THE THEORY OF COLD WORK PEAKS IN IRON ALLOYS.

by

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Abstract.

In order to resolve some anomalies encountered between the results obtained by different workers on the cold work peak of hydrogen in steels, internal friction measurements have been made on deformed iron-nickel-hydrogen alloys and iron-nickel-carbon-hydrogen alloys. A thorough investigation has been carried out on Schoeck's model for the cold work peak, and the theory extended to cover the behaviour of the cold work peak below the concentration at which peak saturation is attained. It is shown that the characteristics of the hydrogen cold work peak in iron alloys then follow Schoeck's model and that the apparent discrepancies reported by different research workers can also be explained on the basis of this model.

Measurement of the diffusion coefficient of hydrogen at subzero temperatures has been carried out using a mass spectrometer, and the results obtained are shown to be identical with those calculated from internal friction measurements. Calculations based on these results are used to obtain the binding energy of hydrogen to dislocations (7.5 ± 0.5 k cal/mole), and activation energies for the cold work peak (1.3 ± 0.5 k cal/mole), for bulk diffusion (9.5 ± 1 k cal/mole) and for diffusion in undeformed iron-nickel alloys (2.0 ± 0.5 k cal/mole).

A study of peak broadening has been used to give a new interpretation for the activation energy of the cold work peak, and to arrive at a more detailed mechanism responsible for this peak.

A peak due to carbon in the iron-nickel-carbon alloys, hitherto not reported, has been identified at about 216°C and some likely mechanisms responsible for the peak are proposed.
Acknowledgements.

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1. Introduction.

The main emphasis in the present work is on the explanation of the apparently contradictory behaviour of the cold work peak with respect to changes in the concentration of hydrogen, reported by various research workers (Sturges & Miodownik, 1969; Miodownik & Sturges, 1969; Gibala, 1966, 1967, 1968, 1970; Ino & Sugeno, 1968). The peak temperature was found to increase with peak height by Gibala, whereas similar experiments performed by Sturges & Miodownik indicated the peak temperature to be independent of the peak height. The explanations put forward by the two groups of authors also differ considerably over a number of fundamental issues, including particularly the distribution of hydrogen in the vicinity of dislocations, and the present work gives a rough estimate of the enhanced solubility of hydrogen due to the presence of dislocations. Both types of behaviour have been reproduced for the hydrogen cold work peak in iron-nickel alloys under controlled conditions and this has led to a satisfactory interpretation of all the experimental work available in this field.

In view of the number of overlapping areas, the literature has been divided into four sections:

(i) A survey of the previous experimental work on the cold work peaks.
(ii) A summary of the existing theories of the cold work peak.
(iii) The main features of the interaction between the dislocations and impurity atoms.
(iv) Internal friction peaks in iron-nickel alloys, with special reference to peaks due to carbon in these alloys.

The literature review is followed by a summary of the present experimental work, which is divided into two sections:

(i) Internal friction experiments.
(ii) Measurement of hydrogen diffusion coefficient using mass spectrometer.

Implications of the results are discussed in conjunction with the results from previous work, and the main conclusions arrived at are summarised in section 9. The appendices include some theoretical derivations, results
from which are used in the main text; a list of computer programmes developed by the author for the present work is also included in the appendices.
2. Phenomenological features of Cold Work Peaks.

The presence of dislocations in a metal affects the internal friction in many ways, and in addition to increasing the background, may give rise to one or more of the following reported types of peaks: (1) The Bordoni peak (Bordoni, 1949; Niblett, 1966), (2) The Niblett-Wilks peak, (3) The Hasiguti peaks (Hasiguti, 1953) and (4) The Köster (Köster et al, 1954) or cold work peak. The cold work peak has a characteristic difference from the other peaks in that the peak height increases when the impurity level is increased, whereas for other peaks the opposite is the case. Excellent reviews of general dislocation damping have been given by Niblett & Wilks (1960) and by Burdett & Queen (1970), and for the purpose of the present work only the cold work peak will be considered in detail.

2.1. The Hydrogen Cold Work Peak in Iron.

Weiner & Gensamer (1957) were the first to report cold work peak due to hydrogen in deformed steel. Hydrogen charged specimens, when deformed, showed a peak at about 105°K, while ageing at 300°K for one day caused the peak to disappear. In annealed specimens, it took four days for the peak to grow to its full height; further ageing at 300°K reduced the peak height, removing the peak altogether after 19 days. The maximum peak height in strained and in annealed specimens was the same, while strain apparently accelerates the entire process. Chang & Gensamer (1953) had earlier reported traces of such a peak at about 100°K in hydrogen charged, annealed specimens of iron containing 0.02% carbon, where a small peak was also found at 100°K prior to hydrogen charging; the peak height reverted to this value after the removal of hydrogen from the specimens. Heller (1961) reported the existence of the hydrogen cold work peak at about 110°K in
relatively pure iron, while Hermant (1966) observed a cold work peak at about 130°K. In the latter case, the peak temperature decreased as the peak decayed, and was completely suppressed by an addition of 0.001% carbon. In some of his specimens, the peak was very high; carbon precipitation was observed in such specimens. Cracks were also observed in some of the specimens after hydrogen charging. The existence of an additional peak at about 170°K can be inferred from the shape of the peak.

