THE FLOW STRESS OF INVAR ALLOYS

Thesis submitted for the degree of Master of Philosophy in the University of Surrey

by

F. Ebrahimi, B.Sc.
Department of Metallurgy and Materials Technology

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ABSTRACT

Iron-nickel Invar alloys containing 30-40% Nickel have an unusually large temperature dependence of the flow stress (0.15 Kg/mm²°K), completely untypical of FCC metals. This behaviour is reported to disappear as the temperature approaches the Curie temperature of these alloys and the present work comprises both practical and theoretical justification of these previously reported results. The effect of grain size on the temperature dependence of the flow stress for the above mentioned alloys has also been investigated and no significant effect has been observed.

A new theoretical approach has been made, which examines interactions between dislocations and magnetization by combining the theories of Weiss and Yamamoto and his co-workers. On the basis of this analysis, specific binary and ternary alloy composition has been selected and tested to allow verification of the developed theory.

A number of predictions of the combined theory have been examined, and a good agreement with the experiments has been observed in most cases, although some predictions have not received experimental confirmation. This leads to the conclusion that the Weiss theory may have to be modified to some extent, but the present work substantiates a basically magnetic origin for the mechanical abnormalities in Invar alloys.
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Iron-nickel Invar alloys containing 30-40% Nickel have an unusually large temperature dependence of the flow stress (0.15 Kg/mm² °K), completely untypical of FCC metals. This behaviour is reported to disappear as the temperature approaches the Curie temperature of these alloys and the present work comprises both practical and theoretical justification of these previously reported results. The effect of grain size on the temperature dependence of the flow stress for the above mentioned alloys has also been investigated and no significant effect has been observed.

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The results described in this dissertation are, to the best of my knowledge, original, except where reference is made to the work of others.

F. Ebrahimi
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1. INTRODUCTION

The face centered cubic iron-nickel alloys in the concentration range 30-40% Ni (generally known as Invar alloys) are anomalous in many respects exhibiting a small thermal expansion, a large pressure dependence of the Curie temperature and saturation magnetization, a positive temperature coefficient of Young's modulus and an abrupt change of magnetization with increased concentration of iron. In addition to these well established physical effects, anomalous behaviour has also been found as a result of plastic deformation, although many of these studies have dealt with the formation of martensite under stress.

Bolling and Richman\(^{(1)}\) appear to be the first investigators who noticed a drastic temperature dependence of the flow stress of Invar type Fe-Ni alloys well away from the region where such effects could be attributed to phase transformations. The mechanical properties of these alloys are characterized by:

a. a large temperature dependence of initial flow stress,

b. the existence of a threshold temperature at which the flow stress dependence upon temperature decreases from steep to which the flow stress is almost independent of temperature,

c. no significant difference in work hardening rate with temperature, unless the temperature is low enough for stress induced martensitic transformation,
d. no clearly defined three stage hardening in single crystals, with a low work hardening rate in stage II \((1.2 \times 10^{-3} \text{ G})\),
e. a positive strain rate sensitivity which is independent of strain \( n = \frac{\partial \ln \sigma}{\partial \ln \varepsilon^*} = 18 \cdot 10^{-3} \), and
f. a uniform dislocation distribution with scarcely any dislocation tangles, when alloys are deformed below the Curie temperature.

Because the normal mechanisms operating in other FCC alloys cannot explain the above properties, it has been suggested\(^{(1)}\) that some kind of interaction between dislocations and magnetization may be responsible. However, the magnitude of magnetostatic dislocation interaction is not high enough to be a possible explanation\(^{(5)}\). Therefore, Yamamoto and his co-workers\(^{(3)}\) proposed a model for the mechanical behaviour of Fe-Ni Invar alloys containing a magnetic friction stress and the peculiar magnetic properties of these alloys. In particular it was suggested that the flow stress is related to the pressure dependence of magnetization.

Although there are many theories through which attempts have been made to describe the Invar anomaly and the associated high pressure dependence of magnetization of Invar alloys, the full consequences of individual theories have hardly been explored in relation to mechanical properties as distinct from physical properties. One of the easiest theories to apply, with the least adjustable parameters, has been proposed by Weiss\(^{(50)}\), which is capable of explaining
the effect of deformation on properties of Invar alloys.

In the present work, tensile tests at different temperatures have been conducted for a series of Fe-Ni, Fe-Ni-Mn and Fe-Ni-C alloys to check the validity of Yamamoto's theory\(^{(3)}\) and provide information with which to check out the applicability of the Weiss theory\(^{(50)}\) of Invar behaviour in the field of mechanical properties.

The theories of Weiss and Yamamoto have been combined together and the pressure dependence of magnetization in Yamamoto's relation is calculated from the Weiss\(^{(50)}\) theory. There is a good agreement between the calculated and experimental values of the slope of flow stress versus temperature. From the Weiss theory, it is expected that cold worked alloys may show a more normal temperature dependence of flow stress, and it will be shown that this is confirmed by the results of experiments on annealed and cold worked alloys.

From the combined theory, a temperature is predicted at which the flow stress is maximum and then decreases with decreasing temperature. This maximum has not received experimental confirmation and leads to the conclusion that the Weiss\(^{(50)}\) theory may have to be modified specially for its use at low temperatures.
2. LITERATURE SURVEY

2.1 PLASTIC DEFORMATION OF IRON-NICKEL FCC ALLOYS

2.1.1 EFFECT OF TEMPERATURE

When ferromagnetic Invar type Fe-Ni alloys are deformed, peculiar deformation characteristics become apparent. There is an unusually large temperature dependence of the flow stress, completely untypical of FCC alloys\(^{(1-3)}\). The variation of the flow stress with temperature for an Invar alloy which transforms to martensite is shown in Fig. 1. On the low temperature side, where the flow stress decreases with decreasing temperature, martensite forms, and for a particular strain, the temperature below which the flow stress decreases with decreasing temperature is defined as \(M_s\^o\)(2). The high temperature side consists of three parts\(^{(3)}\):

a. a plateau part in which the flow stress is almost independent of temperature,
b. a normal temperature dependence, and
c. a region of steep and linear temperature dependence for the flow stress.

There is a threshold temperature, \(T^*\), above which the flow stress dependence upon temperature decreases from "steep" to "normal", which can be obtained by extrapolating the two linear dependences and picking their intersection. There is a good correlation between \(T^*\) and the Curie temperature, \(T_C\), for low nickel concentration alloys and they deviate as nickel concentration is increased (Fig. 2).
Fig. 1. Initial flow stress for Fe-30% Ni determined at 
\[ \varepsilon = 10^{-3} \quad (1) \]
Fig. 2. The variation of Curie temperature, $T_C$, and threshold temperature, $T^*$, with nickel content.
The slope of the steep part of the flow stress versus temperature \( \frac{\Delta \sigma}{\Delta T} \) for Fe-Ni alloys, obtained from different sources, is given in Fig. 3. The slope decreases as nickel concentration is increased, and non-Invar ferromagnetic alloys have a relatively small temperature dependence of the flow stress.

Much of the existing data on plastic deformation is for Fe-Ni-C alloys\(^{(1,2,6,7)}\). Ferromagnetic Fe-Ni-C alloys in Invar composition range show the same drastic change of the flow stress with temperature as Fe-Ni binary Invar alloys (Fig. 4). However, paramagnetic alloys have a normal temperature dependence of the flow stress like ferromagnetic binary alloys with high nickel content (non-Invar).

The temperature dependence of the flow stress of single crystal Fe-Ni alloys has also been investigated\(^{(3)}\). The variation of the shear stress with temperature is shown in Fig. 5, while their slopes \( \frac{\Delta T}{\Delta T} \) are given in Table 1. The work hardening rate in stage II for Invar alloys has been found to be 2 to 3 times lower than the rate of normal FCC alloys\(^{(3)}\).

No significant difference in work hardening rate at low strains with temperature variation has been found\(^{(1)}\) unless the temperature was low enough for stress induced martensite transformation or high enough so that deformation occurred above the Curie temperature. The variation of the flow stress with temperature depends on strain as shown in Fig. 6. For high strains, the temperature dependence of the flow stress decreases as the amount of strain is increased.
Fig. 3. The variation of $\frac{\Delta \sigma}{\Delta T}$ with nickel content.
Fig. 4. Comparison of the flow stress variation with temperature for the following alloys$^2$:

1. Fe-30% Ni ferromagnetic Invar
2. Fe-30% Ni - 0.46% C ferromagnetic Invar
3. Fe-23% Ni - 0.45% C paramagnetic
4. Fe-50% Ni ferromagnetic non-Invar
Table 1. The slopes of $\sigma$ vs. $T$ for single crystalline and polycrystalline Fe-Ni alloys.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\frac{\Delta \sigma}{\Delta T}$, $\frac{Kg}{mm^2 \cdot K}$</th>
<th>$\frac{\Delta T}{\Delta T}$, $\frac{Kg}{mm^2 \cdot K}$</th>
<th>Ref.</th>
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<tr>
<td>wt % Ni</td>
<td>$\Delta T$</td>
<td>$\Delta T$</td>
<td></td>
</tr>
<tr>
<td>29.8</td>
<td>0.14</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>31</td>
<td>0.136 (0.15)</td>
<td>0.06</td>
<td>3</td>
</tr>
<tr>
<td>31.7</td>
<td>0.15</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>32</td>
<td>-</td>
<td>(0.1275)</td>
<td>0.051</td>
</tr>
<tr>
<td>33.3</td>
<td>0.15</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>34</td>
<td>0.121</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>36</td>
<td>0.105 (0.1225)</td>
<td>0.049</td>
<td>3</td>
</tr>
<tr>
<td>37</td>
<td>0.106</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>41</td>
<td>0.078</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>42</td>
<td>0.067 (0.0775)</td>
<td>0.031</td>
<td>3</td>
</tr>
<tr>
<td>45</td>
<td>0.035</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>48</td>
<td>0.06</td>
<td>-</td>
<td>83</td>
</tr>
<tr>
<td>49.2</td>
<td>0.05</td>
<td>-</td>
<td>1</td>
</tr>
</tbody>
</table>

Bracketed values were drawn from single crystalline data by using a factor of 2.5 - See section 5.5).
Fig. 5. The temperature dependence of the flow stress for Fe-Ni Invar alloy single crystals (3). Orientations of single crystals are shown in the triangle.

Fig. 6. The flow stress-temperature curve for Fe-31% Ni at different strains (1).
The dislocation configuration for Fe-Ni Invar alloys deformed below their Curie temperatures is characterised by its uniformity and by a configuration of very straight and squarely bent dislocations. On the other hand, wavy-like and tangled dislocations have been observed for an Invar alloy deformed above Curie temperature and a non-Invar ferromagnetic alloy deformed below Curie temperature. The dislocation configuration for an Invar Fe-Ni alloy deformed below its Curie temperature is shown in Fig. 7.

2.1.2 EFFECT OF STRAIN RATE

The strain rate sensitivity number, n, shows the following behaviour for Fe-Ni alloys and Fe-Ni-C alloys(1,2,6):

a. The carbon free ferromagnetic alloys display positive values of n that are independent of strain, and as \( M_S \) is reached, n increases rapidly with decreasing temperature.

b. Any carbon bearing alloy, ferro- or para-magnetic, exhibits n values that diminish with increasing strain.

Those high carbon ferromagnetic alloys that have been investigated(6) display only positive values of n. However, paramagnetic alloys have a negative value of n over a broad 60-70°K temperature range centered near 290°K. This indicates strain aging associated with carbon. Thus, the magnetic state of austenite influences its response to deformation, and carbon-dislocation interactions seem to be inhibited in the ferromagnetic state(2,6).
The activation volume, calculated from strain rate change tests at different temperatures for Invar alloys, is shown in Fig. 8. The activation volumes determined by experiments on relaxation stress also show the same temperature dependence. The rapid increase of the activation volume at high temperature can be taken to indicate that the assumption of one thermally activated process is inadequate. However, the temperature at which the activation volume increases rapidly does not correspond to a magnetic transition point, so there may be a third factor at work.

2.2 ELASTIC PROPERTIES AND YOUNG’S MODULUS ANOMALY

2.2.1 THE ΔE EFFECT

In ferromagnetic materials, Young's modulus, E, depends both on the strain amplitude and on the intensity of magnetization.

When tension is applied to an unmagnetized ferromagnetic material, its length increases as a result of (1) the purely elastic expansion that occurs in all solids, ε₀, and (2) an expansion resulting from the orientation of domains. In substances with non-zero magnetostrictions, the measured stress-strain relation in an unmagnetized state is therefore non-linear. At first, with increasing strain, the value of Young's modulus decreases because orientation of domains is responsible for some additional elongation. The modulus then goes through a minimum and finally approaches a limiting value E₀.

If the ferromagnetic material is initially magnetized
Fig. 7. Dislocation configuration of the Fe-31% Ni Invar alloy. 
$\varepsilon = 3\%$ at $293^\circ K$ \(^3\).

Fig. 8. Activation volume for the Fe-32% Ni alloy as a function of temperature \(^1\).
to saturation so that magnetostrictive expansion has already occurred, the stress-strain relation will be linear and Young's modulus at saturation will be $E_o$, which is the normal modulus of the material, i.e. the value it would possess if the magnetostriction were zero.

The value of Young's modulus, $E_a$, in the unmagnetized state and at zero external stress is thus always less than its value at saturation, $E_o$, and the difference $E_o - E_a$ is called $\Delta E$ effect.

2.2.2 ELASTIC MODULUS ANOMALY

In the case of normal ferromagnets, such as nickel, the values of $E$ for the saturated magnetic state lie on a curve which merges into the curve for the paramagnetic state without any break at Curie point\(^{(8)}\). The same behaviour can be observed for Fe-Ni alloys containing more than 50% Ni\(^{(9)}\). However, for Fe-Ni FCC alloys with less than 45% nickel, the $E,T$ curve at saturation is very much below the $E,T$ curve extrapolated back from the paramagnetic region\(^{(9)}\). Fig. 9 shows the temperature variation of Young's modulus of 42% Ni showing a marked change of the temperature coefficient of modulus $\frac{1}{E} \cdot \frac{dE}{dT}$ at Curie temperature which is not removed by technical saturation. Other results\(^{(10)}\) on the temperature dependence of Young's modulus of a series of annealed Fe-Ni alloys are shown in Figs. 10 and 11.

In a comprehensive study\(^{(11,12)}\), the polycrystalline elastic constants, i.e. Young's modulus $E$, the shear modulus $G$, and the bulk modulus $B$, have been calculated\(^{(13)}\) from
Fig. 9. Young's modulus of the Fe-42% Ni alloys as dependent on magnetization and temperature(8).

Fig. 10. The temperature dependence of Young's modulus for three Fe-Ni alloys(10).

Fig. 11. Young's modulus of the Fe-36% Ni alloys as a function of temperature(10).
experimental values of the single crystalline constants. The temperature dependence of $E$ and $G$ are very similar and anomaly starts near Curie temperature. However, $B$ varies non-linearly with temperature and anomalous behaviour persists to well above $T_C$.

