200°C for 1 hr.
Carbon extraction replica × 4000

d) Quenched without a field and tempered at 200°C for 1 hr.
Carbon extraction replica × 4000.

FIGURE 79 c and d 1.4C STEEL TEMPERED AT 200°C FOR 1 HR. AFTER QUENCHING IN A FIELD AND WITHOUT A FIELD.
<table>
<thead>
<tr>
<th>Ratio</th>
<th>1.6</th>
<th>2.0</th>
<th>2.5</th>
<th>4.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>10^6 \times 1/\sqrt{1 + 1/4} (T/4)</td>
<td>10^6 \times 1/\sqrt{1 + 1/4} (T/4)</td>
<td>10^6 \times 1/\sqrt{1 + 1/4} (T/4)</td>
<td>10^6 \times 1/\sqrt{1 + 1/4} (T/4)</td>
</tr>
<tr>
<td>2.0</td>
<td>10^6 \times 1/\sqrt{1 + 1/4} (T/4)</td>
<td>10^6 \times 1/\sqrt{1 + 1/4} (T/4)</td>
<td>10^6 \times 1/\sqrt{1 + 1/4} (T/4)</td>
<td>10^6 \times 1/\sqrt{1 + 1/4} (T/4)</td>
</tr>
<tr>
<td>3.0</td>
<td>10^6 \times 1/\sqrt{1 + 1/4} (T/4)</td>
<td>10^6 \times 1/\sqrt{1 + 1/4} (T/4)</td>
<td>10^6 \times 1/\sqrt{1 + 1/4} (T/4)</td>
<td>10^6 \times 1/\sqrt{1 + 1/4} (T/4)</td>
</tr>
</tbody>
</table>

Length changes after 10 minutes of tempering at 1700C for 1.46 steel and

*at 1900C for 1.4Sr steel.*

Table 34 Comparison of contraction in the initial stages of tempering in specimens treated in a 450C furnace and without a first and after the effect of liquid nitrogen quenched in a 300C cold water and without the effect of liquid nitrogen quenched in a 450C furnace and without the effect of liquid nitrogen.
Table 28b Details of experimental procedure for tempering

<table>
<thead>
<tr>
<th>Specimen</th>
<th>1.4C Steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimensions</td>
<td>0.8&quot; in length and .25&quot; diameter</td>
</tr>
<tr>
<td>Austenitising conditions</td>
<td>Temperature 1100°C</td>
</tr>
<tr>
<td></td>
<td>Time 30 minutes</td>
</tr>
<tr>
<td>Quenching media</td>
<td>Flowing stream of water</td>
</tr>
<tr>
<td>Strength of field applied during quenching</td>
<td>6.2 K. Gauss</td>
</tr>
<tr>
<td></td>
<td>(N.B. Field was applied only during quenching and not tempering)</td>
</tr>
<tr>
<td>Tempering temperatures</td>
<td>80, 100, 120 and 140°C</td>
</tr>
<tr>
<td>Method of investigation of tempering kinetics</td>
<td>Dilatometry</td>
</tr>
<tr>
<td></td>
<td>Magnetic analysis</td>
</tr>
<tr>
<td></td>
<td>Hardness tests</td>
</tr>
</tbody>
</table>

Fig. 81 shows the length changes on tempering a 1.4C steel at 140°C starting with a fully martensitic structure. The specimens quenched in a field and without a field after austenitizing, were immediately cooled to liquid nitrogen temperature to transform (as much as possible) any untransformed austenite present to martensite*.

**General features:**

1) The length changes in Fig. 80 and Table 34 show that the overall tempering reaction proceeds very rapidly in the initial stages for both specimens quenched in a field and without a field. The rate of tempering in the initial stages increases with increasing temperature.

* The refrigeration treatment was done without a field.
<table>
<thead>
<tr>
<th>Treatment</th>
<th>1400°C 1 hr</th>
<th>1400°C 1 hr</th>
<th>1000°C (3 hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>725</td>
<td>840</td>
<td>855</td>
<td></td>
</tr>
<tr>
<td>797</td>
<td>740</td>
<td>805</td>
<td>760</td>
</tr>
<tr>
<td>860</td>
<td>740</td>
<td>842</td>
<td>770</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Tempering Treatment</th>
<th>Initial Hardness</th>
<th>Tempering Temperature</th>
<th>Tempering Time</th>
<th>Tempering of Steel</th>
<th>Tempering of Steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>a field (quenched without)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b field (quenched after)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 29: Hardness Changes After Tempering in 1.4C Steel
2) The overall rate of tempering is slowed down when the specimens are quenched in a field; and this is more marked in the initial stages.

The electron micrographs of specimens tempered at 140°C and 220°C Figs. (79 a, b, c, d) also reveal that in specimens initially quenched in a field, tempering has occurred to a lesser extent than in those initially quenched without a field.

3) The tempering curves of fully martensitic specimens (those treated to liquid nitrogen temperature) reveal the same trend i.e. the overall tempering kinetics is slowed in those specimens initially quenched in a magnetic field.

4) A comparison of the tempering curve for specimens quenched in a magnetic field, cooled in liquid nitrogen and then tempered with the tempering curves of specimens quenched in a field and immediately tempered (Fig. 80 and 81) indicates that the initial rate of tempering appears to be accelerated in specimens given prior refrigeration treatment. Prior refrigeration treatment appears to have no significant effect on the rate of tempering in specimens quenched without a field. The implications of this fact are elaborated in Section 7.2.

6.2.2 Hardness measurements

Hardness measurements on some of the quenched and tempered specimens are given in Table 29 and show the following features:

1) The initial hardness of specimens quenched in a field is greater than those specimens quenched without a field by \( \approx 30 \) V.P.N.