Extensive study of hydrogen cold work peak in iron was carried out by Gibala (1967) at a frequency of oscillation of 80 k cycles/sec. The level of cold work in the specimen was varied from 2% to 90%, and the peak height was found to increase with increase in the degree of cold work (Fig 1a), whereas the peak temperature was found to decrease with an increase in cold work (Fig 1b). An increase in concentration of hydrogen increased both the peak temperature and the peak height (Fig 2). Hydrogen concentration was changed by out-gassing hydrogen by holding the specimens at a higher temperature.

All the peaks reported by Gibala were broader than the corresponding single relaxation peaks. Assuming lognormal distribution of relaxation times (Nowick & Berry, 1961), Gibala found that the peak broadening was more sensitive to cold work than to hydrogen concentration (Fig 3). Fig 4 shows a comparison between the experimental results and the theoretical values calculated from the lognormal distribution of relaxation times for a typical peak (Gibala, 1967).

A study of the Snoek peak in conjunction with the cold work peak enabled Gibala (1967) to estimate the relative concentration of hydrogen in sites at the lattice and at the dislocations. He determined the activation energy of the cold work peak to be 8.4 k cal/mole.

Using controlled out-gassing of hydrogen, Sturges & Miodownik (1969) showed that the peak height was proportional to the total concentration of hydrogen in the specimen (Fig 5). The diffusion coefficient of hydrogen in iron was determined at different temperatures and the activation energy
Fig. 1. The effect of cold work on (a) peak height and (b) peak temperature for the hydrogen cold work peak in iron (Gibala, 1967).

Fig. 2. Effects of ageing at 60°C on the hydrogen cold work peak in iron, prestrained 90% and hydrogen charged (Gibala, 1967). (a) As charged, (b) Aged 1 hour, (c) Aged 2 hours, (d) Aged 6 hours and (e) Uncharged.
Fig. 3. Variation of the peak broadening parameter $\beta$ for the hydrogen cold work peak in iron with (a) cold work and (b) hydrogen content (Gibala, 1967).

Fig. 4. Description of the cold work peak in terms of lognormal distribution of relaxation times (Gibala, 1967).

$$x' = Q/2.303 (1/T_p - 1/T)$$
Fig. 5. The relationship between hydrogen cold work peak height in iron and the amount of hydrogen effused out of the specimen (Sturges & Miodownik, 1969).

Fig. 6. Effect of ageing at 298°K on the hydrogen cold work peak in iron (Sturges & Miodownik, 1969). (a) As charged; (b), (c), (d) - After one, two, three ageing cycles.
for diffusion was calculated to be \(7.5 \pm 0.5\) k cal/mole, by plotting the logarithm of the diffusion coefficient against reciprocal of temperature. The temperature of the peak (1100°C) did not vary with changes in hydrogen concentration (Fig 6). As with Gibala's results, the peaks were broader than the corresponding single relaxation peaks, and the peaks appear to be symmetrical.

**Summary:** Thus the main features of the hydrogen cold work peaks in iron alloys can be summarised as follows.

1. The peak height increases linearly with an increase in hydrogen concentration (Fig 5).
2. The increase in peak height with cold work is approximately linear (Fig 1a).
3. The cold work peak temperature decreases, as the amount of cold work is increased (Fig 1b).
4. Changes in peak temperature with concentration of hydrogen are highly sensitive to the actual composition (Table I), the two extreme behaviours being illustrated in figures 2 and 6. In the former, the peak temperature increases with concentration, whereas, in the latter, the peak temperature is independent of concentration.
5. All hydrogen cold work peaks in iron alloys are broader than the corresponding single relaxation peaks. The peak broadening is more sensitive to cold work than to concentration of hydrogen (Fig 3).
6. The experimental results fit well with the values calculated from the theory of lognormal distribution of relaxation times (fig 4); however, there is a small, systematic deviation of the experimental results from the theoretical curve.
7. The peaks are symmetrical relative to the peak temperature on a plot of internal friction vs reciprocal temperature.
Table I. Dependence of Peak Temperature and Activation Energy of Iron-Hydrogen Cold Work Peak on Carbon and Nitrogen Concentration.