The composition dependence of Young's modulus for FCC iron-nickel alloys in the annealed state at room temperature is plotted in Fig. 12, which shows a minimum at 40% nickel. The modulus increases with applied magnetic field but retains the minimum at 40% nickel. This minimum shifts to lower nickel concentration with decreasing temperature, and at $0^\circ$K the minimum is at 35% Ni\(^{(13)}\).

In contrast to $E$ and $G$, the minimum in concentration dependence of $B$ (which corresponds to a maximum in compressibility) does not occur at 35% Ni but at 30% Ni\(^{(13)}\).

Young's modulus and its temperature dependence in Fe-Ni Invar alloys are not only related to composition but also greatly depend upon the working and annealing history of the alloy. Cold work increases the internal stress, $\sigma_i$, while the change of Young's modulus with magnetization is inversely proportional to $\sigma_i^{(8)}$. There is an increase in Young's modulus of deformed binary Invars and a reduction in the positive value of the thermoelastic coefficient compared with the annealed state\(^{(14)}\).

2.3 SUGGESTED EXPLANATIONS OF ABNORMAL PLASTIC DEFORMATION OF INVAR ALLOYS.

2.3.1 BOLLING AND RICHMAN EXPLANATION

Bolling and Richman\(^{(1,2)}\) were the first workers who
Fig. 12. Young's modulus of FCC Fe-Ni alloys at room temperature and $H = 0$ (4).
paid attention to the most unusual deformation of Fe-Ni and Fe-Ni-C Invar alloys. Several phenomena such as magnetic transition, martensitic transformation, and strain aging due to carbon impurities, overlap in the temperature range which has been used for studying the plastic deformation of these alloys (250°- 450°K).

Since a 33% Ni (0.72% C) alloy in which no martensite transformation can be induced, even at 4°K, has also shown a large temperature dependence of the flow stress, it has been stated\(^1\) that the unusual flow stress temperature relationship cannot be a consequence of martensite transformation.

As was explained in section 2.1.2, strain aging has not been observed in ferromagnetic alloys, and this excludes any effect of carbon-dislocation interaction on drastic temperature dependence of the flow stress.

Since paramagnetic austenites do not have a high temperature dependence of flow stress, and a good correlation between Curie temperature and the onset of the unusual temperature dependence of flow stress has been observed, the peculiar deformation behaviour has been considered to be due to the onset of ferromagnetism\(^1\). But the mere property of ferromagnetism is also insufficient because FCC ferromagnetic non-Invar alloys behave quite normally. Unusual behaviour thus seems limited to the Invar alloys, where there is a possible association with anomalous large pressure sensitivity and related properties.

Bolling and Richman\(^1\) have concluded that the rapid
change of flow stress with temperature is dependent upon
dislocation density and the interaction of dislocations with
magnetization. They\(^{(1)}\) have also stated that interactions
between dislocations in the ferromagnetic Invar alloys,
rather than individual dislocations, are peculiar.

2.3.2 EXPLANATIONS BASED ON MAGNETIC INTERACTION

Krey\(^{(5)}\) has calculated the magnetostatic dislocation
interaction within ferromagnetic crystals magnetized to
saturation in order to explain the rapid increase of flow
stress for Invar alloys reported by Bolling and Richman\(^{(1,2)}\).
The results show that such a magnetostatic interaction will
not be strong enough to compete with the elastic interaction
and therefore, the magnetostatic dislocation interaction
is excluded as a possible explanation.

Based on the above conclusion, Yamamoto and his co-
workers\(^{(3)}\) have explained the temperature dependence of
ferromagnetic Invar alloys by the hydrostatic pressure
dependence of the saturation magnetization.

According to Everet and Kussman\(^{(15)}\), the relation
between the change of hydrostatic pressure, \(\Delta P\), and the
magnetization decrease, is given by:

\[
\Delta I = \alpha \cdot I \cdot \Delta P \tag{1}
\]

\[
\alpha = \frac{I}{I} \cdot \frac{\Delta I}{\Delta P} \tag{2}
\]

Edge dislocations are associated with a hydrostatic
pressure, and therefore a region of magnetization decrease
surrounds them. When a dislocation moves it must do work in changing the pattern of magnetization around it. Assuming that $E$ is the energy change when a dislocation moves by a distance $r$, the friction stress for the motion of a dislocation of unit length, $\tau$, can be written as:

$$E = \tau \cdot b \cdot r \quad (3)$$

A molecular field approximation has been used to calculate $E$ from the magnetization decrease by the hydrostatic pressure around edge dislocations\(^{(3)}\).

$$E = -\rho \cdot r \cdot d \int_{I}^{I-\Delta I_d} W \cdot I \cdot dI \quad (4)$$

where $\rho$, $d$, $W$, and $\Delta I_d$ are respectively, the density, the size which indicates the region of magnetization decrease by hydrostatic pressure around an edge dislocation, the molecular field constant, and the quantity of time dependent magnetization decrease for the pressure change. According to the experimental results of Schlosser et al.\(^{(16)}\), a very large relaxation of magnetization decrease is expected. Assuming this relaxation is very large in comparison with the time that dislocation moves the distance, $\frac{V}{d}$, then:

$$\Delta I = \Delta I_d \quad (5)$$

From Eqs. 1 to 5, $\tau$ is then given by:
Yamamoto and his co-workers\(^{(3)}\) have assumed that in Eq. 6 only the magnetization changes with temperature, and the result of their calculation of \(\tau\) for Fe-35% Ni alloy along with experimental results are shown in Fig. 13.

In the early stage of deformation, the flow stress is determined by the process of dislocation intersection with forest dislocations. During this process, screw dislocations are distorted and will have edge components which are accompanied by a hydrostatic pressure. Since the moving dislocation then experiences a magnetic friction, Yamamoto and his co-workers\(^{(3)}\) have considered that the dislocations in Invar alloys will have a tendency to avoid such an edge component. The uniform distribution and rectilinear arrays of dislocations (observed in Fig. 7) are in accordance with this kind of reasoning.

The low work hardening rate in stage II of the stress-strain curve for Invar alloys can also be understood from such dislocation configurations.

### 2.3.3 OWEN AND NILLES EXPLANATION

Recently Owen and Nilles\(^{(17)}\) have studied the strength of some austenitic Fe-Pt alloys which exhibit a strong Invar effect.

The change of flow stress with temperature of Fe-26% Pt (Q 1300) shows a maximum, and the flow stress decreases with decreasing temperature at lower temperatures (Fig. 14).
Fig. 13. The temperature dependence of the flow stress for Fe-35% Ni alloy\(^{(3)}\). The experimental results and calculated values are shown by full circles and open circles, respectively.

Fig. 14. The temperature dependence of the flow stress of Fe-26% Pt alloy quenched from 1573°K\(^{(17)}\).
Owen and Nilles(17) have proposed that temperature
dependence of the Peierls-Nabarro(18,19) can account for the
peculiar temperature variation of the flow stress of Invar
alloys. The Peierls stress $\sigma_p$ is given by:

$$\sigma_p = \frac{2G}{1-\nu} \exp\left(-\frac{2\pi \xi}{b}\right)$$

(7)

where $\xi = \frac{a}{1-\nu}$

$G$ is the shear modulus, $\nu$ is Poisson's ratio, $\xi$ is dislocation
width and $b$ is Burger's vector. Making the assumption that the
flow stress is the sum of an athermal, $\sigma_G$, and a thermal
component, $\sigma_S$, then

$$\left(\frac{\partial \sigma}{\partial T}\right)_\varepsilon \cdot \varepsilon = \left(\frac{\partial \sigma_G}{\partial T}\right)_\varepsilon \cdot \varepsilon + \left(\frac{\partial \sigma_S}{\partial T}\right)_\varepsilon \cdot \varepsilon.$$

The athermal component, $\sigma_G$, changes with temperature
due to the change of shear modulus, $G$, and can be written:

$$\frac{\partial \sigma_G}{\partial T} = \frac{\partial \sigma_G}{\partial G} \cdot \frac{\partial G}{\partial T}$$

On cooling Invar alloys through the Curie temperature the
temperature coefficient of the shear modulus, $\frac{\partial G}{\partial T}$, becomes less
negative and then changes sign from negative to positive, which
makes a corresponding change in the temperature coefficient
of athermal component of the flow stress $\frac{\partial \sigma_G}{\partial T}$. Since $\frac{\partial \sigma_S}{\partial T}$ is
always negative, the temperature coefficient of the flow stress
must become less negative or may even change sign from negative
to positive according to the relative values of $\frac{\partial \sigma_S}{\partial T}$ and $\frac{\partial G}{\partial T}$.
In this way, Owen and Nilles(17) have qualitatively explained
the observed change in the slope of the temperature dependence of the flow stress of the Fe-26% Pt alloy near its Curie temperature. However, it will be shown in Section 5.2 that such a variation of elastic modulus with temperature is not enough to explain the peculiar high temperature dependence of the flow stress for Invar alloys, although it may play some part.

2.4 MAGNETIC PROPERTIES

2.4.1 GENERAL MAGNETIZATION THEORY

Ferromagnetism has been described by P. Weiss\(^{(20)}\) in terms of an internal field, often termed the "Weiss Molecular Field". His theory is an extension of the classical theory of paramagnetism which was developed by Langevin. Assuming that a ferromagnetic substance consists of elementary magnetic particles each of moment \(\mu_A\), when the substance is exposed to a magnetic field of strength \(H\), each particle behaves as if it possessed an average magnetic moment \(\bar{\mu}_A\) given by Langevin equation

\[
\frac{\bar{\mu}_A}{\mu_A} = \frac{I}{I_O} = \coth \left[ \frac{\mu_A \cdot H}{K \cdot T} \right] - \frac{K \cdot T}{\mu_A \cdot H} \tag{8}
\]
In deriving this, the assumptions are made (1) that the elementary magnets may have any direction with respect to the direction of the field, and (2) that they are too far apart to influence each other.

The Langevin equation can be expressed as:

\[ \frac{I}{I_0} = \tanh \frac{\mu_A \cdot H}{K \cdot T} \]  

(9)

Weiss (20) has pointed out that if the elementary magnets have an influence on each other, then there is an additional internal field, NI, in addition to the true field, H. If H is replaced by H + NI in Eq. 9 we have:

\[ \frac{I}{I_0} = \tanh \frac{\mu_A (H + NI)}{K \cdot T} \]  

(10)

Quantum theory alters the first of the above mentioned assumptions by stating that there will be only a limited number of possible orientations. In this case, the quantum analog of the Langevin equation is known as the Brillouin function and is given by:

\[ \frac{I}{I_0} = \frac{2J + 1}{2J} \cosh \left[ \frac{2J + 1}{2J} \right] \frac{1}{2J} \cosh \frac{\alpha}{2J} \]  

(11-a)

\[ \alpha = \frac{Jg (H + NI)}{R \cdot T} \]  

(11-b)

where (2J + 1) is the number of orientations of the magnetic moment with respect to the magnetic field, and g is the
gyromagnetic ratio. Eq. 10 is obtained when $J = \frac{1}{2}$ (appropriate for a single electron spin).

The Curie temperature given by this theory is:

$$T_C = \frac{(J + 1) g \beta N I_0}{3K}$$  \hspace{1cm} (12)

where $\beta$ is the Bohr magneton number. If we assume $g = 2$ and $J = \frac{1}{2}$, then:

$$T_C = \frac{\beta N I_0}{K}$$  \hspace{1cm} (13)

The molecular field constant, $N$, can be determined by measuring the magnetocaloric effect. The change in molecular field constant with temperature in nickel and in iron is shown in Fig. 15. In both elements there is a noticeable increase in the range of 50° - 100°C immediately above the Curie point.

It has been pointed out\(^{(21)}\) that a change in interatomic spacing with temperature will cause a change in the exchange interaction energy and this will be reflected by a change in the molecular field constant.

2.4.2 MAGNETIC PROPERTIES OF IRON-NICKEL ALLOYS.

Iron-nickel FCC alloys have well defined Curie temperatures as are shown in Fig. 16. The measurement of Curie temperature at low nickel content (below 29at% nickel) is difficult because a diffusionless martensitic reaction alters the metastable FCC phase to the ferromagnetic BCC (or BCT) structure. Bolling et al.\(^{(22)}\) have developed an
Fig. 15. Change in molecular field constant, $N$, in nickel and in iron\(^{(8)}\).

Fig. 16. Curie temperature, $T_C$, and martensitic start temperature, $M_s$, of Fe-Ni FCC alloys.
experimental scheme for the determination of virtual Curie temperature down to 0°K in iron-nickel alloys containing carbon. $T_C$ has been determined at various dissolved carbon levels for a given substitutional percent nickel, and then extrapolation to zero carbon has been made in each case. The extrapolated results are shown in Fig. 16, which gives that $T_C = 0°K$ at 25% nickel.

The dependence of magneton number on composition for both BCC and FCC phases in the binary iron-nickel alloy system are shown in Fig. 17. An abrupt decrease of spontaneous magnetization (at 0°K) is observed near 30% nickel.

Iron-nickel FCC alloys do not follow a simple pattern of magnetic behaviour, and as is shown in Fig. 18, the intrinsic magnetization curves depart from the standard "Brillouin Function".

2.4.3 THE EFFECT OF COLD WORK

A decrease in saturation magnetization of Fe-Ni Invar alloys with cold work has been observed\(^{(23-25)}\). The decrease of saturation magnetization is shown as a function of nickel content in Fig. 19; it is very large near 30% nickel, but decreases rapidly as the nickel content increases.

Most models for the Invar anomaly cannot incorporate the effect of cold work, and their authors prefer to conclude that the effect of cold work is due to secondary causes such as precipitation or an induced martensitic transformation.

Recently Yamamoto and his co-workers\(^{(25)}\) have explained
Fig. 17. The variation of the magneton number of BCC (solid points) and FCC (open points) with composition.

Fig. 18. Reduced magnetization plotted against reduced temperature for FCC iron-nickel alloys (51).
this phenomenon by reference to the local hydrostatic stress field around edge dislocations. The density of dislocations, and hence the amount of regions of local hydrostatic field, is higher in plastically deformed metals than in their annealed state, which causes a reduction of saturation magnetization in cold worked Invar alloys. This theory has already been explained in more detail in section 2.3.2.

2.4.4 THE EFFECT OF HYDROSTATIC PRESSURE

There is a sharp decrease of the spontaneous magnetization and the Curie temperature of Fe-Ni Invar alloys when pressure is applied. Initially it was thought that the effect of pressure could be considered to result from the change produced in inter-atomic distance, which is known to be an important parameter in the strength of magnetic interaction. It has been suggested\(^{(26)}\) that for ferromagnetism to exist, the ratio of the distance, \(D\), between neighbouring atoms in the metal crystal, to the radius, \(r\), of the energy shell in which the electron spins are uncompensated, must be larger than 3.0, but not much greater (Fig. 20 Bethe-Slater curve). According to Bozorth\(^{(27)}\), the Bethe-Slater curve is, in effect, a plot of the Curie point as dependent on the ratio of \(D/r\). By applying hydrostatic pressure, the points in Fig. 20 may be considered to move to the left along the curve. However, Patrick\(^{(28)}\) has found that his results for measuring the change of Curie point with hydrostatic pressure are not consistent with the generalized Bozorth interaction curve and has suggested that the conduction electrons may play a role in the interaction.
Fig. 19. The change of saturation magnetization by plastic deformation versus nickel content\(^{(25)}\).