2) Even after a liquid nitrogen treatment of both the specimens quenched in a field and without a field, the hardness of specimens initially quenched in a field is greater than those initially quenched without a field.
3) The hardness of specimens tempered at 100°C for 3 hours and also at 140°C for 1 hour remains greater than the initial as-quenched hardness and this applies for both the specimens initially quenched in a field and without a field.

6.2.3 Determination of retained austenite from second stage tempering

Since the contraction observed during the first stage of tempering is a function of the amount of martensite initially present, and since this is different in steels heat treated with and without a magnetic field, it is necessary to determine the relative percentages of retained austenite. This can be obtained in a number of different ways. The as-quenched hardness gives one measure of retained austenite; another method is direct magnetic analysis, and finally it is possible to obtain an estimate from the characteristics of second stage tempering, which is associated with the decomposition of retained austenite. Some of the specimens initially tempered at lower temperatures were accordingly tempered at 240°C. The decomposition of retained austenite into an aggregate of ferrite and carbide results in an expansion, so that the extent of the dilation at 240°C gives a measure of the retained austenite in the initial structure. There is a slight complication in the case of specimens initially tempered at 140°C. Fig. 82 which shows a contraction in the early stages of tempering at 240°C, reaching a minimum before the curves begin to rise. This can be taken as a result of incomplete first stage tempering at 140°C so that reactions appropriate to this continue for some time in the initial stages at 240°C. This portion of the curve is therefore a resultant of

a) a contraction due to the decomposition of martensite

b) an expansion due to the decomposition of retained austenite.

It is reasonable to assume, as a first approximation, that the decomposition of martensite continues till the point of inflexion is reached (0 & 0'Fig. 82). Since the two curves are very close together at this stage, a reasonable correction can be made by extrapolation for the expansion that would have occurred if the first stage of tempering had not overlapped. The corrected
curves are shown in Fig. 83a*, and can be seen that within reasonable limits the effect of tempering at 240°C for specimens previously tempered at 140°C and 200°C is identical.

A rough estimate can now be made of the ratios of the amount of retained austenite initially present in the specimens quenched in a field and without a field. From the maximum dilation which occurs on tempering at 240°C the rate of second stage tempering appears to be faster for specimens quenched ordinarily, but this is deceptive because

Table 31  Decomposition of retained austenite during the second stage of tempering

<table>
<thead>
<tr>
<th>Specimen treated</th>
<th>Maximum Dilation x 10^6 inch/inch</th>
<th>Ratio L_1/L_2</th>
<th>Time taken to reach the peaks Minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initially quenched without a field and tempered at 240°C</td>
<td>290 (L_1)</td>
<td>10:7</td>
<td>66</td>
</tr>
<tr>
<td>Initially quenched in a field (6.2 K. Gauss) and tempered at 240°C</td>
<td>205 (L_2)</td>
<td></td>
<td>50</td>
</tr>
</tbody>
</table>

there is a greater percentage of austenite present. The last column of Table 31 shows that the time required to reach peak height is in the same ratio as the peak height itself, so the rate of transformation of austenite appears to be the same whether the specimen was quenched with or without a field.

### 6.2.4  Further estimates of the amount of retained austenite

The relative proportions of martensite and retained austenite present in specimens quenched in a field and without a field were estimated

* It is assumed that the first stage of tempering was complete in the specimens initially tempered at 200°C for 1 hr as appears to be indicated by the dilation curves at 200°C.
Table 31a  Estimation of retained austenite by magnetic method.

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hall Probe reading of a fully martensitic specimen</td>
<td>1700 gauss/cm$^3$</td>
</tr>
<tr>
<td>Hall Probe reading of a specimen quenched in a field (6.2 K. Gauss)</td>
<td>1360 gauss/cm$^3$</td>
</tr>
<tr>
<td>Hall Probe reading of a specimen quenched without a field</td>
<td>1270 gauss/cm$^3$</td>
</tr>
<tr>
<td>Percentage of martensite in the specimen quenched in a field</td>
<td>80 (% Austenite 20)</td>
</tr>
<tr>
<td>Percentage of martensite in the specimen quenched without a field</td>
<td>75 (% Austenite 25)</td>
</tr>
<tr>
<td>Relative proportions of retained austenite in specimens quenched in a field</td>
<td>4 : 5</td>
</tr>
</tbody>
</table>
from magnetic analysis (Section 3.5). The relative proportions of austenite from Table (31a) agree reasonably well with the ratio of 7:10 obtained from the second stage tempering results (Section 6.2.3).

It was decided to find out whether the differential Hall probe technique gave the actual saturation magnetization of the specimen. For this purpose the flux density outside a fully martensitic specimen was measured by the probe in a field of 6.2 K. Gauss (the experiment is exactly similar to the one performed in Section 3.5.4 using the same standard).

With a magnetic field \(H\) of 6200 Gauss, the flux density \(B\) just outside the specimen as measured by the Hall probe \(B\) was 7900 Gauss.

From the equation:

\[
B = H + 2I
\]

\[
I = \frac{B - H}{2}\]

which yields a value for \(I\) of 270 Gauss/cm\(^3\). This value is well below the standard value of 1700 Gauss/cm\(^3\) for a fully martensitic structure in a \(1.4C\) steel. This low value can probably be attributed to the fact that for the purposes of consistancy the magnetic analysis was performed on the same specimens as were used for dilatometry; the geometry of the specimens was not really ideal from the point of view of attaining saturation (Section 3.5) and only small field strength was available owing to the limitations of the magnet gap set by the size of the specimen jig. Despite the lack of full saturation it is felt that the relative values are probably accurate enough to compare with other indirect methods of estimating retained austenite.
FIGURE 84 CORRECTED LENGTH CHANGES ON TEMPERING 1.4C STEEL, QUENCHED IN A FIELD (6.2 K. Gauss) AND WITHOUT A FIELD.
(correction applied for the presence of retained austenite)