<table>
<thead>
<tr>
<th>Material</th>
<th>Frequency of test (cps)</th>
<th>Peak temperature (Tp)</th>
<th>Activation energy (k cal/mole)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure iron</td>
<td>2-3</td>
<td>Ageing reduces Tp from 140 to 115°K</td>
<td>7.35</td>
<td>Hermant (1966)</td>
</tr>
<tr>
<td>Ferrovac E C - 0.004% N - 0.0003%</td>
<td>80,000 and 240,000</td>
<td>Cold work reduced Tp from 220 to 160°K, Ageing reduced Tp from 180° to 145°K</td>
<td>8.4 ± 2</td>
<td>Gibala (1967)</td>
</tr>
<tr>
<td>0.02% C Steel</td>
<td>1.1 - 1.7</td>
<td>105-120°K</td>
<td>-</td>
<td>Heller (1961)</td>
</tr>
<tr>
<td>Ferrovac E C - 0.009% N - 0.0001%</td>
<td>2-3</td>
<td>Ageing reduces Tp from 150 to 123°K</td>
<td>7.6 ± 1</td>
<td>Maringer et al (1958)</td>
</tr>
<tr>
<td>1020 Steel</td>
<td>20</td>
<td>100-110°K</td>
<td>6</td>
<td>Weiner &amp; Gensamer (1957)</td>
</tr>
<tr>
<td>(1) Electrolytic iron</td>
<td>2-3</td>
<td>(1) 115°K</td>
<td>-</td>
<td>Chang &amp; Gensamer (1953)</td>
</tr>
<tr>
<td>(2) 1020 Steel</td>
<td></td>
<td>(2) 100-120°K</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Iron 0.018% C - 0.0012% N</td>
<td>1-3</td>
<td>108-112°K</td>
<td>7-8</td>
<td>Sturges &amp; Miodownik (1969)</td>
</tr>
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Extensive studies of iron-carbon-nitrogen cold work peak have been carried out ever since this was first observed by Snoek (1941). At that time the only proposals concerning a mechanism were that the peak was related to the migration of carbon or nitrogen atoms from regions of positive stress to those of negative stress. This section outlines the important features of the iron-carbon-nitrogen cold work peak, and gives a comparison with the characteristics of hydrogen cold work peaks.

Peak Height: Ko (1948) studied the behaviour of the iron-carbon-nitrogen cold work peak, which was observed at 225°C at one cycle/sec, by tempering at various temperatures above the peak temperature. The cold work peak height decreased as the temperature of tempering was increased and disappeared completely when the specimen was recrystallised. Using the frequency shift method, the activation energy responsible for the cold work peak was calculated to be 32 k cal/mole. Similar behaviour after tempering has been reported by Kambar et al (1961), who also showed that the cold work peak at 225°C can be obtained by deforming either nitrided or carburised iron alloys (Fig 7).

Pettaara & Beshers (1967) conducted experiments to determine the mechanism responsible for the decrease in the cold work peak height during tempering and concluded that this was due to recovery rather than due to thermal redistribution of the impurity atoms. The experiment conducted to arrive at this conclusion was as follows. A nitrided, cold worked specimen was tempered at a high temperature followed by ageing for a long time at a lower temperature. Measurements showed that the cold work peak height was characteristic of the higher temperature, and ageing at lower temperature had no effect. If thermal redistribution were to be the reason for the decrease in the height of the cold work peak, ageing at lower temperature ought to have affected the peak height; so this clearly indicates that recovery was the reason for the drop in peak height.

Variation of cold work peak height with changes in carbon and nitrogen
Fig. 7. Cold work peak in deformed iron-carbon and iron-nitrogen alloys (Kamber et al, 1961). (a) Fe-C and (b) Fe-N.

Fig. 8. Dependence of the height of the cold work peak at 200°C on the total concentration of nitrogen and carbon (Küster et al, 1954). (Numbers on the curves refer to the percentage cold work).
concentration and the amount of cold work was first studied by Köster et al (1954). The cold work peak height increased linearly with the impurity content reaching a critical concentration, above which the peak height remained constant (Fig 8). The saturation peak height and the critical concentration could, however, be increased by increasing the cold work. This behaviour has been interpreted by Köster et al to mean that the specific dislocation interstitial configuration causes the cold work peak and any excess of either dislocations or interstitials is ineffective. Linear increase in peak height with an increase in carbon and nitrogen concentration has also been reported by Ino & Sugeno (1967; Fig 9). In addition, they observed that the cold work peak height decreased by increasing the temperature at which the alloy was deformed (Fig 10). Petarra & Beshers (1967) found that the dependence of the cold work peak height on the nitrogen concentration can be divided into three parts (Fig 11). The peak height increased linearly for low concentration of nitrogen (part 1), reaching a saturation value (part 2), as observed by Köster et al (1954). But for still higher concentrations the peak height increased (part 3) with nitrogen concentration. Part 3 of the curve was explained as due to an increase in the dislocation density, resulting from homogeneous precipitation of nitride particles within the lattice. A residual cold work peak observed when the Snoek peak was absent (Petta & Beshers, 1967), was explained to be due to the draining of nitrogen atoms from the lattice, at very low concentration, to the dislocations, as the dislocations offer lower energy sites.