Fig. 20. Bethe-Slater curve relating the exchange energy of magnetization to the distance between atom centers, with fixed diameter of active shell\(^{(8)}\).
The changes of the Curie temperature and the saturation magnetization with hydrostatic pressure found for iron-nickel FCC alloys indicate a rapid increase of $\frac{\partial T_C}{\partial P}$ and $\frac{\partial I_S}{\partial P}$ with decreasing nickel concentration as are shown in Figs. 21 and 22.

Kouvel and Wilson(29) have expressed the pressure dependence of the spontaneous magnetization $\frac{\partial I_0}{\partial P}$ for Fe-Ni FCC alloys as:

$$I_S^{-1} \left( \frac{\partial I_S}{\partial P} \right) = I_0^{-1} \left[ \frac{\partial I_0}{\partial P} \right] - \left( \frac{I_S}{I_0} \right) \frac{\partial I_S}{\partial T} P T_C^{-1} \left( \frac{\partial T_C}{\partial P} \right)$$

(14)

where $\alpha$ is the temperature coefficient of linear expansion and $C_S$ is the volume compressibility. Eq. 14 has been obtained by assuming that:

$$I_S = I_0 f(T/T_C)$$

(15)

and

$$\left( \frac{1}{V} \cdot \frac{\partial V}{\partial H} \right)_P = - \frac{1}{I} \left( \frac{\partial I}{\partial P} \right)_H$$

(16)

where $V$ is the volume and $H$ is the applied field. The calculated values of $\frac{1}{I_0} \cdot \frac{\partial I_0}{\partial P}$ from Eq. 14 are shown as a dashed line in Fig. 22, which indicates a decrease of pressure dependence of magnetization with decreasing temperature for low nickel content alloys. However, the measurements of temperature dependence of $\frac{\partial I}{\partial P}$ for 36.8at%Ni have shown that $\frac{\partial I}{\partial P}$ is independent of temperature below $77^0 K$(30).
Fig. 21. \(-\frac{1}{T_C} \cdot \frac{\partial T_C}{\partial P}\) for FCC Fe-Ni alloys\(^{(28)}\).

Fig. 22. \(-\frac{1}{I_S} \cdot \frac{\partial I_S}{\partial P}\) and \(-\frac{1}{I_0} \cdot \frac{\partial I_0}{\partial P}\) for FCC Fe-Ni alloys.
The ferromagnetic Fe-Ni-Mn alloys also have large magnetic volume effects such as $-\frac{1}{T_C} \frac{\partial^2 T_C}{\partial P} = 1.6 \times 10^{-12} \text{ Kbar}^{-1}$ and $-\frac{1}{I} \frac{\partial I}{\partial P} = 1.6 \times 10^{-2} \text{ Kbar}^{-1}$. The results for Fe$_{65}$ (Mn$_x$ Ni$_{1-x}$)$_{35}$ alloys indicate that in ferromagnetic alloys ($x < 0.3$) the spontaneous magnetization and the Curie temperature decrease appreciably by compression, and fractional change of the spontaneous magnetization $\frac{1}{I} \cdot \frac{\partial I}{\partial P}$ is nearly equal to the fractional change of Curie temperature $-\frac{1}{T_C} \frac{\partial T_C}{\partial P}$ (31).

2.4.5 THEORIES OF INVAR BEHAVIOUR

In general theories explaining the Invar problem can be separated into (a) models of localised states, (b) band theory models, and (c) a combination of these two. The following is a brief resume of the current theories:

(1) Zener's Theory (32)

Zener has suggested that in metals there exist two competing exchange interactions. One is a ferromagnetic coupling of localised atomic spins via itinerant electrons; the other is a direct antiferromagnetic coupling of localised spins due to the overlap of neighbouring wave functions. The former coupling is long ranged and has only a weak dependence on strain, while the latter depends strongly on strain.

Starting with nickel in the transition row of elements, the d shells of elements become larger as one moves to the left, and therefore, for a given interatomic distance, the direct coupling of iron atoms is larger than that of nickel. In the nickel-iron FCC lattice, the overlap of nickel atoms is assumed to be negligible whereas that of iron is large enough to produce antiferromagnetism at a sufficiently high
concentration of iron.

By contrast, parallel spins on neighbouring iron-iron atoms are unfavourable with respect to the highly strain-dependent direct coupling, and will repel one another.

Thus ferromagnetism in FCC iron-nickel alloys will expand the lattice at low temperatures, and contraction will be produced with increasing temperature. This effect will increase with increasing amounts of iron until the concentration is reached where neighbouring spins start to couple antiferromagnetically. Carr and Colling(33) have proposed a qualitative and quantitative theory for the thermal expansion in some Invar type alloys based on these ideas of Zener.

(2) The Model of Kondorsky and Sedov(34)

These workers have explained the Invar problem in terms of a "latent" or "partial" antiferromagnetism of pure iron in the FCC lattice which is similar to Zener's theory(32). If the exchange integral for neighbouring atoms of iron in the FCC lattice is negative, and that of nickel is positive, then between completely ferromagnetic and antiferromagnetic alloys there should be alloys in which a fraction of atoms have anti-parallel spins. This antiferromagnetic interaction between neighbouring iron atoms in Invar alloys changes with composition. Thus the large volume magnetostriction and the para-process susceptibility in strong magnetic fields have been explained(34) by this model.

By developing the Kondorsky hypothesis, Sidorov and co-workers(35) have explained the concentration dependences of the magnetization and Curie temperature of Fe-Ni FCC alloys,
by assuming that exchange interaction between Ni-Ni atoms and Fe-Ni atoms are ferromagnetic, while Fe-Fe atoms interact antiferromagnetically. According to their calculations the spontaneous magnetization moment at \( T = 0^\circ K \) is written as:

\[
M = M_1 + M_2 = N(1-C)\left\{ 1 - \frac{Z^2 \cdot C}{1-C} \right\} \left[ C + \delta(C) \right] \left[ 1-C-\delta(C) \right] \lambda_1 \lambda_2 \mu_1 + 
\]

\[
N \cdot C \left\{ 1-Z \left[ C+\delta(C) \lambda_2 \right] \right\} \mu_2
\]

where:

\[
\lambda_1 = \frac{C_0 + \delta(C_0)}{1-C_0-\delta(C_0)}
\]

\[
\delta(C_0) = \frac{ZC_0^2 + C_0 - 1}{Z \cdot C_0^2}
\]

\[
\delta(C) = -\frac{1}{2} \sum_{0}^{x-1} P_z(n,c) n
\]

\[
P_z(n,c) = \left( \frac{Z}{n} \right) C^n(1-C)^{Z-n}
\]

In these expressions, \( C \) is the concentration of atoms of iron, \( M_1 \) and \( M_2 \) are the magnetic moments at \( T = 0^\circ K \) being created by iron and nickel, respectively, \( N \) is the total number of atoms in the alloy, \( Z = 12 \) is the first coordinate number of the FCC lattice, \( \mu_1 \) and \( \mu_2 \) are the atomic magnetic moments of nickel and iron, \( C_0 \) is the concentration of the iron atoms at which the spontaneous magnetization of the alloy goes to zero, \( x \) varies from 1,2...Z and \( P_z(n,c) \) is the probability
that the nearest neighbours will be of the same type. Their model agrees well with the experimental results on the variation of spontaneous magnetization with nickel concentration. Although such calculations have been made for temperature dependences of magnetization and of the coefficient of expansion, the model is not capable of explaining the temperature dependence of Invar properties directly.

(3) **Model of Tino and Maeda**

Tino and Maeda have suggested that certain Fe-Ni alloys are composed of many regions with different Curie temperatures. Their model is based on the assumption that the Invar region is always very close to the phase boundary between FCC and BCC. Therefore, in Invar alloys there must be some α-phase nuclei or embryos coherent with the γ-phase matrix, and the behaviour of these alloys will be related to the internal stress around the α-embryos dispersed in a γ-matrix. However, this theory does not give a quantitative explanation.

(4) **Theory of Asano and His Co-workers**

Many aspects of Invar anomaly and their own experimental results have indicated that Invar alloys consist of a mixture of magnetic and antiferromagnetic phases. This has led them to propose a concentration fluctuation model. In this model it is assumed that by increasing the temperature, the regions of different Curie temperatures transform successively to the paramagnetic state; each individual atom is permanently in either the ferromagnetic or paramagnetic state.

(5) **Shiga's Model**

Shiga begins by postulating that ferromagnetic iron has
a permanent moment while antiferromagnetic iron has an induced moment which disappears in the absence of the exchange field, so the atomic state of the iron depends on its surroundings. Shiga has considered that the change of spin polarization in the 3d band induces a change in volume and the thermal behaviour of Invar alloys is a consequence of large volume dependence of the band energy. The neutron scattering measurements of Collins have been interpreted as support for this theory.

(6) **Itinerant Magnetism Models**

Wohlfarth has interpreted the magnetic volume effects of the Invar alloys on the basis of the weak itinerate electron ferromagnetism, relating the physical properties of the material to the width of d band and to the effective interaction between electrons.

Katsuki and Terao have also discussed this problem on the basis of the band model but also take fluctuation of the local composition into account.

(7) **Other Segregation Models**

Schlosser has proposed a model which includes the influence of other metallurgical factors on the Invar anomaly. He has considered that there exist three regions in Fe-Ni Invar alloys, locally ordered FeNi3, pure Fe in FCC lattice, and a transition part where iron atoms have different electronic structures. On the basis of this model the electronic state of an iron atom is affected by the exchange field, the number of nickel nearest neighbours, and the degree of order, but it is not clear how far these are equilibrium or non-equilibrium effects.
The theories mentioned so far have been successful in explaining some of the anomalous behaviour of Invars, in most of the cases by qualitative interpretations, and where quantitative explanations have been given, the theory has a large number of parameters and it is very hard to apply it for calculating different Invar properties. However, the theory given by Weiss (47–50) not only explains the anomalous thermal expansion but also explains a large number of other Invar anomalies. Weiss's hypothesis has some advantages over the other theories. Firstly, it is based on the behaviour of pure iron and one does not have to change the model in relation to pure iron or when adding other elements. Secondly, all of the Invar properties can be directly interpreted by this model with least adjustable parameters. Therefore, special attention has been given to this theory in the present work and it will be discussed in the next section.

2.4.6 WEISS THEORY

Weiss (47–50) has proposed the idea that there are two electronic configurations of iron atoms in a face-centered cubic lattice. These two states, \( \gamma_1 \) and \( \gamma_2 \), are separated by a specific energy difference, \( \Delta E_{\gamma_1\gamma_2} \), and are in equilibrium with each other in a manner corresponding to a two level Schottky excitation. If iron were to exist entirely in one of these two forms, the properties obtained from alloy extrapolation would be as shown in Table 2. In pure iron the antiferromagnetic state, \( \gamma_1 \), is the ground state, but with increasing temperature the ferromagnetic state, \( \gamma_2 \), will be excited. In this model the individual atoms exhibit both
Table 2. Properties of gamma iron obtained by extrapolation from alloy data\(^{(50)}\).

<table>
<thead>
<tr>
<th>Gamma State</th>
<th>Crystal Structure</th>
<th>Lattice Parameter (Å)</th>
<th>Magnetic Structure</th>
<th>Spin per Atom (µB)</th>
<th>Curie or Neel Temp. (°K)</th>
<th>Elastic Modulus (dyne/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma_1 )</td>
<td>FCC</td>
<td>3.54</td>
<td>Antiferromagnetic</td>
<td>-0.5</td>
<td>-80</td>
<td>2.4 ( \times ) 10(^{12} )</td>
</tr>
<tr>
<td>( \gamma_2 )</td>
<td>FCC</td>
<td>3.64</td>
<td>Ferromagnetic</td>
<td>-2.8</td>
<td>-1800</td>
<td>1.5 ( \times ) 10(^{12} )</td>
</tr>
</tbody>
</table>
states on a time transient basis, which is quite different from models suggested by Shiga\(^{41,42}\) and Asano\(^{38-40}\) and his co-workers.

Weiss\(^{50}\) has extended this concept to binary Fe-Ni alloys by postulating a variation of \(\Delta E_{\gamma_1 \gamma_2}\) with nickel content. When iron is alloyed with sufficient nickel, the ferromagnetic state, \(\gamma_2\), is stabilized at \(T = 0^\circ\text{K}\) and the antiferromagnetic state, \(\gamma_1\), can be excited thermally. The suggested energy separation of \(\gamma_1\) and \(\gamma_2\) levels, \(\Delta E_{\gamma_1 \gamma_2}\), of the iron atom in a face-centered cubic lattice as a function of nickel concentration is shown in Fig. 23. The value - 0.0355 ev for pure gamma iron has been determined from the \((P,T)\) curve for the \(\alpha \rightarrow \gamma\) transition in iron while the concentration of nickel for which \(\Delta E_{\gamma_1 \gamma_2}\) passes through zero and becomes positive has been determined from the experimental saturation magnetization curves\(^{51,52}\), as well as the hyperfine field of the FCC Fe-Ni alloys as determined by Mossbauer measurements\(^{53}\). This point has been taken at 29at\% nickel where there is a sudden loss of ferromagnetism.

The ratio of the \(\gamma_1\) and \(\gamma_2\) at temperature \(T\) is given by:

\[
g = \frac{f}{1-f} = \left[ \frac{g_0}{g_1} \right] \frac{\Delta E_{\gamma_1 \gamma_2}}{e^{\frac{R}{T}}} \tag{18}
\]

where \(g\) is the probability of the lower energy state being occupied, \(f\) is the corresponding fraction of iron atoms in the lower energy state, and \(g_0\) and \(g_1\) are the degeneracies of the lower and upper states, respectively. If the number
Fig. 23. The energy separation of the \( \gamma_1 \) and \( \gamma_2 \) levels of iron atoms in a FCC lattice as a function of nickel content. Negative values of \( \Delta E^{\gamma_1 \gamma_2} \) indicate the \( \gamma_1 \) level as the lower level\(^{(50)}\).
of permitted spin orientations is equal to \((2S+1)\) (where \(S\) is the appropriate quantum number), then it can be written that:

\[
g^* = \frac{g_0}{g_1} \approx \frac{(2S_0+1)}{(2S_1+1)} \approx \frac{(2I_0+1)}{(2I_1+1)}
\]  

In Eq. 19 it is assumed that the orbital contribution can be neglected, and Weiss\(^{(50)}\) has pointed out that the value of \(g^*\) below both Curie and Neel temperatures tends to be unity. The theoretical value of \(g^*\) expected from Eq. 19, 2.1, is very close to the value 1.79 derived from a thermodynamic basis.