M1 M2 M3 M4 ..... Quenched in a field of 6.2 K. Gauss and tempered without a field at 80°, 100°, 120°C and 140°C respectively

O1 O2 O3 O4 ..... Quenched without a field and tempered at 80°, 100°, 120° and 140°C respectively.
FIGURE 86  CALCULATION OF ACTIVATION ENERGY FOR THE KINETICS OF THE FIRST STAGE OF TEMPERING

<table>
<thead>
<tr>
<th>$\Delta L/L \times 10^6$</th>
<th>$Q_{mag}$ K.Cals</th>
<th>$Q_{ord}$ K.Cals</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>200</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>300</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>400</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>
6.2.5 Determination of activation energy for first stage tempering

The contraction observed during tempering is due to the decomposition of martensite corresponding to its volume fraction. A correction therefore has to be made to convert these volume fractions to unity so that the length changes correspond to the decomposition of 100% martensitic structures.

The volume fraction of martensite in specimens quenched in a field and without a field has been shown to be 0.8 and 0.75 respectively (Table 31a). Fig. 84 shows the corrected length changes on tempering specimens quenched in a field and without a field.

The overall activation energy for the first stage of tempering was then calculated from the corrected dilation curves (Fig. 84) assuming the following relationship between time (t), fraction transformed (f) and temperature T.

\[
\frac{1}{t} = F(f) \exp \frac{-Q_f}{RT} \quad \text{2.55}
\]

where \(Q_f\) is the activation energy corresponding to a fraction transformed \(f\). To establish the value of \(Q_f\) the differential form of the equation is used:

\[
\frac{\partial \ln t}{\partial \sqrt{T}} = \frac{Q_f}{R} \quad \text{2.56}
\]

A contraction \(\Delta l/1\) should correspond to the decomposition of a specific fraction \(f\) of the total amount of martensite present, and hence can be taken as a criterion for the fraction \(f\).

A graph of \((\ln t) \quad \Delta l/1\) against \(\sqrt{T}\) was drawn (Fig. 86) and the activation energies for the overall first stage tempering calculated for various \(\Delta l/1\) values, for both specimens quenched in a field and without a field (Table 32).
Table 32 Activation energy values for first stage tempering

<table>
<thead>
<tr>
<th>$\Delta L/1 \times 10^6$</th>
<th>$Q_e$ (K-cals) (for specimens quenched in a field)</th>
<th>$Q_e$ (K-cals) (for specimens quenched without a field)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>200</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>300</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>400</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>

The activation energy of 18 Kilo calories obtained for the first stage of tempering compares favourably with the activation energy values obtained by Gerdien (122) and Robert et al (91). The increase in activation energy (from 18 to 20 Kilo calories) as the tempering reaction progresses follows a trend similar to the observations made by King and Glover (89) and Roberts (91) who however found values slightly higher than 18 Kilo calories (23 K~cal). This is probably due to the different experimental techniques used in the two methods.

The similar activation energy values obtained for specimens quenched in a field and without a field add further evidence that no additional mechanisms are required to explain the decomposition of primary martensite during first stage tempering after a magnetic quench.

6.2.6 Tempering kinetics of a Fe 1C 1.5Cr alloy

The tempering experiments were repeated (but not in the same detail) with a Fe 1C 1.5Cr alloy, using a higher field strength. Dilatometric specimens were quenched in a transverse field of 16 K. Gauss, (the axis of the specimen being at right angles to the centres of the poles) and then tempered at 130°C and 150°C. In order to eliminate any possible
FIGURE 87 LENGTH CHANGES (ΔL/L) ON TEMPERING Fe-1Cr ALLOY,
QUENCHED IN A FIELD AND WITHOUT A FIELD.

DILATATION x 10^6 (ΔL/L)

TIME IN MINUTES

- Quenched in a field (16 K. Gauss) and tempered 130°C
- Quenched in a field (16 K. Gauss) and tempered 150°C
- Quenched without a field and tempered 130°C
- Quenched without a field and tempered 150°C
FIGURE 88 LENGTH CHANGES ON TEMPERING Fe 1C 1.5Cr ALLOY, QUENCHED IN A MAGNETIC FIELD (16 K. Gauss) AND WITHOUT A FIELD AND THEN COOLED TO LIQUID NITROGEN TEMPERATURE.

M - Quenched in a field (16 K. Gauss) and tempered at 150°C after liquid nitrogen treatment

O - Quenched without a field and tempered at 150°C after liquid nitrogen treatment
effects due to the decomposition of retained austenite during the first stage of tempering, some of the water-quenched specimens were immediately cooled to liquid nitrogen temperature, and then tempered at 130° and 150°C. The results are shown in Figs. 87 and 88 which confirm the trend observed in the case of 1.4C steel. A quantitative assessment of the effect of the higher field is difficult to make as the tempering characteristics of the two steels are different.

6.2.7 Magnetic analysis of tempered specimens

Further information on the tempered specimens was obtained using the differential Hall probe technique. A fully martensitic structure, obtained by first quenching in water and subsequently giving a refrigeration treatment, was used as the primary standard. It was subsequently found that in order to compare the results with dilatometric curves, allowances had to be made for the different amounts of retained austenite in specimens quenched in a field and without a field. For this purpose the results were recalculated with separate as-quenched standards (one with a magnetic heat treatment and one without) which automatically gave the required correction without having to substitute values for the differences in retained austenite.

Calculations

Let the differential gaussmeter reading between the standard and the tempered specimen be $x$ gauss/cm$^3$.

Let the differential gaussmeter reading between the standard and the specimen quenched in a magnetic field be $a$ gauss/cm$^3$.

and let the corresponding reading between the standard and the specimen quenched without a field be $b$ gauss/cm$^3$.