Linear dependence of peak height with carbon concentration has been found in martensite (Chernikova, 1957) and in mixed structures, martensite and austenite (Krishtal & Golovin, 1959). Ino & Sugeno (1967) showed, the orientation dependence of the cold work peak height to be negligible and Petarra & Beshers (1967) found that the grain size had no effect on the cold work peak height.

**Peak Temperature:** A linear increase in peak temperature with an increase
Fig. 9. Dependence of the cold work peak height in iron-nitrogen-carbon alloys on the total interstitial content (Ino & Sugeno, 1967).

Fig. 10. Effect of temperature of deformation on the nitrogen cold work peak in iron (Ino & Sugeno, 1967). Deformed at (a) 200°C, (b) 30°C and (c) -70°C.
Fig. 11. Relationship between the cold work peak height and the Snoek peak height in iron-carbon-nitrogen alloys (Petarra & Beshers, 1967). (a) 30.1% deformation and (b) 14.8% deformation.

Fig. 12. Dependence of the cold work peak temperature on the carbon concentration in hardened steels (Krishtal et al, 1959).
of carbon and nitrogen concentration has been reported by Mura, Tamura & Brittain (1961) and similar behaviour has been observed by Chernikova (1957) and Krishtal & Golovin (1959; Fig 12) in hardened steels. Petarra & Beshers (1967) found a linear dependence for low nitrogen concentration, beyond which the peak temperature remained unaffected (Fig 13). Ino & Sugeno (1967), however, observed that the peak temperature varied as the logarithm of the sum of carbon and nitrogen concentration (Fig 14). They also found that the peak temperature changed from 200°C to 260°C for specimens with \( \langle 100 \rangle \) and \( \langle 110 \rangle \) axes.

Sugeno, Sakamoto & Ino (1963), working on iron-nitrogen alloys, found that the peak temperature decreased, when the amount of cold work was increased.

**Comparison of Carbon-Nitrogen Cold Work Peak and Hydrogen Cold Work Peak in Iron:** Main characteristics of the iron-carbon-nitrogen cold work peak are summarised in Table II; and a comparison is made below with the important features of the hydrogen cold work peak.

1. **Peak height:** For low concentrations, the peak height increases linearly, with the impurity concentration for both iron-carbon-nitrogen and iron-hydrogen cold work peaks. Saturation of peak height beyond a critical concentration has been observed for iron-carbon-nitrogen cold work peak, whereas, such an effect has not been found in the case of iron-hydrogen cold work peak. For both peaks the peak height could be increased by increasing the amount of cold work, at a given impurity concentration.

2. **Peak temperature:** For iron-carbon-nitrogen cold work peaks both a linear and a logarithmic dependence of peak temperature with carbon and nitrogen concentration have been reported. In addition, above a critical concentration, the iron-nitrogen cold work peak temperature was found to be independent of nitrogen concentration. For iron-hydrogen cold work peak, the peak temperature has been reported to increase with hydrogen concentration, by Gibala (1967); an entirely different behaviour, namely, the peak
Fig. 13. Variation of the cold work peak temperature with the Snoek peak height in iron-nitrogen-carbon alloys (Petarra & Beshers, 1967). (Numbers on the curves refer to the percentage cold work).

Fig. 14. Dependence of the iron-carbon-nitrogen cold work peak temperature on the total concentration of nitrogen and carbon (Ino & Sugeno, 1967).
Table II. Variation of the Peak Height and Peak Temperature of Iron-Carbon-Nitrogen Cold Work Peaks with Concentration and Cold Work.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Dependence of Peak Temperature</th>
<th>Dependence of Peak Height</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increase in Concentration</td>
<td>Linear increase</td>
<td>Linear increase</td>
<td>Krishtal et al (1959); Chernikova (1957); Mura et al (1961).</td>
</tr>
<tr>
<td>- DO -</td>
<td>- DO -</td>
<td>Linear increase for low concentrations, reaching a saturation value for higher Concentrations.</td>
<td>Köster et al (1954)</td>
</tr>
<tr>
<td>- DO -</td>
<td>Logarithmic increase</td>
<td>Linear increase</td>
<td>Ino &amp; Sugeno (1967)</td>
</tr>
<tr>
<td>- DO -</td>
<td>Linear increase for low concentrations, reaching a saturation value for high concentrations.</td>
<td>Linear increase for low concentrations, reaching a saturation value and an increase again for very high concentrations.</td>
<td>Petarra &amp; Beshers (1967)</td>
</tr>
</tbody>
</table>
temperature to be independent of concentration, has been reported by Sturges & Miodownik (1969).