By using a reasonable variation of energy separation of the two levels with concentration, Weiss\(^{(50)}\) has obtained quantitative agreement for many different properties of the Fe-Ni alloy system, as in Fig. 24 which shows the calculated and observed lattice parameter for pure gamma iron and several Fe-Ni alloys as a function of \(T\).

The \(\gamma_1/\gamma_2\) theory predicts an additional change in saturation magnetization with temperature, as well as the thermal uncoupling of spins. In the Brillouin-Langevin function:

\[
\frac{I}{I_0} = \tanh \left( \frac{I/I_0}{T/T_C} \right)_{H=0}
\]

\(I_0\) will vary with temperature by altering the ratio of \(\gamma_1\) and \(\gamma_2\) and for Fe-Ni alloys this can be expressed in the form:

\[
\frac{I_{\text{max}}}{T} = \left[ 0.6x + \frac{2.8(1-x)g}{1+g} + \frac{0.5(1-x)}{1+g} \right]
\]  

(21)
Fig. 24. The calculated and observed lattice parameter of some Fe-Ni alloys as a function of temperature (50).
where $x$ is the atomic fraction of nickel. The calculated and observed magnetization curves against reduced temperature for two Fe-Ni alloys are shown in Fig. 25, evidencing appreciable departure from the Brillouin curve of pure nickel.

The Curie temperature of transition metals and alloys can be expressed by: \(^{(36)}\):

$$T_C = 113.5 \frac{|Z^\uparrow - Z^\downarrow|}{\ln(I_{T}^{\text{max}} + 1)}$$ (22)

where $Z^\uparrow$ is the number of nearest neighbours with spin aligned in the direction favoured by the sign of the exchange integral and $Z^\downarrow$ is the number whose spin is opposed. $|Z^\uparrow - Z^\downarrow|$ is affected by $\Delta E$, and for FCC lattices\(^{(50)}\):

$$|Z^\uparrow - Z^\downarrow| = 12 \left[ 1 - \frac{(1-x)}{1+\gamma} \right] \left[ 1 - \frac{2(1-x)}{1+\gamma} \right]$$ (23)

By using Eqs. 21-23 the curve in Fig. 26 has been obtained which shows a good agreement with experimental data.

The application of pressure introduces a $\Delta V$ term in the energy separation of the $\gamma_1$ and $\gamma_2$ levels favouring the $\gamma_1$ (low volume) level. The observed and calculated\(^{(54)}\) pressure dependence of the saturation magnetization for Fe-Ni alloys at 300 K is shown in Fig. 27.

Miodownik\(^{(55-58)}\) has applied this theory to explain anomalies in thermodynamic and magnetic properties of FCC Fe-Ni-Cr, Fe-Ni-C, Fe-Mn and Fe-Co alloys, and also the elastic properties of FCC Fe-Ni alloys.
Fig. 25. The calculated and observed magnetization curves against reduced temperature for two Fe-Ni FCC alloys and pure nickel \(^{(50)}\).

Fig. 26. The calculated and observed values of the Curie temperatures of FCC Fe-Ni alloys against nickel content \(^{(50)}\).
Fig. 27. Pressure dependence of the saturation magnetization for Fe-Ni alloys at 300ºK (58).
The effect of deformation on some properties of Fe-Ni alloys has been explained\(^{(59)}\) by Weiss model, while the other available theories do not seem to be able to consider the effect of deformation in a suitable manner. An increase in Young's modulus combined with a reduction in saturation magnetization caused by deformation, has been explained by assuming that deformation leads to an increased proportion of iron atoms in the \(\gamma_1\) state. Evidence for this effect has been obtained by Mossbauer experiments both in Fe-Ni and Fe-Ni-Mn alloys\(^{(60)}\). However a reduction of \(\frac{\Delta E}{E^2}\) and the small shift in \(T_c\) are not consistent with such an increase in the proportion of \(\gamma_1\). Hayes and Miodownik\(^{(59)}\) have suggested that although deformation increases the number of atoms in the \(\gamma_1\) state, it also effectively freezes the thermal equilibrium between \(\gamma_1\) and \(\gamma_2\). Any form of locking for the \(\gamma_1/\gamma_2\) equilibrium will have a tendency to make these alloys behave more normally. For example, the reduced magnetization curve of Ni-Span C approaches the standard \(J=\frac{1}{2}\) Heisenberg relationship more closely than the quenched material, where the spontaneous magnetization in the latter case is undoubtedly temperature dependent\(^{(59)}\).

Davies and Magee\(^{(61)}\) have explained the small volume change in martensitic transformation and the steep \(M_s\) composition dependence found in Invar alloys on the basis of Weiss model.

There is increasing evidence for the coexistence of ferromagnetic and antiferromagnetic behaviour in iron alloys, and the two \(\gamma\) state model provides a useful quantitative
insight into the underlying principles governing the anomalous properties of Invars.

2.5 MARTENSITIC TRANSFORMATION IN IRON-NICKEL ALLOYS

2.5.1 MARTENSITIC START TEMPERATURE

The experimental results on martensitic start temperature, \( M_s \), of Fe-Ni alloys is shown in Fig. 16. The \( M_s \) temperature of Fe-Ni FCC alloys is markedly influenced by austenitizing temperature and austenite grain size\(^{(62,63)}\). It has been observed that when the austenite grain size is small, the \( M_s \) temperature increases with increasing grain size but when the austenite grains are coarse, the \( M_s \) temperature is independent of grain size\(^{(63)}\). The variation of \( M_s \) temperature with grain size in Fe-31\% Ni and austenitizing temperature in Fe-31\% Ni-0.23\% C are shown in Figs. 28 and 29, respectively.

The effect of ternary alloying additions on the \( M_s \) temperature can be estimated from whether they are \( \gamma \) stabilizing or gamma-loop elements and also from their effect on the magnetic properties of Fe-Ni alloys. The effect of alloying on the \( M_s \) temperature cannot be regarded as a mere temperature shift of the \( M_s \)-composition curve for a basic binary system (e.g. Fe-Ni in this instance).

Carbon\(^{(64)}\) and manganese\(^{(65)}\) decrease the \( \alpha+\gamma \) transformation when they are substituted for nickel, and cobalt increases the \( M_s \) temperature when it replaces nickel\(^{(66)}\).

2.5.2 THE EFFECT OF APPLIED STRESS

Martensitic transformation is strongly promoted by an
Fig. 28. The variation of $M_S$ temperature with grain size in the Fe-31% Ni alloy \cite{63}.

Fig. 29. The variation of the $M_S$ temperature with the austenitizing temperature in the Fe-31% Ni-0.23% C \cite{62}.
applied plastic deformation in a range of temperature above $M_S$. For comparable values of the applied stresses, dynamic stresses promote the transformation to a much greater extent than static stresses$^{(67)}$.

Bolling and Richman$^{(6)}$ have studied dynamic and static martensite formation in Fe-Ni and Fe-Ni-C alloys. They have defined two martensite start temperatures: $M_S^\varepsilon$, which is the martensite start temperature for specimens prestrained at strain level $\varepsilon$ at a certain temperature, and $M_S^\sigma$, which is the peak stress in the curve of flow stress versus temperature (Fig. 1) and arises in dynamic response to imposed change. Two regimes are separated by $M_S^\sigma$, the regime of lower temperatures $T < M_S$ which has been distinguished as a temperature range for stress-aided transformation, and the other interval $T_0 > T > M_S^\sigma$ ($T_0$ is the equilibrium temperature between martensite and austenite) which has been distinguished as transformation-aided plasticity. Ferromagnetic Fe-Ni FCC alloys show different behaviour in comparison with paramagnetic alloys. In ferromagnetic alloys, $M_S^\varepsilon$ is not affected by the amount and the temperature of prestrain, and also no evidence of martensite formation has been observed at temperatures between $T_C$ and $M_S^\sigma$. Thus, it has been concluded$^{(1,6)}$ that the nucleation of martensite is inhibited by ferromagnetism.

2.5.3 MARTENSITE MORPHOLOGY

Two major types of martensite, lath and plate, form in iron base alloys as a result of the shear type and diffusion-less martensite transformation of the high temperature stable
FCC solid solution. These two morphological types of martensite differ in fine structure, unit shape, microstructure and formation. For Fe-Ni alloys, it has been suggested\(^{(68)}\) that the morphological transition is governed by the temperature of transformation. With a decrease in \(M_s\) to below 0°C, slip becomes difficult and twinning is preferred, this giving rise to the transition from lath martensite to plate martensite. However, Brook and Entwistle\(^{(69)}\) have proposed that nickel content determines the morphology.

The results of Davies and Magee\(^{(70)}\) show that ferromagnetism is a necessary but not sufficient condition for plate martensite, since many ferromagnetic austenites form lath martensite. They have suggested that the correlation of morphology with ferromagnetism arises because of the "Invar strengthening" which occurs in these austenites below \(T_C\) and because strong austenites tend to form plate martensite.

2.6 RELEVANT THEORIES OF FLOW STRESS

Experimental results show that the plasticity in metals is of a dual nature, athermal and thermal. Different types of deformation mechanisms such as dislocation drag, thermally activated, athermal, and diffusion-controlled mechanisms are operative over all test conditions and it is not readily possible to isolate satisfactory individual mechanisms for experimental examination.

Briefly: i) Alloys deform by diffusion controlled mechanisms at temperatures above about one-half of their melting point. ii) At low temperatures, and for nominal rates of strain, plastic flow in crystals is usually dominated
by a series of thermally activated mechanisms. III) In the case of athermal mechanisms, dislocations can only be moved mechanically and the process cannot be facilitated by thermal fluctuations.

2.6.1 THE SEEGER MECHANISM(71)

The flow stress is normally considered to be made up of a component \( \tau_G \) which is independent of temperature (apart from the variation of the shear modulus, \( G \), with temperature), and a component \( \tau_S \) which increases with decreasing temperature.

Thus:

\[
\tau = \tau_G + \tau_S \tag{24}
\]

The flow stress will change with temperature, \( T \), and strain rate, \( \varepsilon^* \) depending on the type of barriers which oppose mobile dislocations. Seeger(71) has derived an expression for the flow stress as a function of \( T \) and \( \varepsilon^* \) as follows:

\[
\tau(T) = \tau_G + \frac{U_0 - K \cdot T \ln \left( \frac{N A b \nu_0}{\varepsilon^*} \right)}{V} \quad \text{when } T < T^* \tag{25}
\]

\[
\tau = \tau_G \quad \text{when } T > T^* \tag{26}
\]

and

\[
T^* = \frac{U_0}{K \ln \left( \frac{N A b \nu_0}{\varepsilon^*} \right)} \tag{27}
\]

where \( V \) is activation volume, \( N \) is the number of mobile dislocations per volume, \( A \) is the average area swept by the dislocation, \( \nu_0 \) is the frequency which the dislocation tries to...
overcome the barrier, and \( U_0 \) is the local energy barrier. Eq. 25 shows that if the activation volume is small in each process, the sensitivity both to temperature and strain rate is high. The flow stress predicted from this equation is shown in Fig. 30. At high temperatures, the \( \tau_g \) term remains unaltered as the temperature is changed.

It is known that in most FCC metals the yield stress is not very sensitive to temperature, but temperature has a big effect on strain hardening. However, there are several forces which contribute to the yield stress, but to a different extent in different metals. For example, pure aluminium has a high temperature dependence of flow stress in comparison with pure copper\(^{(72)}\). This may be the result of the high stacking fault energy of aluminium which eases the cross slip of dislocations since cross slip is a thermally activated process.

2.6.2 THE ROLE OF SOLID SOLUTION HARDENING

Measurement of the yield stress variation of alloys with temperature shows that most solutes can raise the temperature sensitivity\(^{(73)}\). The results of measurements on copper and copper-zinc alloys indicate that the dependence of the flow stress increases with increasing zinc concentration. While the critical shear stress of copper is independent of temperature, copper-30% Zinc has a temperature sensitivity of about \( 0.01 \text{ kg/mm}^2 \) \(^{(74)}\). By contrast, the results of some measurements on aluminium alloys have shown that flow stress rises less rapidly with decrease in temperature in the alloys than in pure metal\(^{(75)}\). This may be due to the effect of alloying
Fig. 30. The temperature dependence of the flow stress predicted from Seeger's equation (71).
on cross-slip (see previous section) as there will then be less scope for the thermally activated mechanism to operate on lowering the temperature.

A major effect of alloying is to raise the yield stress. It has been variously suggested that the appropriate measure of this is: (a) the difference in atomic size between solvent and solute (b) a difference between the elastic properties of the solute and the matrix atoms.

Mott and Nabarro(76) have developed a theory based on the first assumption where an extra force is needed to push the dislocations past the strained regions surrounding the solute atoms. The effect of the internal stress field can be considered by introducing the parameter $\theta$, defined as:

$$\theta = \frac{1}{a} \cdot \frac{da}{dc}$$

(28)

where $a$ is the lattice parameter and $\frac{da}{dc}$ is the change in the lattice parameter of the solid solution with atomic concentration of the solute. The critical resolved shear stress for two different assumptions of the length of the moving dislocation loop is then given by:

$$\tau_a = G \cdot \theta^2 \cdot c$$

(29)

$$\tau_b = G \cdot \theta^{4/3} \cdot c$$

(30)

where $G$ is the shear modulus and $c$ is the atomic concentration of the solute. Both of these equations predict the
linear dependence on concentration and given a relation of the following type:

\[
\frac{d\tau}{dc} = K' \cdot \theta^n \quad \text{(31)}
\]

Fleischer\(^\text{(77)}\) has investigated the strengthening of copper-base alloys and has shown that both the size effect and the difference in modulus are effective in solution hardening. He has considered that the flow stress is proportional to \((\varepsilon'_G - \alpha \varepsilon_b)\) where:

\[
\varepsilon'_G = \varepsilon_G / (1 + |\varepsilon_G|/2) = \frac{1}{G} \cdot \frac{dG}{dc} \left(1 + \frac{1}{2G} \left| \frac{dG}{dc} \right| \right)^{-1} \quad \text{(32)}
\]

\[
\varepsilon_b = \frac{1}{b} \cdot \frac{db}{dc} \quad \text{(33)}
\]

These results imply that elastic interaction with screw dislocations controls the extent of solution hardening.

A further effect arising from the relative valency of the solvent and solute atoms also appears to be of significance from the work of several investigators\(^\text{(78,79)}\).

For substitutional solute atoms in a FCC crystal where the volume change is relatively small, the modulus effect seems to be the most significant.
3. EXPERIMENTAL PROCEDURE

3.1 MATERIALS AND SPECIMEN PREPARATION

Iron-nickel alloys of the specifications given in Table 3 were annealed at 1373°K for 4 days in vacuum to ensure chemical homogeneity. The carbon bearing alloys were quenched from 1373°K in an oil bath to inhibit the formation of carbides. The diameter of alloy number 1 was reduced to 8 mm by subsequent swaging and annealing at 1173°K in vacuum. Standard rod specimens were then machined (Table 4-c) from a 50% cold worked rod. The thickness of sheet-form alloys was reduced to 0.8 mm by subsequent cold rolling and annealing. Standard flat specimens (Table 4-d) were then machined from 50% cold rolled sheets. The specimen dimensions used by previous investigators are also shown in Table 4.