Since the decomposition of primary martensite into epsilon carbide and low carbon martensite leads to a decrease in the effective saturation magnetization of the specimen, $(x - a)$ and $(b - x)$ should be respectively...
TREATMENT: 1.4 C STEEL QUENCHED IN A FIELD AND WITHOUT A FIELD AND TEMPERED AT 80°, 100°, 120° and 140°C

FIGURE 85  CORRELATION BETWEEN LENGTH CHANGES AND MAGNETIC MEASUREMENTS
proportional to the decomposition of martensite in specimens quenched in a field and without a field. The results are tabulated in Table 30.

6.2.8 Correlation between magnetic analysis and dilatometry

The decomposition of primary martensite during the first stage of tempering leads to a contraction. Hence the terminal contraction (i.e., contraction at the end of tempering) obtained by dilatometry should in some way be related to the magnetic readings \((a - x)\) and \((b - x)\) (Table 30). It can be seen from Fig. 85 that both the extent of contraction and the decrease in magnetization are lower in specimens quenched in a field (and subsequently tempered without a field). However, the points in Fig. 85 are very close to a single line which seems to indicate that the basic mechanism of tempering is the same for specimens quenched in a field as well as for those quenched without a field. The direct proportionality of magnetic and dilatometric readings makes it unlikely that more than one mechanism needs to be invoked to account for the tempering characteristics.

Table 30 Magnetic analysis of tempered specimens.

<table>
<thead>
<tr>
<th>Tempering Temperature and Time</th>
<th>Quenched in a field and tempered (x-a)</th>
<th>Quenched without a field and tempered (x-b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(80^\circ C) (86 hrs)</td>
<td>218</td>
<td>305</td>
</tr>
<tr>
<td>(100^\circ C) (3 hrs)</td>
<td>17</td>
<td>145</td>
</tr>
<tr>
<td>(120^\circ C) (3 hrs)</td>
<td>101</td>
<td>231</td>
</tr>
<tr>
<td>(140^\circ C) (1hr)</td>
<td>202</td>
<td>270</td>
</tr>
</tbody>
</table>
SECTION 7 DISCUSSION OF FURTHER RESULTS

7.1 Hardness histograms

7.1.1 Relation of hardness increase to martensite formation

It was shown in Section 5.2.3 that when the transformation takes place in a magnetic field the $M_s$ is raised, and the whole transformation curve is shifted to higher temperatures by this amount (Fig. 90). It follows therefore that at any temperature in the transformation range, the amount of martensite formed in a field should be greater than without a field. As a first approximation it can be assumed that the hardness of the quenched structure is proportional to the amount of martensite present. The difference in the percentage of martensite formed due to the field is given by the points of intersection of the room temperature ordinate with the transformation curves ($A$, $A'$ (Fig. 90). Taking alloy 1 (Fe 1C 1.5Cr) as an illustration, extrapolation of the transformation curves to room temperature gives 80% martensite in the structure when the transformation takes place in a field and 75% martensite when the transformation takes place without a field. Hence the expected increase in hardness in a structure quenched in a magnetic field would be due to the addition 5% martensite formed.

Given characteristic hardness values for martensite and retained austenite, an estimate can now be made of the difference in hardness due to the field. Assuming the hardness of martensite of Fe 1C 1.5Cr alloy to be 900 V.P.N. and the hardness of retained austenite for the same alloy be 250 V.P.N. (104) the hardness of a structure containing 80% martensite would be 770 V.P.N. and the hardness of a structure containing 75% martensite would be 737 V.P.N. The difference in hardness of 33 V.P.N. is slightly greater than the experimentally observed hardness increase of 25 V.P.N. for this alloy. Although the difference between 33 V.P.N. and 25 V.P.N. can well be regarded as experimental error, there is the possibility that this discrepancy arises because of the initial assumption that the hardness difference is only due to a difference in the amount of martensite present which implies that the intrinsic
FIGURE 90 SCHEMATIC REPRESENTATION OF MARTENSITE FORMATION CURVES WITH A FIELD AND WITHOUT A FIELD.
hardness of martensite formed with and without a field remains the same. Consideration of the first stage tempering results indicates that a magnetic field is likely to inhibit auto tempering (Section 7.2.6). Since the hardness of martensite is increased by the early stages of tempering there will be a tendency for intrinsic hardness of martensite quenched in a magnetic field to be lower than is normally attained at the same cooling rate. This then will affect the increase in hardness of the specimen as a whole due to an increased amount in the total percentage of martensite present.

For a 1.4C steel the $M_s$ should be around $110 - 120^\circ C$ (127); and one could expect about 5% extra-martensite at room temperatures in structures transformed in a magnetic field. Hence similar changes in hardness can be expected to those obtained for the Fe 1C 1.5Cr alloy.

The histograms for the Fe 0.3C 2.8Ni 0.6Cr and 0.6Mo alloy show a considerable overlap, and the hardness increase if any is very small. This can be related to the fact that the $M_s$ temperature for the alloy is $\approx 320^\circ C$; the room temperature ordinate (Fig. 90) will therefore cut out the transformation curves at B and B', where the difference between the amount of martensite formed in a field and without a field is very small.

7.1.2 Tentative explanation for the more uniform hardness in samples quenched in a field

Variations in hardness on quenching can be attributed to a number of factors, notably variation in quenching rate from specimen to specimen, or from point to point within the specimen. If the magnetic field affects the efficiency of the quenching medium, this would result in a more uniform martensitic structure (126 and 14). This argument will not hold for an air cooling steel, but in fact the most noticeable improvement in uniformity are to be found in the water quenched steels.

An alternative explanation can be based on the relative rates of martensite formation at different temperatures. Referring to Fig. 90, let the ordinate corresponding to room temperature cut the transformation
curves in a field and without a field at A and A' respectively. Let the percentage of martensite formed be represented by \( \% M_1 \).