3. Ageing behaviour: In the iron-nitrogen alloys, the decrease in peak height after tempering, is due to recovery; similar work in iron-hydrogen is complicated because of hydrogen effusion at temperatures above that of hydrogen cold work peak.

4. Peak broadening: The peak broadening for hydrogen cold work peak as reported by Gibala (1967) is very large compared to that of carbon-nitrogen cold work peaks in iron.

2.3. Hydrogen Cold Work Peaks in Alloys containing Additional Substitutional Elements.

Maringer et al (1958) investigated the effect of hydrogen charging on Ferrovac E (Fe-0.009% C) and on 4340 steel (Fe-0.38% C - 1.75% Ni - 0.75% Cr - 0.24% Si). In as drawn specimens, a peak was observed at about 140°K, after hydrogen charging for one to ten minutes. The peak observed was relatively small, when the specimen was tempered before introducing hydrogen.

Peterson et al (1967) observed two peaks in hydrogen charged austenitic steel (24% Cr, 21% Ni, 0.06% C) at 205°K and 225°K, at a frequency of 80 k cycles/sec. These peaks grew in size up to five days after charging at room temperature and disappeared after ageing for five months at room temperature (Fig 15). They tentatively suggested that the 225°K peak might be a cold work peak in austenitic structure. Later work showed that 10% deformation at 77°K, decreased the height of both peaks in hydrogen charged specimens (Peterson et al, 1969).

Kinel et al (1968) detected a peak in hydrogen charged iron-silicon alloys at about 160°K using 520 cycles/sec. They calculated the activation energy responsible for the peak to be 5400+ 200 cal/mole. However, they obtained a similar peak in specimens strained 2% and which were not charged with hydrogen (Fig 16). The authors concluded that the peak was due to
Fig. 15. Internal friction peaks in austenitic steels before and after hydrogen charging (Peterson et al., 1967). (a) 4 hours (b) 5 days and (c) 5 months after charging; (d) uncharged.

Fig. 16. Cold work peak in silicon-iron alloys (Kinel et al., 1968). (a) Hydrogen charged (b) 2% deformed (uncharged).
deformation only, and the peak also appeared after hydrogen charging, because hydrogen produced deformation and was only indirectly responsible for the peak.

**Summary:** Experiments of Peterson et al (1967; 1969) and Maringer et al (1958) show that the behaviour of the hydrogen cold work peak in iron alloys is not very sensitive to either changes in structure or additional substitutional elements. The peak observed by Kinel et al (1968) in iron-silicon, could not be compared with hydrogen cold work peaks, because this peak was present even in the absence of hydrogen and this behaviour is different from all the other known cold work peaks.

**2.4. The Nature of Cold Work Peaks in other Alloys.**

Examples of cold work peaks in some other systems are given here to show that the characteristics of the cold work peaks vary considerably in different alloys.

A cold work peak in tantalum-oxygen system was detected by Schoeck & Mondino (1963) at 340°C at a frequency of 0.45 cycle/sec. Variation of the cold work peak height with the degree of deformation is shown in Fig. 17. The peak height was found to reach a maximum value, which was proportional to the initial concentration of oxygen in free solid solution. The activation energy for the relaxation process responsible for the cold work peak was found to be $36 \pm 3$ k cal/mole. The ageing behaviour of the peak was studied at different temperatures (Fig. 18), the frequency being adjusted in such a way that the peak temperature was always maintained to be the same as the temperature of ageing. The decay of the peak height initially followed the $t^{2/3}$ law, the rate being lower at later stages. From this data, they calculated the activation energy for the decay of the peak to be equal to $28 \pm 3$ k cal/mole which compared very favourably with the value of the activation energy for diffusion of oxygen in tantalum, 26 k cal/mole.

A cold work peak observed in niobium at 500°C at about one cycle/sec by Boone & Wert (1963) was attributed to the interaction of dislocations with
Fig. 17. Variation of the cold work peak height with deformation in tantalum-oxygen alloys (Schoeck & Mondino, 1963). Oxygen originally in solid solution: (a) $3.5 \times 10^{-3}$ wt. percent, (b) $7 \times 10^{-3}$ wt. percent and (c) $10^{-2}$ wt. percent.

Fig. 18. Ageing behaviour of the cold work peak in tantalum-oxygen alloys (Schoeck & Mondino, 1963).
clusters of nitrogen atoms; the peak height was proportional to the nitrogen concentration. The relaxation strength of nitrogen atoms at dislocation sites contributing to the cold work peak height was about ten times that at the lattice sites contributing to the Snoek peak height. The peak temperature decreased with a decrease in nitrogen concentration, and was not very sensitive to the degree of deformation (Fig 19). The peak was about 1.5 times broader than the corresponding single relaxation peak. The activation energy of the peak was determined to be 48 k cal/mole.