In the first set of experiments, the specimens were annealed at 1173°K for 20 minutes in vacuum. In the second set, different grain sizes were produced in specimens of alloy number 2 by austenitizing at 1273°K, 1173°K, and 973°K for 30 minutes. In the third set, no further heat treatments were given to the specimens after machining and they were tested in the cold worked state.

3.2 TESTING METHOD

Tensile tests were carried out on an Instron Model 1115 and a Hounsfield Tensometer Model E at Arya-Mehr and Surrey Universities, respectively (Fig. 31).

Grips with universal joints which allow a perfect alignment were used to test flat specimens (Fig. 32). The rod
Table 3. Specification of received alloys.

<table>
<thead>
<tr>
<th>No.</th>
<th>Alloy</th>
<th>Composition wt %</th>
<th>Source</th>
<th>Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>Ni 36 C-Mn-Si</td>
<td></td>
<td>1&quot; Rod</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>Ni 31 C-Mn-Si</td>
<td></td>
<td>1/16&quot; Thick Sheet</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>Ni 26 C 0.4 Mn-Si</td>
<td></td>
<td>1/16&quot; Thick Sheet</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>Ni 36 C 0.15 Mn 0.5 Si</td>
<td>Henry Wiggin Ltd.</td>
<td>1/8&quot; Thick Sheet</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>Ni 34.9 C 0.12 Mn 3.5 Si</td>
<td>Johnson Matthey Research Center</td>
<td>0.128&quot; Thick Sheet</td>
</tr>
</tbody>
</table>
Table 4. Specimen dimensions for tensile test.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. Yamamoto (3)</td>
<td>Wire of 1.5mm diameter. Tensile stress has been conducted in an Instron.</td>
</tr>
<tr>
<td>b. Bolling and Richman (1)</td>
<td>Wire of 2.0mm diameter and 2 inch length. Tensile test has been conducted in an Instron with shoulderless specimens arranged for 1 inch gauge length between serrated jaws.</td>
</tr>
<tr>
<td>c. Present Work Rod Specimen</td>
<td>A gauge length of ½&quot; has been used. Tensile tests were conducted in an Instron with screwed grips.</td>
</tr>
<tr>
<td>d. Present Work Flat Specimen</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 31. The apparatus for tensile test.
Fig. 32. The grips with universal joint.
specimens of alloy number 1 were screwed into threaded end grips.

Yielding of the specimens was indicated schematically in Fig. 33-a. The yield stress was defined by the intersection of the extrapolated plastic and elastic regions. Duplicate specimens were tested at most test temperatures and usually gave values within 2 percent of one another.

Since some of the previous data had been obtained by applying systematic temperature changes to a single specimen, this procedure was also applied to alloys 1 and 2. Single specimens of these alloys were tensile tested at the highest temperature, then partially unloaded to change the temperature, and retested at the new temperature. Information from such tests was derived in the following fashion: The yield stress of the starting temperature was taken as a baseline to which the changes in stress measured at the next temperature were added consecutively. The cumulative stress value was taken as the initial flow stress at each temperature (Fig. 33-b).

For measurement of strain rate, the gauge length on three specimens was measured before and after testing using a travelling microscope with an accuracy of ± 0.001 mm, and time was indicated from the chart speed.

3.3 TEMPERATURE MEASUREMENT

Test temperatures were variously obtained as follows:

a) 523 °K to room temperature in baths of heated silicone oil, monitored by a temperature controller.
b) 273°K to 261°K in baths of acetone-ice mixture.
c) 243°K to 193°K in baths of acetone or alcohol cooled with CO₂ ice or liquid nitrogen.
d) 148°K to 123°K in baths of pentane or distilled petroleum cooled with liquid nitrogen.
e) 77°K in baths of liquid nitrogen.

A copper-constantan thermo-couple was calibrated with boiling water, an ice water mixture, CO₂ ice and liquid nitrogen, and was attached to the specimen. A potentiometer was used for indicating the temperature. In the case of temperatures near room temperature, checks were made using a stem thermometer. In this way temperature was measured with a precision of ± 2°C. Specimens were held in the bath for 15 minutes after a constant temperature was obtained to ensure temperature uniformity.

3.4 METALLOGRAPHY AND GRAIN SIZE MEASUREMENT

A microscopic examination was made after testing each specimen to check the grain size and also to detect the presence of any martensite that might have formed during the test, especially in iron-rich alloys.

Two samples were cut from each tensile test specimen, one from the shoulder and one from the gauge length. After polishing, specimens were etched with a solution containing 30% Acetic Acid + 20% Nitric Acid to reveal the structure.

The grain size was measured by Hilliard's intercept method. A 10 cm diameter test circle was placed on the ground screen of a microscope and the number of intersections were counted. The mean intercept is defined as:
Fig. 33. a) Observed yielding behaviour of tested alloys (except for the carbon bearing alloy which shows a serrated yielding because of strain-aging) and definition of yield stress. b) Schematic stress-strain curve for a systematic temperature change.
Here $P$ is the total number of grain boundary intersections made by circles of 10 cm diameter, $M$ is the magnification and $n$ is the number of circles. The ASTM grain size number was calculated from Hilliard's equation as:

$$N = 10.00 - 6.64 \log L$$

The results of the above measurement were compared with the results obtained from standard ASTM grain size charts.
4. RESULTS

4.1 TEMPERATURE DEPENDENCE OF THE INITIAL FLOW STRESS

Initial flow stress values (obtained as described in section 3.2) for alloys tested at different temperatures are given in Figs. 34, 35, 36, and 37. The results for Fe-31% Ni and Fe-36% Ni alloys in the annealed state show good agreement with previous results. The difference in the absolute values between the present results and the work of Yamamoto\(^{(3)}\) is due to different austentizing temperatures and hence different grain sizes.

It has been shown\(^{(1)}\) that the temperature dependence of the flow stress determined from a systematic temperature change test on one specimen is the same as the temperature variation of the flow stress with many specimens. The Fe-36% Ni alloy was tested in these two ways and as can be seen in Fig. 35, a good correlation can be observed.

The (Fe-36% Ni)\(_{0.97}\) Mn\(_{0.03}\) alloy in the annealed state shows nearly the same drastic temperature dependence of the flow stress as Fe-31% Ni (Fig. 33). By contrast, the Fe-26% Ni-0.4% C alloy (paramagnetic) has a small temperature dependence of the flow stress just as has been observed for other paramagnetic alloys (Fig. 37).

4.2 THE EFFECT OF GRAIN SIZE

The effect of grain size on the temperature dependence of the flow stress was studied in an Fe-31% Ni alloy. Since the martensite start temperature depends on the grain size\(^{(63)}\), this investigation allows mechanical testing of specimens at
Fig. 34. Variation of the initial flow stress with temperature for the Fe-31% Ni. ▲-Ref. 1(Fe-31.7% Ni), △-Ref. 3, ○-Present work (annealed state, grain size 32 μm), ■-Present work (cold worked state, (ε* = 5·10^{-4} 1/sec).
Fig. 35. Variation of the initial flow stress with temperature for the Fe-36% Ni alloy.

$\varepsilon^* \approx 5 \cdot 10^{-4} \text{ 1/sec}$
Fig. 36. Variation of the initial flow stress with temperature for the (Fe-36% Ni)\textsubscript{0.97 Mn \textsubscript{0.03}} alloy. ($\varepsilon \cdot \tilde{\varepsilon} = 5 \times 10^{-4} \text{ 1/sec}$)
Fig. 37. Variation of the initial flow stress with temperature for the Fe-26% Ni-0.4% C alloy in the annealed state. ($\dot{\varepsilon} = 5 \times 10^{-4} 1/sec$)
lower temperatures without the formation of martensite. The variation of the flow stress with temperature for three different grain sizes is shown in Fig. 38. No significant effect of grain size on temperature dependence of the flow stress can be detected.

Martensite formed below 200³⁰K for the two small grain sizes and below 255³⁰K for the specimen with largest grain size. Such martensite formation was detected by a serrated stress-strain curve and also by microscopic examination.

The $M_S^0$ temperatures obtained in the present work for the two small grain sizes are lower than the previous $M_S$ values reported for Fe-31% Ni alloy\(^{(63)}\), but this may be due to the presence of carbon in the specimens. With a 53 μ grain size, the $M_S$ is higher than reported\(^{(63)}\) values because this specimen was tested by using the technique of incremental temperature, and since deformation promotes martensite, a higher $M_S$ can be expected in such circumstances.

### 4.3 THE EFFECT OF COLD WORK

Cold worked specimens (50% cold worked at room temperature) were tested and the results of the variation of the initial flow stress with temperature for three different alloys in the cold worked state along with values for the annealed state are given in Figs. 34, 35, and 36. As can be observed, cold work decreases the temperature dependence of the flow stress for Fe-31% Ni drastically. Its effect in the Fe-Ni-Mn alloy is considerable but there is no effect in the Fe-36% Ni alloy. Table 5 gives the slope of $\sigma$ vs. $T$ curves for the annealed and cold worked states of these alloys.
Fig. 38. The effect of grain size on the temperature dependence of the flow stress for the Fe-31% Ni alloy. (ε = 5·10^{-4} l/sec)
Table 5. The slope of the variation of initial flow stress with temperature in the steep region for tested alloys.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Annealed</th>
<th>50% Cold Worked</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-31% Ni</td>
<td>0.193</td>
<td>0.08</td>
</tr>
<tr>
<td>Fe-36% Ni</td>
<td>0.13</td>
<td>0.14</td>
</tr>
<tr>
<td>Fe-26% Ni-0.4% C</td>
<td>0.042</td>
<td>-</td>
</tr>
<tr>
<td>(Fe-36% Ni)<em>{0.97}Mn</em>{0.03}</td>
<td>0.165</td>
<td>0.116</td>
</tr>
</tbody>
</table>
It can be seen that the Fe-31% Ni alloy in the cold worked state behaves like a paramagnetic alloy.

4.4 MICROSTRUCTURES

The microstructures for three different grain sizes of the Fe-31% Ni alloy are given in Fig. 39. Fig. 40 gives the microstructure of the same alloy (53 μ grain size) deformed at 200°K, which shows that martensite has been formed at this temperature.

The microscopic examination of cold worked Fe-31% Ni specimens tested at different temperatures did not reveal any martensite formation down to a testing temperature of 250°K.

The microstructure of the Fe-26% Ni-0.4% C alloy after quenching is shown in Fig. 41. It appears homogeneous and no carbide can be detected in this alloy.
Fig. 39. The microstructures of the Fe-31% Ni alloy.
(a) Grain size 21.6 μm, (b) Grain size 31.7 μm, (c) Grain size 53 μm.
Fig. 40. The microstructure of the Fe-31% Ni alloy deformed at 200°K (grain size 53 μm) showing the martensite.

Fig. 41. The microstructure of the Fe-26% Ni-0.4% C alloy after quenching from 1373°K.
5. DISCUSSION

5.1 COMPARISON OF THE MECHANICAL BEHAVIOUR OF IRON-NICKEL INVAR ALLOYS WITH THAT OF OTHER FCC ALLOYS

It is known that most FCC alloys have a small temperature dependence of the flow stress and alloying increases this dependence to some degree\textsuperscript{(73)}. Fig. 42 shows the variation of the flow stress with temperature for Fe-31\% Ni, Fe-26\% Ni-0.4\% C, Fe-45\% Ni and Cu-30\% Zn alloys. We see that the Invar alloy (31\% Ni) has a drastic temperature dependence of the flow stress, however both ferromagnetic non-Invar (Fe-45\% Ni) and paramagnetic (Fe-26\% Ni-0.4\% C) alloys have nearly the same behaviour as a normal FCC solid solution (Cu-30\% Zn). Thus the Invar Fe-Ni alloys have an anomalous large temperature dependence of the flow stress, despite the fact that neighbouring Fe-Ni compositions give a quite normal variation of the flow stress with temperature. In previous investigations\textsuperscript{(1-3)} the temperature dependence of the flow stress of Fe-Ni alloys has been compared with that of pure copper, where the flow stress is nearly temperature independent and probably the smallest among other FCC metals\textsuperscript{(72)}. This has led to the consideration that iron-nickel alloys in general have a higher temperature dependence, which takes attention off the particularly striking behaviour in the vicinity of Invar.

Another way in which Invar alloys differ from the usual behaviour of FCC metals is that the temperature dependence of the flow stress generally increases as the plastic strain is increased (or in other words the rate of work hardening decreases with increasing temperature). However for Fe-Ni Invar
Fig. 42. Temperature dependence of the shear stress, $\tau$, for the following alloys:

1. Fe-31% Ni* Present Work
2. Fe-26% Ni-0.4% C* Present Work
3. Fe-45% Ni* Ref. 7
4. Cu-30% Zn Ref. 74

(* Values were drawn from polycrystalline data by using a factor of 2.5 - see section 5.5).
alloys, the temperature dependence of the flow stress decreases as the plastic deformation is increased (see Fig. 6). This means that for these alloys, the rate of work hardening increases as the temperature is increased, which cannot be explained by normal theories of work hardening.

Thirdly, the effect of grain size on the variation of the flow stress with temperature for the Fe-31% Ni alloy was investigated and no significant effect was observed (Fig. 38); although it has been reported that in most metals the temperature dependence of the flow stress decreases as the grain size is increased\(^{(72)}\). Fig. 43 shows the variation of the flow stress with temperature for copper with different grain sizes and we see how significant the effect of grain size is in this more typical FCC metal.

5.2 POSSIBLE ROLE OF THE NON-MAGNETIC VARIABLES ON THE ABNORMAL PLASTIC DEFORMATION OF IRON-NICKEL INVAR ALLOYS

Before considering the effect of internal magnetic fields on the drastic temperature dependence of the flow stress of Invar alloys, attempts were made to verify whether this behaviour is in any way a consequence of changes in several other factors with temperature. In the following a brief survey on the possible effect of such factors is given.

a) Young's Modulus:

The effect of temperature dependence of Young's modulus on the variation of the flow stress with temperature for iron-nickel Invar alloys was checked. In the temperature range of 273\(^{\circ}\)K-573\(^{\circ}\)K, as the temperature is increased, the modulus of Fe-(30-42)% Ni alloys increases and the modulus of Fe-(42-52)% Ni
alloys decreases\(^{(10)}\). Fig. 44 shows the temperature dependence of the flow stress for 45% Ni and 36% Ni alloys corrected for changes in Young's modulus and as can be seen, the difference in slopes is increased. Thus, the correction for the variation of modulus does not help to explain the high temperature dependence of Fe-Ni alloys in Invar region.

b) Stacking Fault Energy:

The stacking fault energy of a metal may contribute to the temperature dependence of its flow stress; a high SFE will tend to increase the variation of the flow stress with temperature. The stacking fault energies of iron-nickel alloys are given in Table 6, which shows a reduction of the SFE by decreasing the nickel content.