Then the slopes of the curves at A and A' are \( \frac{d \% M}{dT} \) at A and \( \frac{d \% M}{dT} \) at A'. Variations in quenching conditions are less likely to be effective at A than at A', because \( \frac{d \% M}{dT} \) at A' \( \frac{d \% M}{dT} \) at A'. Hence one is likely to get a structure with a greater uniformity of hardness values when the room temperature ordinate intersects the transformation curves at a position corresponding to A and A' (Fig. 90), which is the case for Fe 1C 1.5Cr and 1.4C steels. One of the weaknesses of this explanation is that it depends on there being a marked difference in slopes of the displaced martensite curves which is only possible in a particular range of temperatures, whereas the overall martensite structure in fact produced by transformation over a much larger range of temperature.

### Occurrence of a double martensite peak in the hardness curves

The two hardness peaks obtained for martensite are interesting, but difficult to explain. However, the factors that are likely to produce two different types of martensite of different hardness levels can be listed as follows:

1) mixtures of twinned martensite and acicular or lath martensite
2) mixtures of auto tempered martensite and virgin or untempered martensite
3) differential hardness of the interface between two plates and individual martensite plates
4) mixtures of martensite and non-martensite products.

The double hardness peaks obtained may be a combination of all these factors; there is insufficient evidence to distinguish between possibilities (1), (2) and (3) as far as microhardness is concerned. In case of water-quenched steels (Fig. 74 and 76) the most likely explanation is some
degree of slack quenching to give non-martensite products. This would be in keeping with the increase in uniformity of hardness obtained on quenching in a magnetic field, if it is assumed that this improves the efficiency of fluid quenching media (Section 7.1.2).

7.1.4 Comparison of hardness results and explanations with previous work

There does not seem to be any previous work on the effect of magnetic field on the hardness of quenched steels. Most previous workers investigated the effect of a magnetic field on other mechanical properties, such as tensile strength yield strength and impact strength. The investigations of Bernsteyn et al (7) reveal that a magnetic field of 16 K. Gauss when applied during the martensitic transformation of nickel steels (C 0.03 - 1.1%, Ni5 - 16%) reduces the amount of retained austenite by 8%. This should correspond to a hardness difference of the same order as that obtained in the current investigation.

Bernsteyn (13) and Jahn (14) who obtained some improvement in tensile strength and other mechanical properties due to quenching in a magnetic field, associated this with the refinement of martensite plates through magnetostrictive stresses. There does not seem to be any need to invoke such a hypothesis when the effect of quenching in a magnetic field on the martensitic transformation and the resulting changes observed in hardness can be more easily explained by the simple thermodynamic model outlined in Section (5.2.3). More over there is the problem of obtaining sufficiently high energy values from magnetostrictive effects to appreciably affect nucleation and growth (Section 2.9.2).

7.2 Explanation of the effect of quenching in a magnetic field on the kinetics of the first stage of tempering

7.2.1 Summary of results and observations

The effects of quenching in a magnetic field on the decomposition of martensite during the first stage of tempering can be summarised as follows:

1) The tempering kinetics are slowed down in specimens quenched in a magnetic field.
Fig 92. Possible additional sites for nucleation of epsilon carbide.

1. Martensite formed in a field.
2. Martensite formed without a field.
2) Magnetic analysis, hardness and metallographic investigations revealed that at room temperature, specimens quenched in a magnetic field contain about 5% more martensite than those quenched without a field. It is significant to note that although the volume fraction of martensite is slightly greater in specimens initially quenched in a field, the contraction observed during the first stage of tempering is less. This confirms that the rate of tempering is slowed down in specimens initially quenched in a field.

3) The activation energies for the first stage of tempering are of the same order of magnitude 18 Kcal/mol for both the structures (i.e., those quenched in a field and without a field). This implies that the basic mechanism involved in the decomposition of martensite is likely to be the same in both conditions.

4) The results of a refrigeration treatment before tempering for specimens initially quenched in a field and without a field, are summarised in Table 34. A comparison of the extent of contraction that has occurred after ten minutes of tempering, reveals that the tempering reaction proceeds more rapidly in the initial stages in those specimens quenched in a magnetic field, and treated to liquid nitrogen temperature before tempering. The initial rate of tempering in specimens without a field is not much affected after liquid nitrogen treatment. It should be remembered here that the refrigeration treatment was performed without a magnetic field in both cases, so that the specimens quenched in a magnetic field now contain a mixture of martensites formed with and without a field, whereas the other specimens will consist totally of martensite formed without a field. Refrigeration treatment of a structure quenched initially in a field produces additional martensite (i.e., martensite formed without a field) which not only tempers faster but in all likelihood also provides nucleation sites for martensite plates previously formed in a field (Fig. 92); the overall increase in tempering rate in the initial stages can therefore be explained without

* Metallographic investigations were done only for the Fe 1C 1.5Cr alloy.
altering the conclusion that martensite formed in a field tempers at a slower rate, when compared to that formed without a field. The nature of such nucleation sites will be discussed further in Section 7.2.3.

7.2.2 Factors likely to delay the tempering reaction

The reaction Primary martensite → Low carbon martensite + $\epsilon$-carbide can be spilt into the following sequences (Section 2.7.1):

1) Segregation of carbon atoms to defects such as twin boundaries, dislocations (and possibly domains).
2) Formation of $\epsilon$-carbide platlets.
3) Transformation of b.c.T martensite into low carbon cubic martensite.

Consequently factors which might delay the tempering reactions in specimens previously quenched in a magnetic field are:

a) A change in substructure of martensite.

b) Interaction of carbon atoms with the partially ordered domains and residual magnetic stresses.

c) Alteration in embryonic nucleation sites for $\epsilon$-carbide during martensitic transformation.