Lamotte & Wert (1964) made similar studies on Ta-O, Ta-N, Nb-O and Nb-N cold work peaks. The Ta-O cold work peak, however, decayed very rapidly at the peak temperature and could not be detected after the first heating cycle. The specimens had to be aged below the peak temperature to study the ageing behaviour. Cold work in the specimens was 50% compared to 12% in those used by Shoeck & Mondino (1963).

Arons et al (1967) observed a composite peak (Fig 20) in deformed palladium-hydrogen alloys; the behaviour of this peak was similar to that of the iron-hydrogen cold work peak reported by Gibala (1967). However, this composite peak consists of two peaks, one at 75°K and the other at 105°K (2.7 cycle/sec). Palladium-hydrogen alloy has two F.C.C. phases, alpha and beta, and these two peaks appear only under the special conditions as tabulated in Table III.

Table III. Peaks in Palladium hydrogen alloys. (Arons et al., 1967).

<table>
<thead>
<tr>
<th>Phase</th>
<th>State of deformation</th>
<th>Existence of peaks (2.7 c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>75°K peak</td>
</tr>
<tr>
<td>Alpha</td>
<td>Undeformed</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Deformed</td>
<td>No</td>
</tr>
<tr>
<td>Beta</td>
<td>Undeformed</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>Deformed</td>
<td>Yes</td>
</tr>
</tbody>
</table>
Fig. 19. Effect of deformation on the cold work peak height in niobium-nitrogen alloys (Boone & Wert, 1963). (Nitrogen in weight percent shown on the curves).

Fig. 20. Ageing behaviour of the composite peak due to hydrogen in β palladium-hydrogen alloys (Arons et al, 1967). (a) As strained; (b) After ageing for 68 hours at 20°C; (c) After additional ageings of 64 hours at 100°C and 24 hours at 185°C.
Conclusions:

1) In the case of the Ta-O cold work peak, the peak height increases with deformation, for small values of deformation, reaching a saturation value. However, transition from one stage to the other is not as sharp as in the case of the concentration dependence of the cold work peak height (compare Fig 17 and Fig 8).

2) The mechanism responsible for the decrease in the cold work peak height in Ta-O alloys and in Fe-C-N alloys are different. In the former, the decrease in the peak height is due to strain ageing whereas in the latter, the decrease is due to recovery.

3) In the Nb-N alloys, the cold work peak height is independent of deformation above 5% (Fig 19), whereas in other cases this is observed only above a much higher level of deformation.

4) The mechanism responsible for the Nb-N cold work peak is the interaction of dislocations with clusters of impurity atoms, as against single atoms in other cases.

5) The behaviour of the composite peak in Pd-H alloy shows that it is easy to be misled by the apparent similarity in the behaviour of the cold work peaks and composite peaks.

2.5. Conclusions.

The experimental results given in Section 2 show that, theories put forward to explain the cold work peaks have to take into account the variation of peak temperature and peak height with

(a) change in the impurity concentration,

(b) change in the level of deformation,

and (c) ageing.

Although the behaviour of the peak height is nearly the same for many cold work peaks, there are some discrepancies in the reported behaviour of the peak temperature. Ageing behaviour is very dependent on the alloy system and depending on the temperature at which ageing is performed, the dominant factor responsible for the observed ageing characteristics may be
(a) thermal unpinning of impurity atoms (b) strain ageing (c) recovery.

A detailed discussion of the existing cold work peak theories is given in Section 3; but most of the basic theories may have to be modified to explain the characteristics of the cold work peaks in alloys where precipitation is found to occur.
3. Theories of the Cold Work Peak.


Extensive discussion of the basic theory of internal friction is given by Nowick (1953) and Entwistle (1962) and only a few of the basic relationships are mentioned here.

If the strain developed in a body in response to a stress is not a single valued function of stress, then there will be some loss of energy, when a periodic stress is applied to the body. If the energy lost per cycle is $\Delta E$ and the average vibrational energy of the body during the cycle is $E$, then

$$Q^{-1} = \frac{\Delta E}{2\pi E}$$  \hspace{1cm} (1)

If $\delta$, the logarithmic decrement for the free decay of amplitude of oscillation is defined as

$$\delta = \frac{1}{n} \ln \left( \frac{A_0}{A_n} \right)$$  \hspace{1cm} (2)

where $A_0 =$ initial amplitude of oscillation

$A_n =$ amplitude after $n$ oscillations

then it can be shown that,

$$Q^{-1} \propto \frac{\delta}{\pi}$$  \hspace{1cm} (3)

This is valid only if $Q^{-1}$ is very small compared to one, which is, however, usually the case.