As can be seen in Table 6, there is also not a great difference in the temperature dependence of the SFE between Invar and non-Invar alloys (there is a tendency for the SFE to rise again at high temperatures in very iron-rich alloys but this is not so at low temperatures). The conclusion is therefore that the unusual mechanical properties of Invar alloys are not related to their SFE.

c) Activation Volume:

Following the theories of yield strength, we see that the large yield stress and high temperature sensitivity of BCC crystals are due to a large Peierls force and a small activation volume. The magnitude of the activation volume for Fe-Ni alloys at room temperature is of the order of 100 \(b^3\) which is in fact high compared with values\(^{(72)}\) of 9\(b^3\) and 7\(b^3\) for pure iron and carbon steel, respectively. Moreover there is no
Fig. 43. The effect of grain size on the variation of yield stress of copper polycrystals with temperature.

Fig. 44. The temperature dependence of the flow stress corrected for changes in Young's modulus. Dashed curves are $\sigma$ vs. $T$ and full curves are $\frac{\sigma}{E}$ vs. $T$. 
Table 6. The stacking fault energy of iron-nickel alloys at two different temperatures.

<table>
<thead>
<tr>
<th>Composition % Ni</th>
<th>SFE at RT (Ref. 88)</th>
<th>SFE at 1100°C (Ref. 89)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>206</td>
<td>119</td>
</tr>
<tr>
<td>90</td>
<td>221</td>
<td>103</td>
</tr>
<tr>
<td>80</td>
<td>209</td>
<td>93</td>
</tr>
<tr>
<td>70</td>
<td>175</td>
<td>72</td>
</tr>
<tr>
<td>60</td>
<td>142</td>
<td>59</td>
</tr>
<tr>
<td>50</td>
<td>-</td>
<td>48</td>
</tr>
<tr>
<td>40</td>
<td>-</td>
<td>37</td>
</tr>
<tr>
<td>34</td>
<td>-</td>
<td>36</td>
</tr>
</tbody>
</table>
significant difference between the activation volume of Invar alloys and other Fe-Ni alloys. Thus the peculiar properties of Invar alloys are not reflected in the activation volume.

d) Peierls Force:

It is difficult to evaluate the Peierls force precisely. If we assume that in Eq. 7, \( a = b \) and taking \( v = 0.4 \) and \( G = 5 \cdot 10^3 \text{ Kg/mm}^2 \) (13), the maximum of Peierls force is approximately \( 0.5 \text{ Kg/mm}^2 \), which is five times less than the reported shear stress at room temperature for Fe-Ni Invar alloys.

In the temperature range of 273°K-473°K, the shear modulus of Fe-Ni Invar alloys has a positive temperature dependence (13). This gives a decrease of Peierls force with decreasing temperature, which is in contrast with the drastic increase of the flow stress for these alloys.

Hence, the change of Peierls force with temperature is unlikely to contribute to the peculiar temperature dependence of the flow stress of iron-nickel Invar alloys.

e) Atomic Mismatch Parameter:

According to Fleischer (77) the variation of the flow stress with solute concentration is proportional to a mismatch factor \( \varepsilon_s = (\varepsilon_G - \alpha \varepsilon_b) \) (section 2.6.2), which arises from the different elastic properties of the matrix and solute, or

\[
\frac{d\tau}{dc} = A \cdot \varepsilon_s \quad (36)
\]

Since for Fe-Ni alloys \( \frac{dG}{dc} \), and hence \( \varepsilon_s \), changes considerably with temperature, attempts were made to explain the
temperature dependence of the flow stress of these alloys by reference to the Fleischer\textsuperscript{(77)} theory. However as is shown in Fig. 45, the variation of $\frac{dG}{dc}$ with temperature is not significantly different in Invar and non-Invar alloys (e.g. in 30% and 47% nickel alloys). Therefore, qualitatively the Fleischer\textsuperscript{(77)} theory predicts the same behaviour for all compositions of nickel and cannot explain the particularly high temperature dependence of the flow stress for Invar alloys.

5.3 THEORETICAL TREATMENT

5.3.1 PRIMARY CONSIDERATIONS

It has been shown that none of the mechanical factors which were described in the previous section can explain the anomalous plastic deformation of Fe-Ni Invar alloys. It is reasonable therefore to return to the observation that the rapid variation of the flow stress with temperature has a good correlation with Curie temperature (Fig. 2). There are however deviations as the nickel content is increased and both ferromagnetic non-Invar and paramagnetic alloys behave quite normally. Thus the unusual plastic deformation of iron-nickel alloys must be related to the onset of ferromagnetism but it is still necessary to show why the effect is limited to Invar alloys.

The Yamamoto\textsuperscript{(3)} theory is the only successful quantitative one which gives some account of the abnormal temperature dependence of the flow stress of Invar alloys under consideration. However, it takes for granted the values of certain magnetic parameters in the Fe-Ni system. The Yamamoto theory can be verified by the Weiss theory which
Fig. 45. Variation of shear modulus with nickel content\textsuperscript{(13)}. 
has the advantage that many such magnetic properties and other characteristics of the Fe-Ni system can be calculated from some fundamental properties of iron, and increasing evidence is becoming available for the coexistence of ferromagnetic and antiferromagnetic behaviour in iron alloys\(^{(82)}\). An example of using the Weiss\(^{(50)}\) theory for calculating different properties of Fe-Ni alloys is shown in Appendix I which gives the calculated and experimental values of molar volume of Fe-Ni alloys, where very good agreement can be observed.

Moreover, it will be shown that a combination of Weiss\(^{(50)}\) and Yamamoto\(^{(3)}\) theories is capable of explaining the effect of deformation on properties of Invar alloys in a more successful way than the Yamamoto\(^{(3)}\) theory alone.

5.3.2 THE EFFECT OF INTERNAL MAGNETIC FIELDS OF THE FLOW STRESS

According to Yamamoto and his co-workers\(^{(3)}\), the change of the flow stress with temperature of Fe-Ni alloys is only due to magnetic friction, where the friction stress is given by:

\[
\tau_{\text{mag}} = \frac{W}{D} \cdot \Delta P \cdot \rho \cdot d \cdot \alpha \cdot I^2 \tag{37}
\]

and\[
\alpha = \frac{1}{I} \cdot \frac{\Delta I}{\Delta P} \tag{38}
\]

where the definitions are the same as in Eq. 6. It is assumed that \(\tau_{\text{mag}}\) changes with temperature only through the variation of magnetization, \(I\).

In the present work, the flow stress of a ferromagnetic
material is considered to be made as follows:

\[ \tau = \tau' + \tau_{\text{mag}} \]  
(39)

\[ \tau' = \tau_G + \tau_S \]  
(40)

\( \tau' \) is the stress due to various mechanical factors, and consists of a temperature independent component, \( \tau_G \), and a component \( \tau_S \) that increases with decreasing temperature. \( \tau_{\text{mag}} \) is the strength due to magnetic friction which arises from the drag due to the creation of a region of decreased magnetization around the edge dislocation and can be calculated from Eq. 37.

### 5.3.3 COMBINATION OF YAMAMOTO AND WEISS THEORIES

According to Yamamoto and his co-workers\(^{(3)}\), \( \alpha \) in Eq. 37 is temperature independent; however, according to the Weiss theory, this parameter changes significantly with temperature. Therefore, a combination of Yamamoto\(^{(3)}\) and Weiss\(^{(50)}\) theories has been adopted to evaluate the magnetic component of flow stress.

From the Weiss\(^{(50)}\) theory, the spontaneous magnetization of Fe-Ni alloys, is given by:

\[ t_{\text{T}}^{\text{max}} = \left[ 0.6x + \frac{2.8(1-x)g}{1+g} + \frac{0.5(1-x)}{1+g} \right] \]  
(41)

\[ g = g^* \exp \left( \frac{\Delta E_1 \gamma_2 + PAV}{R \cdot T} \right) \]  
(42)

where the symbols are the same as were described in section 2.4.6.
By differentiating $I_T^{\text{max}}$ with respect to pressure, we obtain:

$$\frac{dI_T^{\text{max}}}{dP} = \frac{dI_T^{\text{max}}}{d\gamma} \cdot \frac{d\gamma}{dP} \quad (43)$$

$$\frac{d\gamma}{dP} = \frac{\Delta V}{R \cdot T} \cdot g \quad (44)$$

$$\frac{dI_T^{\text{max}}}{d\gamma} = \frac{2.3(1-x)}{(1+g)^2} \quad (45)$$

$$\frac{dI_T^{\text{max}}}{dP} = \frac{2.3(1-x)g\Delta V}{R \cdot T(1+g)^2} \quad (46)$$

$$\alpha = \frac{1}{I_T^{\text{max}}} \cdot \frac{dI_T^{\text{max}}}{dP} \quad (47)$$

$\alpha$ was calculated for various nickel compositions at different temperatures by the introduction of the following quantitative factors, taken essentially from Weiss\(^{(50)}\):

$\gamma^*$, the degeneracy factor, was taken as 1 for Fe-Ni alloys below their Curie temperatures.

$\Delta V$, the difference in volume of the $\gamma_1$ and $\gamma_2$ states, was taken as:

$$\Delta V = [(3.64)^3 - (3.54)^3] \cdot 10^{-24} \cdot \frac{6.02 \cdot 10^{23}}{4} \quad (\text{cm}^3 \text{ mole}^{-1})$$

$\Delta E_{\gamma_1\gamma_2}$, the energy difference between the $\gamma_1$ and $\gamma_2$ states, was obtained from Fig. 23 (converted to $\frac{\text{cal}}{\text{mole}}$).

In the calculation of $\gamma$ it was assumed that $P\Delta V$ is negligible (at low pressures) compared to $\Delta E_{\gamma_1\gamma_2}$.

The calculated temperature and composition dependences of
α are shown in Figs. 46 and 47. As can be seen, the absolute value of α and also its temperature dependence is relatively small for normal ferromagnetic Fe-Ni alloys, but rises to abnormally high values for Invar alloys.

Since α is also temperature dependent, the magnetic component of the flow stress will vary with temperature through the change of the α • I^2 term, whose temperature dependence is shown in Fig. 48. It can be observed that α • I^2 varies markedly with temperature for low nickel alloys and gives low values with a small temperature dependence as the nickel concentration is increased and the Invar region is passed.

A further feature shown by Fig. 45 is the existence of a maximum (T_{max}) in α • I^2 vs. T curves. This should be reflected in a corresponding maximum in the flow stress curve, but this has not been observed either in previous experiments or in the present results for Fe-31% Ni and Fe-36% Ni alloys. There are, however, several factors which contribute to the absence of such an effect in binary iron-nickel alloys:

a) At low nickel concentrations, where α • I^2 is the largest, T_{max} is below the martensitic transformation temperature, M_s, and cannot be observed.

b) At higher nickel concentrations, where T_{max} is above the M_s, the values of α • I^2 are correspondingly small.

c) The basic temperature dependence of the non-magnetic component of the flow stress must also be considered, which will tend to outweigh the effect of the magnetic component at very low temperatures and higher nickel contents (leaving merely a curvature in the flow stress rather than a maximum).
Fig. 46. The calculated temperature dependence of $\alpha$ for various Fe-Ni alloys.
Fig. 47. The composition dependence of $\alpha$ for three different temperatures.
Fig. 48. The $\alpha \cdot I^2$ values plotted against reduced temperature.
Clearly we need experimental demonstration of the maxima predicted by Fig. 48., but binary iron-nickel alloys are not the best for this purpose.

5.3.4 PREDICTION OF A SUITABLE ALLOY

In order to observe experimentally the maximum in the curve of the flow stress versus temperature, the alloy should have:

a) a high intrinsic value of $\alpha \cdot I^2$,

b) a high temperature dependence of $\alpha \cdot I^2$, and

c) $T_C > T_{\text{max}} > M_S$.

The theory developed here requires a low value of $\Delta E^{Y_1Y_2}$ in order to maximise $\alpha \cdot I^2$, but it also turns out that $T_{\text{max}}$ decreases as $\Delta E^{Y_1Y_2}$ is decreased, and this makes it increasingly likely that $M_S > T_{\text{max}}$.

Thus, the effect of several ternary additional elements on $\Delta E^{Y_1Y_2}$, $T_{\text{max}}$, $M_S$ and $T_C$ was examined with a view towards finding alloys in which a maximum in the flow stress-temperature curve might be more easily detected.

Following the procedure used by Weiss (50) in the binary Fe-Ni system, Miodownik (55) extended the relations for a ternary system as:

$$I_T^{\text{max}} = \left[ 0.6x + \frac{2.8(1-x-y)g}{1+g} + \frac{0.5(1-x-y)}{1+g} + I_y \cdot y \right]$$

(48)

$$|Z^+ - Z^+| = 12 \left[ 1 - \frac{(1-x-y)}{1+g} \right]\left[ 1 - \frac{2(1-x-y)}{1+g} \right]$$

(49)

where $I_y$ and $y$ are the effective spontaneous magnetization and the atomic fraction of the ternary element $y$, respectively.
Differentiating Eq. 48 with respect to pressure gives:

\[
\frac{dI_T^{\text{max}}}{dP} = \frac{2.3(1-x-y) \Delta V \cdot g}{R \cdot T (1 + g)}
\]  \hspace{1cm} (50)

The addition of a third element to the Fe-Ni system also changes the \( \Delta E_{Y_1Y_2} \), and depending on whether \( \gamma_1 \) or \( \gamma_2 \) is stabilised, \( \Delta E_{Y_1Y_2} \) is decreased or increased. Miodownik(55) has adopted the following procedure to evaluate \( \Delta E_{Y_1Y_2} \) for an alloy:

1) Experimental values of \( I_0 \) and \( T_C \) are entered into Eq. 23 to yield a value of \( |Z^+ - Z| \).

2) This value is then entered into Eq. 49 to yield a value of \( g \).

3) This value of \( g \) is entered into Eq. 48 to yield a value of \( I_T^{\text{max}} \) appropriate to \( T_C \).

4) The process is repeated with the new value of \( I_T^{\text{max}} \) so obtained, until the value of \( I_T^{\text{max}} \) remains essentially unchanged.

5) The value of \( g \) which leads to a constant \( I_T^{\text{max}} \) is then entered into Eq. 42, setting the temperature equal to Curie temperature, \( T_C \), and yields a value of \( \Delta E_{Y_1Y_2} \).

The above process gives a self-consistent set of values of \( g \) (or \( \Delta E_{Y_1Y_2} \)) and \( I_T^{\text{max}} \).

Since a high temperature dependence of the flow stress for Fe-Ni-10% Co(70), Fe-Ni-C(2), and Fe-Ni-Mn(70) alloys has been reported, and also information on the values of \( \Delta E_{Y_1Y_2} \) or magnetic properties for these alloys was available, calculations were made to find \( \alpha \cdot I_T^2 \) and \( T_{\text{max}} \) for these alloys.
Fe-Ni-10% Co Alloys: The Curie temperatures of these alloys were obtained from two different sources and are shown in Fig. 49. Since there is a significant difference between the data of these sources, an average was used for the calculation.