These possibilities will now be discussed individually.

7.2.3 The effect of a magnetic field on martensite substructure

Thin foil transmission electron microscopy investigations have shown that martensite plates can consist either of an array of fine twins or a dense dislocation network (77); these are attributed to the mode of inhomogeneous shear in the shape deformation in the theories of
martensite crystallography. When twinning is involved the shape deformation is an invariant plane strain and martensite takes the form of plates. A more non-planar or needle-like morphology may result when the inhomogeneous shear deformation is slip. In addition it is possible to obtain a transition from one kind of substructure to the other at a critical temperature.

The influence of such transformation substructures on the nucleation and growth of \( \zeta \)-carbide is not clearly established, but transmission electron micrograph studies of tempered martensites in Fe-Ni-C alloys reveal that twins do not appear to be preferential nucleation sites for \( \zeta \)-carbide, which is found to grow parallel to (100) planes. An increase in twin substructure could therefore inhibit \( \zeta \)-nucleation relative to other dislocation substructures. Recent investigations on the effect of pressure on martensite transformations have shown that the substructure depends on the relative positions of the \( M_s \) temperature and slip/twinning transition temperature and therefore the substructure will be a function of the \( M_s \). An analogous situation obviously holds for the \( M_s \) shifts produced due to an applied magnetic field.

However it is unlikely that the small shift in the \( M_s \) produced by a magnetic field (with the field strengths used in the present work) could significantly affect the transformation substructure, unless the \( M_s \) temperature is fortuitously close to the slip/twinning transition temperature.

7.2.4 The effect of a magnetic field on residual stresses

A magnetically-quenched structure contains partially ordered domains, and regions of residual magnetic stresses associated with the various anisotropy energies which have had to be overcome during magnetization (Section 2.9.2). These stressed regions can provide competitive sites for segregation of carbon atoms so that the migration of carbon atoms to regions which act as nuclei for \( \zeta \)-carbide platelets is reduced.
Wilson (84) has found an analogous situation while studying the effect of cold working martensite on the precipitation of ε-carbide, where the normal precipitation of ε-carbide in the first stage of tempering is suppressed. This is attributed to the segregation of carbon atoms to dislocations, due to the strong interaction that exists between the two, and therefore less carbon atoms will be available for precipitation (for details refer to Section 2.7.3).

7.2.5 The effect of a magnetic field on the driving force for ε-carbide nucleation

One way in which a magnetic field can reduce ε-carbide nucleation, is by preventing or slowing down the necessary pre-precipitation reactions. This hypothesis is based on the fact that in the presence of a magnetic field a ferromagnetic phase has additional stability, and any reaction which is in competition with the formation of a ferromagnetic phase is less favoured. Magnetization data shows that the formation of ε-carbide is accompanied by a reduction in saturation magnetization (Section 2.7.8) so that application of the same principles already used for describing the Ms shift in terms of a magnetic energy factor JH, would lead to a reduced driving force for the reaction $\xi \rightarrow \alpha + Fe_{2.4}C$.

The normally very fast rate of tempering in the initial stages suggests that potential nuclei are already formed during quenching. The observations of Turkale (83) reveal a continuous carbide film at the austenite/martensite interface in the early stages of tempering of a 0.42C 1.9Mn steel.

If in steels quenched in a magnetic field reactions involving the segregation of carbon atoms to interface dislocations are slowed down, fewer 'potential nuclei' will be available for precipitation of ε-carbide. Hence the overall tempering kinetics will be slowed down in the initial stages.

It would be a bold assumption to assert that the total nucleation of ε-carbide and the effect of quenching in a magnetic field are entirely described by this simple picture; but it is suggested that by quenching in a magnetic field some of several 'potential nucleation sites' is removed or reduced.
7.2.6 The role of auto tempering

The hypothesis outlined in the previous Section has obviously a close connection with the phenomenon of auto tempering, which is likely to occur in ferrous martensite transformations (containing an interstitial element such as carbon or nitrogen). Auto tempering can be considered as the onset of first stage tempering during quenching operation. Hence the effect of a magnetic heat treatment on the kinetics of auto tempering and first stage tempering should be similar, and indeed the hypothesis advanced in previous Sections required that some degree of auto-tempering has occurred during quenching. It would be very difficult to explain the tempering effects otherwise since no field was actually applied during the tempering operation itself.

7.2.7 Comparison with previous work

The results obtained in the current investigation agree with those of Bernsteyn et al (7) who also found that quenching in a magnetic field delays the subsequent decomposition of martensite during the first stage of tempering (Section 2.3). Bernsteyn et al (7) observed that when the specimens were initially quenched without a field, but subsequently tempered in a magnetic field, the decomposition of martensite was also slowed down. No explanation was offered for these results, which are however consistent with the hypothesis invoked in Section 7.2.5. A reduction in the driving force for the nucleation of $\varepsilon$-carbide, based on the relative saturation magnetization of the reaction products relative to pure martensite, would obviously be equally relevant to the case where the field is applied during the tempering operation.

The observation made by Bernsteyn et al (7) that tempering in a magnetic field accelerated the decomposition of retained austenite during the second stage tempering, is also consistent with the hypothesis invoked in Section 7.2.5.

Although it is not possible to give a quantitative treatment of tempering effects it appears that qualitatively it is not necessary to invoke any further assumptions than those used to explain the effect of a magnetic field on transformation during quenching.
SECTION 8 CONCLUSIONS

1) A magnetic field of 16 K. Gauss applied to low alloy steels during quenching produces a shift in the $M_s$ temperature of $\approx 5^\circ C$ and an associated increase of 4-9% in the percentage of martensite formed below the $M_s$.

2) The magnitude of these effects can be accurately predicted by a simple thermodynamic model which is based on adding a single magnetic energy term $H (J_\alpha - J_\gamma)$ to the free energy balance.