Internal friction arises from one or both of the following:

(a) An instantaneous internal rearrangement, bringing about a sudden change in the level of strain at a particular value of the stress. This is sometimes referred to as internal friction due to static hysteresis. Some examples of this type of internal friction are encountered in Granato & Luke's (1956) theory of unpinning of dislocations and changes in internal friction during various types of transformations (Garber et al, (i) 1968; (ii) 1968).
(b) A time lag between stress and strain due to anelasticity (Nowick, 1953; Stanley & Hughes, 1965). Even when the stress is in the elastic range, a component of the strain called the anelastic strain, is time dependent, and therefore is not proportional to the stress.

\[ \varepsilon_2(t) = \varepsilon_2(0) + \sum_i \Delta \varepsilon_i \gamma_i(t) \]  

where \( \varepsilon_2(0) \) = anelastic strain at time \( t = 0 \)

\[ \gamma_i(t) = 1 - \exp\left(-\frac{t}{\tau_i}\right) \]

Here the \( \tau_i \)'s are the characteristic constants called relaxation times, corresponding to relaxation processes responsible for the time dependent anelastic strain.

3.1.1. Relaxation Strength.

Relaxation strength \( \Delta_m \) is defined by the following equation:

\[ \Delta_m = \frac{(M_u - M_R)}{M_R} \]

where \( M_u \) = unrelaxed modulus

\( M_R \) = relaxed modulus.

But by definition,

\[ M_u = \frac{\sigma}{c_1 + \varepsilon_2(0)} \quad \text{and} \quad M_R = \frac{\sigma}{c_1 + \varepsilon_2(\infty)} \]

where \( c_1 \) = elastic strain

Using equations (4) and (5) the above two equations can be written as,

\[ M_u = \frac{\sigma}{c_1 + \varepsilon_2} \]  

and,

\[ M_R = \frac{\sigma}{c_1 + \varepsilon_2 + \sum \Delta \varepsilon_i} \]  

Substituting this in equation (6) we have,

\[ \Delta_m = \sum \Delta \varepsilon_i / \left( c_1 + \varepsilon_2 \right) \]  

If, however, time is measured from the instant the stress is applied, then \( \varepsilon_2 \) the elastic strain at time \( t = 0 \) is zero. Therefore equation (9) becomes,

\[ \Delta_m = \sum \Delta \varepsilon_i / c_1 \]
3.1.2. Single Relaxation Peak.

In the case of a periodic stress, there is a permanent lag between the stress and the strain. If the lag angle is $\phi$, it can be shown that (Entwistle, 1962),

$$\tan \phi = \frac{\Delta E}{(2\pi E)}$$

In general $\phi$ is very small compared to one and then,

$$Q^{-1} = \frac{\Delta E}{(2\pi E)} \approx \phi \approx \frac{\phi}{\pi}$$

(11)

For a single relaxation process, it can be shown that

$$Q^{-1} = \frac{\Delta}{\omega \tau} \left\{ 1 + (\omega \tau)^2 \right\}$$

(12)

where $\omega$ = angular frequency of the periodic stress

$\tau$ = relaxation time.

A plot of $Q^{-1}$ against $\ln (\omega \tau)$ has a maximum at $\omega \tau = 1$, the maximum value of $Q^{-1}$ being

$$Q_{\text{max}}^{-1} = \frac{\Delta}{\omega^2}$$

(13)

(Fig 21). The width $W$ at half the peak height is an important parameter and for a single relaxation peak, $W$ is given by (Stanley & Hughes, 1965),

$$W = 2\sqrt{3}$$

(14)

The best example of a well established single relaxation peak is the Snoek peak (Snoek, 1941) due to the reorientation of interstitial impurities in free solid solution (Polder, 1945).

3.1.3. Peak Broadening

If the anelastic strain is due to more than one relaxation process, then (Nowick & Berry, 1961; Zener, 1948),

$$Q^{-1} = \frac{\Delta}{\omega \tau} \left\{ f(\tau_i) \right\} \frac{\omega \tau_i}{\left[ 1 + (\omega \tau_i)^2 \right]}$$

(15)

where $f(\tau_i) = \text{fraction of the relaxation processes having } \tau_i \text{ as the relaxation time}$

the summation being carried over all the relaxation times and

$$\sum f(\tau_i) = n$$

where $n = \text{number of relaxation processes}

\text{responsible for the anelastic strain.}$
When the relaxation time has a continuous spectrum of values, it is convenient to use \( \ln \tau \) as the independent variable rather than \( \tau \) itself (Zener, 1948). Thus if \( \Phi(\ln \tau) \, d(\ln \tau) \) is the fraction of the total number of relaxation processes, for which the logarithm of the relaxation time lies between \( \ln \tau \) and \( \ln \tau + d(\ln \tau) \), then, equation (15) gives

\[
Q^{-1} = \Delta_m \int_{-\infty}^{+\infty} \Phi(\ln \tau) \, \omega \tau / \left[ 1 + (\omega \tau)^2 \right] \, d(\ln \tau) \tag{16}
\]

with

\[
\int_{-\infty}^{+\infty} \Phi(\ln \tau) \, d(\ln \tau) = 1 \tag{17}
\]

For comparison with experiments, it is convenient to write \( \tau \) in terms of temperature and the activation energy for the relaxation processes. Thus,

\[
\tau = \tau_0 \exp \left( \frac{Q}{RT} \right) \tag{18}
\]

where \( \tau_0 \) and \( Q \) are temperature independent variables

- \( Q \) = activation energy
- \( R \) = universal gas constant
- \( T \) = temperature on the absolute scale.