The effective spontaneous magnetization of cobalt was assumed to be the same as cobalt in binary Fe-Co alloys, \( I_{Co} = 1.7 \mu_B \).

The \( \Delta E_{Y_1Y_2} \) values for binary Fe-Co alloys have been calculated by Miodownik and are shown in Fig. 50; it has also been suggested that on the basis of electron concentration, \( e/c \), the effect of cobalt on \( \Delta E_{Y_1Y_2} \) is half the effect of nickel. In the present work, \( \Delta E_{Y_1Y_2} \) values for Fe-Ni-Co alloys were obtained in two ways; firstly, by assuming that the effect of cobalt is half the effect of nickel, i.e.,

\[
\frac{\Delta E_{Y_1Y_2}}{Fe-xNi-yCo} = \frac{\Delta E_{Y_1Y_2}}{Fe-(x + \frac{1}{2}y)Ni}
\]

and secondly, the slope of increasing \( \Delta E_{Y_1Y_2} \) by adding Co in binary Fe-Co (Fig. 50) was measured and \( \Delta E_{Y_1Y_2} \) for Fe-Ni-Co was calculated as:

\[
\frac{\Delta E_{Y_1Y_2}}{Fe-xNi-yCo} = \frac{\Delta E_{Y_1Y_2}}{Fe-xNi} + y \cdot \frac{d(\Delta E_{Y_1Y_2})}{dy_{Co}}
\]

The mean value of the two \( \Delta E_{Y_1Y_2} \) was entered into Eq. 48 to yield \( I^\text{max}_T \). This value of \( I^\text{max}_T \) was used as a starting value for the Miodownik procedure of calculating \( \Delta E_{Y_1Y_2} \). These calculations were done because no experimental data on spontaneous magnetization of Fe-Ni-10% Co was available, and on the
Fig. 49. The variation of $T_C$, $T_{max}$ and $T_m$ with nickel content for Fe-Ni-10% Co alloys. The Curie temperatures are from Ref. 8 (open circles) and Ref. 61 (full circles).
Fig. 50. The difference in energy between the two $\gamma$ states of iron for Fe-Co binary alloys. The average change of $\Delta E_{\gamma_1\gamma_2}$ by adding cobalt is about 64 cals/mole per one percent of cobalt.
other hand, the assumption made for $I_{T}^{\text{max}}$ through the mean value of $\Delta E_{Y_{1}Y_{2}}$ helped to minimize the volume of calculations. As is shown in Table 7, the self-consistent $\Delta E_{Y_{1}Y_{2}}$ values are nearly equal to the values obtained from the assumption that the effect of cobalt is half the effect of nickel.

The $\alpha$ factor was calculated for three Fe-Ni-10% Co alloys. Since experimental data for $I_{T}$ was not available it was calculated from the following relation:

$$I_{T} = I_{T}^{\text{max}} \left[ 1 - \left( \frac{T}{T_{C}} \right)^{6} \right] \quad (53)$$

The $\alpha \cdot I_{2}$ values at $T_{\text{max}}$ are given in Table 8, and Fig. 49 shows the $T_{\text{max}}$, $M_s$ and $T_{C}$ for these alloys. At about 29.5% Ni, the $M_s$ temperature is equal to $T_{\text{max}}$, where $\Delta E_{Y_{1}Y_{2}}$ and $\alpha \cdot I_{2}^2$ are the same as for an Fe-34.5% Ni binary alloy. This is not a better situation than the Fe-Ni alloys, since the Fe-33% Ni alloy also does not transform to martensite and has higher $\alpha \cdot I_{2}$ values (which also have a higher temperature coefficient). What is really required is an alloy which has the same temperature dependence of $\alpha \cdot I_{2}^2$ as Fe-30at% Ni but which does not transform to martensite, and Fe-Ni-Co alloys do not seem to have such properties.

**Fe-Ni-C Alloys:** Ternary additions of carbon decrease $M_s$ while they increase the Curie temperature of Fe-Ni alloys. The effect of the addition of carbon on $\Delta E_{Y_{1}Y_{2}}$ for ternary alloys was calculated by using the relationship:

$$\Delta E_{Y_{1}Y_{2}}^{\text{Fe-xNi-yC}} = \Delta E_{Y_{1}Y_{2}}^{\text{Fe-xNi}} + y \cdot \frac{d\Delta E_{Y_{1}Y_{2}}}{dy} \quad (54)$$
Table 7. Comparing the $\Delta E^{\gamma_1 \gamma_2}$ values obtained in different ways.

$\Delta E_{1}^{\gamma_1 \gamma_2}$ and $\Delta E_{2}^{\gamma_1 \gamma_2}$ are obtained by Eqs. 51 and 52, respectively, and $\Delta E_{3}^{\gamma_1 \gamma_2}$ is the self-consistent value obtained by Miodownik (55) procedure.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\Delta E_{1}^{\gamma_1 \gamma_2}$</th>
<th>$\Delta E_{2}^{\gamma_1 \gamma_2}$</th>
<th>$\Delta E_{3}^{\gamma_1 \gamma_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe–32% Ni–10% Co</td>
<td>800</td>
<td>980</td>
<td>~800</td>
</tr>
<tr>
<td>Fe–30% Ni–10% Co</td>
<td>655</td>
<td>790</td>
<td>~640</td>
</tr>
<tr>
<td>Fe–28% Ni–10% Co</td>
<td>412</td>
<td>560</td>
<td>~530</td>
</tr>
</tbody>
</table>
Table 8. The results of calculation for Fe-Ni-10% Co alloys.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$T_c$ (°K)</th>
<th>$\alpha \cdot I^2 \cdot 10^{14}$ $\mu_B$ (dyne/cm²)</th>
<th>$T_{\max}$ (°K)</th>
<th>$M_s$ (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-28% Ni-10% Co</td>
<td>515</td>
<td>1552</td>
<td>~175</td>
<td>370</td>
</tr>
<tr>
<td>Fe-30% Ni-10% Co</td>
<td>550</td>
<td>1380</td>
<td>~190</td>
<td>282</td>
</tr>
<tr>
<td>Fe-32% Ni-10% Co</td>
<td>600</td>
<td>930</td>
<td>~250</td>
<td>80*</td>
</tr>
</tbody>
</table>

* Extrapolated value.
where y is the atomic fraction of carbon. The increase of $\Delta E^{Y_1 Y_2}$ due to addition of carbon is about 80 cals/mole per one atomic percent of carbon.(56)

The $\alpha \cdot I^2$ values at different temperatures were calculated for a series of Fe-Ni-C alloys using Eqs. 50, 47, and 53. The results of such calculations for three Fe-Ni-C alloys are given in Table 9, which shows that carbon also is not the most suitable alloying addition.

Fe-Ni-Mn Alloys: Ternary additions of manganese decrease the $M_s$ and Curie temperatures of Fe-Ni alloys slightly(31,82,84). Manganese is antiferromagnetic and stabilises the $\gamma_1$ state, and the $\Delta E^{Y_1 Y_2}$ values for Fe-Mn alloys show a significant decrease of $\Delta E^{Y_1 Y_2}$ by adding manganese (Table 10)(85). Calculations were done for some Fe-Ni-Mn alloys, and the compositions of these alloys were so selected that they would have the minimum $\Delta E^{Y_1 Y_2}$ values and also, based on previous work(31,82,84), they do not transform to martensite. In these initial calculations it was assumed that the effect of Mn on $\Delta E^{Y_1 Y_2}$ is the same for both pure iron and Fe-Ni alloys and the effective spontaneous magnetization of manganese is $I_{Mn} = -4.3 \mu_B$, with the results shown in Table 11. It can be seen that based on the above assumptions, Mn is a useful ternary addition element. Alloys with about 36% Ni and 2% Mn should have a high value of $\alpha \cdot I^2$ with a $T_{max}$ that is above $M_s$ and also is not so low that tensile test cannot be conducted easily. In other words the addition of Mn makes it possible to test alloys with high nickel concentrations which do not transform to martensite and yet have high values of $\alpha \cdot I^2$. Thus, an alloy of Fe-Ni-Mn was
Table 9. The results of calculation for Fe-Ni-C alloys.

$T_c$ and $M_s$ values are obtained from Ref. 64.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$T_c$ (°K)</th>
<th>$\alpha \cdot I^2 \cdot 10^{14}$ ($\mu_B^2$ dyne/cm²)</th>
<th>$T_{\text{max}}$ (°K)</th>
<th>$M_s$ (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-26.7% Ni-2% C</td>
<td>310</td>
<td>-6000</td>
<td>&lt; 50</td>
<td>176</td>
</tr>
<tr>
<td>Fe-28.4% Ni-2.3% C</td>
<td>400</td>
<td>2500</td>
<td>125</td>
<td>-</td>
</tr>
<tr>
<td>Fe-30% Ni-2% C</td>
<td>460</td>
<td>1883</td>
<td>150</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 10. The $\Delta E_{1Y2}^Y$ values for Fe-Mn binary alloys, used in initial calculations drawn from (56) derived from antiferromagnetic alloys.

<table>
<thead>
<tr>
<th>Mn Concentration (Atomic Fraction)</th>
<th>$\Delta E_{1Y2}^Y$ Cal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-860</td>
</tr>
<tr>
<td>0.01</td>
<td>-1057</td>
</tr>
<tr>
<td>0.02</td>
<td>-1242</td>
</tr>
<tr>
<td>0.04</td>
<td>-1590</td>
</tr>
<tr>
<td>0.06</td>
<td>-1845</td>
</tr>
<tr>
<td>0.08</td>
<td>-1955</td>
</tr>
</tbody>
</table>
Table 11. The results of calculation for Fe-Ni-Mn alloys.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Tc (°K)</th>
<th>$a \cdot I^2 \cdot 10^{14}$ (μB)</th>
<th>$\mu_B$ (dyne/cm²)</th>
<th>Tmax (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-35% Ni-3% Mn</td>
<td>460</td>
<td>5359</td>
<td>50</td>
<td>125</td>
</tr>
<tr>
<td>Fe-35% Ni-2% Mn</td>
<td>500</td>
<td>3000</td>
<td>125</td>
<td>70</td>
</tr>
<tr>
<td>Fe-32.4% Ni-7.79% Mn</td>
<td>392</td>
<td>3652</td>
<td>70</td>
<td></td>
</tr>
</tbody>
</table>
selected in order to check for the existence of the maximum in the temperature dependence of the flow stress curve expected from the developed theory.

5.4 QUALITATIVE CORRELATION OF EXPERIMENTAL DATA WITH THEORY

5.4.1 BINARY IRON-NICKEL ALLOYS

The theory developed so far allows a correlation between the observed and expected slopes, $\frac{d\tau}{dT}$, in the region between $T_C$ and $T_{\text{max}}$. The composition dependence of the $\frac{d(\alpha \cdot I^2)}{dT}$ (Fig. 48) has the same trend as $\frac{d\tau}{dT}$, i.e., it increases as the nickel concentration decreases, and it will be shown later (section 5.5) that these slopes also correlate quantitatively.

The maximum in the flow stress-temperature curve, expected from the developed theory, was not observed for tested Fe-Ni binary alloys. In Fig. 34, for Fe-31% Ni in the annealed state, there is some indication of a curvature in the flow stress curve, but because of martensitic transformation, the flow stress at lower temperature could not be measured. However for Fe-Pt alloys, which should theoretically behave in a similar way as Fe-Ni alloys, a maximum in temperature dependence of the flow stress has been observed, although here there may be additional effects present due to ordering.

5.4.2 TERNARY Fe-Ni-Mn ALLOYS

In practice the selected Fe-Ni-Mn alloy shows a relatively high temperature dependence of the flow stress, which is higher than for the Fe-36% Ni alloy but less than for the 31% Ni alloy. Based on the assumption made for $\Delta E_{11}^Y_{12}^Y$ of this alloy (section 5.3.4), a higher temperature dependence was expected. Moreover,
the predicted maximum in the flow stress curve was not observed down to the temperature of liquid nitrogen. In section 5.3.4 it was assumed that the effect of manganese on $\Delta E^{\gamma_1 \gamma_2}$ is the same for iron and Fe-Ni binary alloys. These values of $\Delta E^{\gamma_1 \gamma_2}$ were subsequently checked for the self-consistency between $I_{T \text{max}}^{\gamma_1 \gamma_2}$ and $T_C$ for three Fe-Ni-Mn Invar alloys for which the experimental values of Curie temperature and spontaneous magnetization were available. The results are shown in Table 12, and it can be seen that in contrast to the situation in binary Fe-Mn alloys, the effect of Mn on $\Delta E^{\gamma_1 \gamma_2}$ in Fe-Ni-Mn alloys is very small. From these results the (Fe-36% Ni)$_{0.97}$-Mn$_{0.03}$ alloy can be expected to act effectively as a binary Fe-35% Ni alloy and therefore have a much smaller magnetic component.

5.4.3 THE EFFECT OF COLD WORK

Some of the effects of cold work on the physical properties, including changes in Young's modulus, have been attributed to changes in the population of the two gamma states\(^{58}\). The argument used is that although deformation increases the number of iron atoms in the $\gamma_1$ state (which has an intrinsically higher modulus), it also effectively freezes the thermal equilibrium between $\gamma_1$ and $\gamma_2$ to some degree. This is equivalent to saying that deformation introduces an activation energy barrier for the $\gamma_1/\gamma_2$ equilibrium which will have a tendency to reduce all Invar effects due to changes in the ratio of the two states with temperature.

The present experimental results show that the temperature dependence of the initial flow stress for the Fe-31% Ni alloy is reduced drastically by cold work and it has nearly a
Table 12. Comparison of the $\Delta E$ values for Fe-Ni-Mn alloys.
$T_c$ values are from Refs. 31 and 82.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$T_c$ (°K)</th>
<th>$\Delta E_{1}^{\gamma}$ (cal/mole)</th>
<th>$\Delta E_{2}^{\gamma}$ (cal/mole)</th>
<th>$\Delta E_{3}^{\gamma}$ (for binary Fe-Ni) (cal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-29.3% Ni-4.9% Mn</td>
<td>320</td>
<td>-800</td>
<td>180</td>
<td>200</td>
</tr>
<tr>
<td>Fe-39.74% Ni-9.63% Mn</td>
<td>470</td>
<td>50</td>
<td>650</td>
<td>1220</td>
</tr>
<tr>
<td>Fe-32.4% Ni-1.79% Mn</td>
<td>392</td>
<td>217</td>
<td>270</td>
<td>420</td>
</tr>
</tbody>
</table>

* values obtained by combining $\Delta E$ values from FeNi(50) and $\Delta E$ values from Fe-Mn (Table 10).
normal temperature dependence; the (Fe-36% Ni)\textsubscript{0.97-Mn\textsubscript{0.03}} alloy in the cold worked state has a lower temperature dependence of the initial flow stress than in the annealed state but this reduction is less than the reduction for the Fe-31% Ni alloy; and cold work does not affect the slope of the variation of the initial flow stress with temperature for the Fe-36% Ni alloy.