3) It has been shown how the experimentally determined $M_s$ shift can be utilised to determine the slope of $\Delta F^{\gamma \rightarrow \alpha}$ curve at $M_s$ and that this constitutes a useful way of experimentally checking the validity of theoretical predictions of the entropy of transformation at the $M_s$ temperature.

4) It has been confirmed that the entropy of transformation appears to be directly proportional to the rate of martensite formation below the $M_s$. This fundamental correlation between the increment of transformation (as defined by the slope of the linear portion of the transformation curve) and the change of driving force with temperature first recognised by Brook, Entwisle and Ibrahim, is a useful step in bridging the gap between the thermodynamics and kinetic approaches to martensitic transformation.

5) An attempt is made to evaluate the latent heat of martensite formation from the recalescence effects associated with the periodic application of a field below the $M_s$. The heat of transformation values can be combined with the entropy of transformation (obtained from the $M_s$ shifts) to evaluate the driving force, $\Delta F^{\gamma \rightarrow \alpha}$ at $M_s$. The value so obtained ($260 \pm 100$ cal/mol) compares favourably with the current theoretical estimates of the driving force required to initiate martensite transformation at the $M_s$. 
6) The increase in hardness of 20-30 V.P.N. obtained at room temperature in three steels after quenching in a magnetic field has been shown to be associated with the shift in the whole transformation curve to higher temperatures in the presence of a magnetic field.

7) Quenching in a magnetic field delays the decomposition of martensite during the first stage of tempering even when no field is applied during tempering. The delay is consistent with a decrease in the number of potential \( \varepsilon \)-carbide nuclei generated during quenching. This is in turn attributed to the reduction in the driving force for \( \varepsilon \)-carbide formation which results from the relative saturation magnetization values of martensite and its tempered products.

8) It has been shown that the application of a magnetic field provides a convenient way of introducing a well defined additional energy increment into the system. This can be used to measure the effects of small changes in driving force on both quenching and tempering reactions and offers certain theoretical and practical advantages over the use of alternative methods such as the application of hydrostatic pressure.
SUGGESTIONS FOR FURTHER WORK

1) The $M_s$ shifts and transformation curves should be reetermined using higher fields to confirm the results obtained using a field of 16 K. Gauss.

2) The effect of a periodic application of a field in the transformation range should be repeated using a differential calorimetric method, so that the rise in temperature due to extra-martensite formed can be determined more accurately; this in turn would enable a more accurate evaluation of the heat of transformation.

3) Thin foil transmission electron microscope studies of martensites formed in intense magnetic fields should be made to find out whether there is any change either in the morphology or crystallography of martensite formed in a field. This should also help in developing a more refined model of the role played by magnetic field (applied during quenching) in delaying the kinetics of the first stage of tempering.

4) Careful experiments may allow a determination of the difference in free energy when one mol of austenite transforms to a) martensite (b.c,T lattice) and b) supersaturated ferrite (b.c.c. lattice) of the same composition. This would settle present ambiguities in the theoretical estimate of the free energy contribution due to preferential ordering of carbon atoms when b.c.T martensite is formed, which is a major source of uncertainty in free energy calculations dealing with martensitic transformations.
REFERENCES


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<table>
<thead>
<tr>
<th>No.</th>
<th>Author(s) and Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>93.</td>
<td>F.E. Werner et al, Trans ASM 42 823 (1957).</td>
</tr>
</tbody>
</table>
95. B.L. Averbach and M. Cohen Trans. ASM 41 1024 (1949).
104. H. Haneman Arch Eisenhutten 15 403 (1942).


Table 4  The Effects of pulsating magnetic fields on martensite transforms in steels.

<table>
<thead>
<tr>
<th>Alloy Composition</th>
<th>Specimen dimensions mm</th>
<th>Field Strength K. Gauss</th>
<th>Variables Studied</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe 0.5C 23Ni 1.5Cr</td>
<td>10 x 10 x 60</td>
<td>350</td>
<td>magnetic field strength</td>
</tr>
<tr>
<td>Fe 0.5C 22Ni</td>
<td>L - 25</td>
<td>0-170</td>
<td>(i) field strength</td>
</tr>
<tr>
<td>Fe 0.5C 22Ni 2Cr</td>
<td>d - 3</td>
<td></td>
<td>(ii) no. of pulses</td>
</tr>
<tr>
<td>Fe C- Ni- Cr alloys</td>
<td>C (0.25 - 1.25)</td>
<td></td>
<td>(i) effect of field strength on $M_s$</td>
</tr>
<tr>
<td></td>
<td>Ni (3 - 24)</td>
<td>0-350</td>
<td>(ii) effect of field strength on the amount of martensite formed</td>
</tr>
<tr>
<td></td>
<td>Cr (2 - 12)</td>
<td></td>
<td>(i) application of magnetic field strength</td>
</tr>
<tr>
<td>Fe 0.5C 22Ni 2Cr</td>
<td>L - 15</td>
<td>0-500</td>
<td>(i) stabilization of austenite, stabilized to various degrees by plastic deformation</td>
</tr>
<tr>
<td></td>
<td>d - 3</td>
<td></td>
<td>(ii) stabilization of austenite, stabilized by isothermally soaking above $M_s$</td>
</tr>
</tbody>
</table>

Technique used for investigation ... magnetic.
<table>
<thead>
<tr>
<th>Commercial Housefield Specimens</th>
<th>0.4C Sheet</th>
<th>1.4C Sheet</th>
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</thead>
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<tr>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.6 ^C6 0.6</td>
<td>0.5 0.2</td>
<td>1.39</td>
</tr>
<tr>
<td>2.8 ^C6 0.2</td>
<td><strong>0.3</strong></td>
<td><strong>0.3</strong></td>
</tr>
<tr>
<td>1.5</td>
<td><strong>0.05</strong></td>
<td><strong>0.5</strong></td>
</tr>
<tr>
<td>C</td>
<td><strong>0.05</strong></td>
<td><strong>0.5</strong></td>
</tr>
<tr>
<td>Mn</td>
<td><strong>0.05</strong></td>
<td><strong>0.5</strong></td>
</tr>
<tr>
<td>Si</td>
<td><strong>0.05</strong></td>
<td><strong>0.5</strong></td>
</tr>
<tr>
<td>Cr</td>
<td><strong>0.05</strong></td>
<td><strong>0.5</strong></td>
</tr>
<tr>
<td>Nb</td>
<td><strong>0.05</strong></td>
<td><strong>0.5</strong></td>
</tr>
</tbody>
</table>

**Chemical Compositions %**

**Table 15** Composition of Steels
Field was applied during quenching only

Some of the specimens were tempered at 240°C.

<table>
<thead>
<tr>
<th>Property</th>
<th>Temperature</th>
<th>Transverse</th>
<th>16</th>
<th>1° C 7° C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness (3)</td>
<td>70 and 170</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnetic anisotropy (2)</td>
<td>30 and 40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1) Diffusivity</td>
<td>170, 190</td>
<td>Axial</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Investigation methods</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Direction of field</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>External quenching temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alloy</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 16: Procedures relating to quenching, field strength and temperature
Table 17 Variation of extra martensite formed with the degree of cooling below the $M_s$.

<table>
<thead>
<tr>
<th>$(M_s - T)^\circ C$</th>
<th>Extra Martensite %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Alloy 1</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>20</td>
<td>9</td>
</tr>
<tr>
<td>30</td>
<td>7</td>
</tr>
<tr>
<td>40</td>
<td>5</td>
</tr>
<tr>
<td>50</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 23 Heat of Transformation values (Voranchikin).

<table>
<thead>
<tr>
<th>Steel</th>
<th>$\Delta J$ gauss/gm</th>
<th>$\Delta H/\Delta T$ K. Gauss/degree</th>
<th>$T_o ^\circ K$</th>
<th>$L$ cal/gm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4C 2Cr 20Ni</td>
<td>190</td>
<td>2</td>
<td>230</td>
<td>2.2</td>
</tr>
<tr>
<td>0.6C 4Cr 8.5Ni 3Si 1.1Mo</td>
<td>150</td>
<td>6</td>
<td>480</td>
<td>11</td>
</tr>
</tbody>
</table>
Table 22 Relevant magnetic properties and $M_s$ temperatures in the vicinity of Fe-30%Ni alloys.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$M_s$ $^0\text{K}$</th>
<th>Curie Temperature for $\langle \Theta \rangle_\alpha$</th>
<th>Curie Temperature for $\langle \Theta \rangle_\gamma$</th>
<th>Bohr Magneton $\langle \xi \rangle_\alpha$</th>
<th>Bohr Magneton $\langle \xi \rangle_\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>31.3%</td>
<td>240$^0\text{K}$</td>
<td>720$^0\text{K}$</td>
<td>370$^0\text{K}$</td>
<td>2.0</td>
<td>1.85</td>
</tr>
<tr>
<td>32.3%</td>
<td>130$^0\text{K}$</td>
<td>710$^0\text{K}$</td>
<td>430$^0\text{K}$</td>
<td>1.85</td>
<td>1.85</td>
</tr>
<tr>
<td>Composition</td>
<td>Ratio $\frac{\sigma^\text{M}_s}{\sigma_o}$</td>
<td>Ratio $\frac{\sigma^\text{M}_s}{\sigma_o(\gamma)}$</td>
<td>Effective $\langle \beta \rangle_\alpha$</td>
<td>Effective $\langle \beta \rangle_\gamma$</td>
<td>J $^\alpha$</td>
</tr>
<tr>
<td>31%</td>
<td>0.95</td>
<td>0.65</td>
<td>1.9</td>
<td>0.8</td>
<td>1.45</td>
</tr>
<tr>
<td>32.3%</td>
<td>0.99</td>
<td>0.90</td>
<td>1.85</td>
<td>1.45</td>
<td>1.45</td>
</tr>
</tbody>
</table>

* using $H = 350 \text{ K. Gauss Ref (12)}$

$\beta = 5586 \text{ ergs/gauss/mol Ref}$
Table 26  Thermodynamic data associated with the effect of pressure on the $M_s$ transition

<table>
<thead>
<tr>
<th>Composition (%)</th>
<th>Pressure (Kbar)</th>
<th>$\Delta V^{\rightarrow\leftarrow}(M_s)$ (cc/mol)</th>
<th>$\Delta T/\Delta P$ ($^\circ$K/Kbar)</th>
<th>$\Delta E$/Kbar (cal/mol/Kbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure iron</td>
<td>5</td>
<td>0.09</td>
<td>8.3</td>
<td>2.1</td>
</tr>
<tr>
<td>pure iron</td>
<td>40</td>
<td>0.16</td>
<td>4.0</td>
<td>3.8</td>
</tr>
<tr>
<td>pure iron</td>
<td>110</td>
<td>0.31</td>
<td>6.2</td>
<td>7.4</td>
</tr>
<tr>
<td>0.41/$w/o$ C</td>
<td>42</td>
<td>0.18</td>
<td>5.2</td>
<td>4.3</td>
</tr>
<tr>
<td>0.75/$w/o$ C</td>
<td>42</td>
<td>0.20</td>
<td>3.7</td>
<td>4.8</td>
</tr>
<tr>
<td>1.23/$w/o$ C</td>
<td>42</td>
<td>0.23</td>
<td>6.2</td>
<td>5.5</td>
</tr>
</tbody>
</table>