Interestingly enough, the effect of cold work on the $\frac{AE}{B_H}$ of the Fe-36% Ni alloy also indicates that there is relatively little effect of cold work on the temperature dependence of this quantity, although cold work reduces the absolute magnitude of this parameter\textsuperscript{(58)}. It is reasonable to assume that as the value of the basic energy difference between the two gamma states, $\Delta E_{\gamma_1\gamma_2}$, approaches zero, any such locking effects will become more and more important. Since Weiss\textsuperscript{(50)} has assumed $\Delta E_{\gamma_1\gamma_2} = 0$ at about 30% nickel, the result of the effect of cold work on the temperature dependence of the initial flow stress for the Fe-31% Ni alloy is not unexpected.

5.4.4 CORRELATION WITH OTHER SOURCES

Another way of checking the validity of Eq. 46 and 47 is to check whether the maximum predicted for $\frac{dI}{dP}$ can be detected. Unfortunately no reliable experimental study on the temperature dependence of $\frac{dI}{dP}$ was available. According to the Maxwell equation $-\frac{\partial I}{\partial P} \cdot \frac{1}{V} = \frac{\partial}{\partial T} \frac{3}{V} \frac{\partial V}{\partial H}$, where $I$ is the magnetic moment of the sample, $V$ is its volume, $T$ is temperature, $P$ is the pressure and $H$ is the applied magnetic field. The temperature and magnetic field dependences of the forced volume magnetostriction of an Invar alloy at low temperatures have indeed
shown that its forced volume magnetostriction decreases drastically with decreasing temperature\(^{(46)}\). However, the measurement of temperature dependence of \(\frac{dT}{dP}\) on a 36.8at% Ni alloy, has shown that \(\frac{dT}{dP}\) is effectively independent of temperature below 77°K\(^{(30)}\), quite unlike the results obtained for the temperature dependence of the forced volume magnetostriction.

It is difficult to account for this discrepancy if the Maxwell relation is to hold. Therefore some other factor must have been omitted, or there is some strong variation of exchange forces with temperature as suggested by Hausch\(^{(12)}\). This has the advantage that shear and bulk moduli could behave quite differently, but the incorporation into the Yamamoto equation is difficult. According to the Weiss picture some adjustment could be made by assuming partial freezing of the \(\gamma_1/\gamma_2\) equilibrium. In other words, at low temperatures when hydrostatic pressure is applied, the \(\gamma_2\) (high volume) state does not transform to the \(\gamma_1\) (low volume) state in the proportion which is expected from theory and an equilibrium state is not reached. Scholsser et al\(^{(46)}\) have also concluded that the failure of the Maxwell equation indicates the freezing in of a higher temperature state but the nature of the states differs considerably from those postulated by Weiss\(^{(50)}\).

It is therefore not possible at the present time to be sure whether the maximum predicted by the Weiss theory is really there; however, the next section shows that some quantitative predictions can be successfully made from the Weiss–Yamamoto formula.
5.5 QUANTITATIVE CORRELATION OF EXPERIMENTAL DATA WITH THEORY

Irrespective of the presence or absence of a maximum in the flow stress curve, the combined theory of Weiss\(^{(50)}\) and Yamamoto\(^{(3)}\) allows a quantitative correlation between the observed and expected slopes for \(\frac{dT}{dT}\) in the region between \(T_C\) and \(T_{\text{max}}\), provided it is possible to separate \(\tau_{\text{mag}}\) from the total value of \(\tau\).

As can be seen in Table 5, the slope of the flow stress is nearly the same for Fe-26% Ni-0.4% C (paramagnetic), Fe-31% Ni (ferromagnetic Invar, cold worked) and Fe-49.2% Ni (ferromagnetic non-Invar). It is assumed that this slope is the normal (non-magnetic) temperature dependence of the flow stress for Fe-Ni alloys and is taken as \(\frac{dT}{dT}\)\(_{\text{normal}}\). Thus:

\[
\frac{dT_{\text{mag}}}{dT} = \left(\frac{dT}{dT}\right)_{\text{obs}} - \left(\frac{dT}{dT}\right)_{\text{normal}} \quad (55)
\]

In this way the slope, \(\frac{dT_{\text{mag}}}{dT}\), for each composition can be obtained by subtraction of the normal slope from the observed temperature dependence of the flow stress.

On the other hand, \(\frac{dT_{\text{mag}}}{dT}\) can be calculated as follows:

\[
\tau_{\text{mag}} = C \cdot \alpha \cdot I^2 \quad (56)
\]

where

\[
C = \frac{W}{b} \cdot \Delta P \cdot \rho \cdot d \quad (57) \quad \text{(section 5.3.2)}
\]

and

\[
\frac{dT_{\text{mag}}}{dT} = C \cdot \frac{d(\alpha \cdot I^2)}{dT} \quad (58)
\]

where \(C\) is assumed to be constant. The necessary values of \(C\)
were then obtained for different compositions in two ways using Eqs. 57 and 58, respectively as shown below.

5.5.1 CALCULATION OF C

The first calculation of C requires the introduction of the following quantities:

1) The molecular field constant \( W = \frac{3K \cdot T_C}{I_0^2} \), where: \( K \) = Boltzman's constant,
\( T_C \) = Curie temperature and
\( I_0 \) = spontaneous magnetization \(^{(8)}\).

2) The slip vector \( b \approx \frac{a}{\sqrt{2}} \), where: \( a \) = lattice parameter.

3) The size of the region of magnetization decrease around an edge dislocation \( d \approx 100 b \)^{(3)}.

4) The hydrostatic pressure around an edge dislocation which is given by

\[
\Delta P = \frac{\sigma_x + \sigma_y + \sigma_z}{3} = \sigma_{\text{hyd}}
\]

(59)

where \( \sigma_x, \sigma_y \) and \( \sigma_z \) are the stresses around an edge dislocation at positions \( x, y \) and \( z \)^{(72,73)}.

In turn,

\[
\sigma_{\text{hyd}} = -\frac{Gb(1+\nu) \sin \theta}{3\pi (1-\nu) r}
\]

(60)

where \( r, \theta \) = polar coordinates,
\( G \) = shear modulus, and
\( \nu \) = Poisson's ratio \( \approx 0.4 \).
We then have

\[
\overline{\sigma}_{\text{hyd}} = - \frac{Gb(1 + \nu)}{3(1 - \nu)} \left[ \int_{r_0}^{R} \frac{dr}{r} \int_{0}^{\pi} \sin \theta \, d\theta \right] \int_{r_0}^{R} dr \int_{0}^{\pi} d\theta
\]

and

\[
\Delta P = - \frac{2Gb(1 + \nu) \ln \frac{R}{r_0}}{3\pi^2(1 - \nu)(R - r_0)}
\]  

(61)

where: \( R = \) half of the dislocation separation \( \approx 10^{-4} \text{cm} \) (73), 
\( r_0 = \) radius of the core of the dislocation \( \approx 10^{-3} \text{cm} \) (73).

By using the above parameters, the following result is obtained:

\[
C_{\text{cal}} = \frac{1.8984 \cdot 10^6 \cdot T_C \cdot G \cdot a \cdot \rho}{A \cdot I_0^2}
\]  

(62)

\( T_C (^\circ \text{K}), \ G \left( \frac{\text{dynes}}{\text{cm}^2} \right), \ a \ (\text{cm}), \ \rho \left( \frac{\text{gr}}{\text{cm}^3} \right), \ A \left( \frac{\text{gr}}{\text{mole}} \right), \ I_0 \ (\mu_\text{B}) \)

It is considered that \( C \) is independent of temperature, and the error arising from the assumption that \( G, a \) and \( \rho \) are temperature independent, is negligible.

For the second method using Eq. 58, the experimental temperature dependence of resolved shear stress was drawn largely from polycrystalline data whereas the theoretical prediction basically holds only for single crystals. A conversion factor from Sachs\(^{86}\) was therefore used to correlate theory and experiment. In the case of 31\% Ni for which both single crystalline and polycrystalline data was available, use of this same conversion factor gives a satisfactory
answer.

It can be seen from Table 13 that there is remarkably good quantitative agreement between the calculated and experimental results. One of the reasons why the results of the 31% Ni alloy are not in such close agreement as for higher nickel concentration alloys is that with decreasing nickel content the spontaneous magnetization, \( I_0 \), drops extremely rapidly and the value of \( C_{\text{cal}} \) is very sensitive to this factor.
Table 13. The values of C calculated by two methods. C and $C_{cal}$ are calculated from Eqs. 58 and 62, respectively.

<table>
<thead>
<tr>
<th>Composition (wt % Ni)</th>
<th>$\left(\frac{dT}{d\tau}\right)_{obs}$ (Kg/mm² °K)</th>
<th>$\left(\frac{dT}{d\tau}\right)_{mag*}$ (Kg/mm² °K)</th>
<th>$\frac{d(\alpha \cdot I^2)}{dT}$ dyne/cm²</th>
<th>$C = \frac{d\tau/dT}{d(\alpha \cdot I^2)/dT}$</th>
<th>$C_{cal}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>41</td>
<td>0.039</td>
<td>0.019</td>
<td>2.05</td>
<td>$0.925 \cdot 10^{12}$</td>
<td>$1.006 \cdot 10^{12}$</td>
</tr>
<tr>
<td>36</td>
<td>0.052</td>
<td>0.032</td>
<td>3.5</td>
<td>$0.914 \cdot 10^{12}$</td>
<td>$0.954 \cdot 10^{12}$</td>
</tr>
<tr>
<td>34</td>
<td>0.054</td>
<td>0.034</td>
<td>4.4</td>
<td>$0.777 \cdot 10^{12}$</td>
<td>$1.040 \cdot 10^{12}$</td>
</tr>
<tr>
<td>31</td>
<td>0.065</td>
<td>0.045</td>
<td>6.1</td>
<td>$0.737 \cdot 10^{12}$</td>
<td>$1.568 \cdot 10^{12}$</td>
</tr>
</tbody>
</table>

* $\left(\frac{dT}{d\tau}\right)_{mag} = \left(\frac{dT}{d\tau}\right)_{obs} - \left(\frac{dT}{d\tau}\right)_{normal}$, the normal temperature dependence was taken as the slope for Fe-49.2% Ni, i.e. 0.02 Kg/mm² °K (see Table 1).
On the basis of the experimental results and the theoretical treatment it may be concluded that:

1) Iron-nickel alloys have an anomalous large temperature dependence of the initial flow stress in the vicinity of Invar Composition.

2) Grain size does not have a significant effect on the variation of the initial flow stress with temperature for Invar alloys.

3) Cold worked Invar alloys show a lower temperature dependence of the flow stress than in the annealed state.

4) This abnormal mechanical behaviour of Invar alloys has a basically magnetic origin.

5) None of the usual factors of mechanical origin, which contribute to the temperature dependence of the flow stress, are capable to explain the drastic change of the initial flow stress with temperature for Invar alloys.

6) The combination of Weiss and Yamamoto theories which has been developed here shows good agreement with the experimental results in most of the test situations.

7) The Weiss theory ($\gamma_1/\gamma_2$ hypothesis) can account for the basic effect of deformation although it may have to be modified for use at low temperatures.
A number of observations made during this work suggest some further investigation.

1. In order to check the existence of the predicted maximum in the initial flow stress versus temperature curve, an Fe-Ni-Mn alloy with about 33% Ni and 4% Mn may be more suitable than some of the compositions tested so far.

2. Further experimental study on the variation of the pressure dependence of the saturation magnetization \( \frac{dI}{dp} \) at lower temperatures for Invar alloys may clarify whether the \( \gamma_1/\gamma_2 \) theory fails at low temperatures or the Yamamoto theory should be modified in some other way.

3. Further study of the dislocation density of the Invar alloys may provide information which can be used for verification of the Yamamoto theory concerning the effect of deformation on the properties of Invar alloys.

4. If the unusual mechanical behaviour of Invar alloys has a magnetic origin, the application of an external magnetic field will produce a change in their responses to mechanical factors. Hence, the testing of Invar alloys under high magnetic fields may help to understand the contribution of magnetization to mechanical behaviour of these alloys.
APPENDIX 1

ON THE CHANGE OF MOLAR VOLUME WITH COMPOSITION

IN IRON-NICKEL FCC ALLOYS

Iron-nickel FCC alloys do not follow a simple linear composition dependence of the molar volume, and an excess volume term has been used to describe the pattern of the change of their molar volume with temperature \(^{(91)}\).

On the basis of Weiss\(^{(50)}\) theory, the molar volume of iron-nickel alloys can be calculated as follows:

\[
V = xV_{Ni} + [(1-x) V^*_{Fe}] [1 + 3\alpha (T-290)]
\]

where \( \alpha = 14 \cdot 10^{-6} [1 + 6 \cdot 10^{-4} (T-290)] \)

\(V_{Ni}\) = the molar volume of pure nickel and \(x\) = the atomic fraction of nickel.

In Eq. i the \(V^*_{Fe}\) term changes with both temperature and composition through the change of \(g\) with these variables.

Assuming that at \(x = 0.29\) the energy separation between the \(\gamma_1\) and \(\gamma_2\) states is zero\(^{(50)}\), then we can write for \(x < 0.29\) (\(\gamma_1\) the ground state):

\[
V^*_{Fe} = \frac{1}{1+g} V_{Fe}^{\gamma_2} + \frac{g}{1+g} V_{Fe}^{\gamma_1}
\]

\[
g = e^{\frac{\Delta E_{Y_1Y_2}}{R \cdot T}} \quad \text{T} < T_C
\]

\[
g = \frac{1}{1.79} e^{\frac{\Delta E_{Y_1Y_2}}{R \cdot T}} \quad \text{T} > T_C
\]
and for $x > 0.29$ ($\gamma_2$ the ground state):

$$V^*_\text{Fe} = \frac{1}{1+g} \, V_{\gamma_1}^\text{Fe} + \frac{g}{1+g} \, V_{\gamma_2}^\text{Fe}$$  \hspace{1cm} (iii)

$$g = \frac{\Delta E_{\gamma_1\gamma_2}}{R \cdot T} \quad \text{if} \quad T < T_C$$

$$g = 1.79 \, e^{\frac{\Delta E_{\gamma_1\gamma_2}}{R \cdot T}} \quad \text{if} \quad T > T_C$$

In deriving the above equations it is assumed that the degeneracy ratio of the $\gamma_1$ state to the $\gamma_2$ state is unity and 1.79 below and above the Curie temperature, respectively (see section 2.4.6).

The molar volumes calculated from Eq. i for four different temperatures as a function of composition are shown in Figs. i, ii, iii and iv. The experimental values of the molar volume from other sources are also included in these figures. As can be observed there is an excellent agreement between theory and experimental results. Such calculations can be done for very high temperatures and pressures, where the experimental conditions cannot be obtained.
Fig. 1. The molar volume of FCC iron-nickel alloys as a function of composition at 288°K.
Fig. ii. The molar volume of FCC iron-nickel alloys as a function of composition at 373°K.
Fig. iii. The molar volume of FCC iron-nickel alloys as a function of composition at 473°K.
Fig. iv. The molar volume of FCC iron-nickel alloys as a function of composition at 673°K.
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