Assuming a Gaussian distribution for the logarithm for the relaxation times,

\[
\Phi(z) = \frac{1}{\beta \sqrt{\pi}} \exp \left[ - \left( \frac{z}{\beta} \right)^2 \right] \tag{19}
\]

with

\[
z = \ln \left( \frac{\tau}{\tau_m} \right) \tag{20}
\]

where \( \tau_m \) = most probable value of the relaxation time

\[
1/\beta = \text{Gaussian distribution parameter}
\]

one can obtain,

\[
\delta_n = 6/\beta_p = f_2(x, \beta)/f_2(0, \beta) \tag{21}
\]

where \( \delta_n \) = normalized logarithmic decrement

\( \delta \) = logarithmic decrement at \( T^0K \)

\( \delta_p \) = logarithmic decrement at the peak temperature \( T^0K_p \)

The parameter \( x \) and the function \( f_2(x, \beta) \) are defined by the following equations:
\[ x = \left( \frac{Q_m}{R} \right) \left[ \frac{1}{(1/T) - (1/T_p^2)} \right] \]  

Equation (21) cannot be solved analytically for \( \beta \). Nowick & Berry (1961) have tabulated the values of \( f_2(x, \beta)/f_2(0, \beta) \) for different values of \( x \) from \( \beta = 0 \) to \( \beta = 7 \). A comparison of these values with the values of \( \delta_n \) calculated from experimental values using the first half of equation (21), can be used to obtain an approximate value of \( \beta \). A number of corrections have to be applied for an accurate determination of \( \beta \); however, for small values of internal friction and peak broadening, equation (21) gives reasonably accurate value for \( \beta \).

3.1.4. Temperature dependence of Peak Broadening.

The relaxation time \( \tau \) consists of two parameters (see equation 18), \( Q \) and \( \tau_0 \). Therefore it is interesting and useful to see how the distributions in \( Q \) and \( \tau_0 \) affect the value of the peak broadening parameter \( \beta \), separately and collectively. For such an analysis two cases may be distinguished (Nowick & Berry, 1961).

**Case (a) When the distribution in \( Q \) and \( \tau_0 \) are related to each other through a common parameter:**

In this case it can be proved that the individual broadening parameters, \( \beta_{\tau_0} \) for the distribution in \( \ln \tau_0 \) and \( \beta_Q \) for the distribution of \( Q \), are related to the total broadening parameter \( \beta \) according to the following equation:

\[ \beta = \beta_{\tau_0} + \beta_Q \sqrt{(RT)} \]  

Thus a plot of \( \beta \) against \( 1/T \) is a straight line and \( \beta_{\tau_0} \) and \( \beta_Q \) can be determined from such a plot.

**Case (b) When the distribution in \( \ln \tau_0 \) and \( Q \) are independent of each other:**

In this case if we assume that both the distributions are Gaussian, then it can be shown that

\[ \beta^2 = \beta_{\tau_0}^2 + \beta_Q^2 (RT)^2 \]
Thus a plot of $\beta^2$ against $1/T^2$ is a straight line with slope equal to $(\beta_0/R)^2$ and the intercept on the $1/T^2 = 0$ axis is $\beta_0^2 \gamma'_0$.

When $\beta$ is independent of temperature, the two cases merge together and the peak broadening is entirely due to a spread in the value of $\gamma'_0$. These features are summarised in Table IV.

**Table IV. Implications of temperature dependence of $\beta$ (Nowick and Berry, 1961).**

<table>
<thead>
<tr>
<th>Dependence of $\beta$ on the temperature, $T$</th>
<th>Broadening is due to distribution in</th>
<th>Whether the distribution in $\gamma'_0$ &amp; $Q$ are related to each other</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$ independent of $T$</td>
<td>$\gamma'_0$</td>
<td>--------</td>
</tr>
<tr>
<td>$\beta$ vs $1/T$ is a straight line</td>
<td>$\gamma'_0$ and $Q$</td>
<td>Yes</td>
</tr>
<tr>
<td>$\beta^2$ vs $1/T^2$ is a straight line</td>
<td>$\gamma'_0$ and $Q$</td>
<td>No</td>
</tr>
</tbody>
</table>

An analysis of this sort can give a good insight into the physical mechanism responsible for broadened internal friction peaks.

**3.2. Cold Work Peak Theories.**

Several theories have been put forward to explain the features of the cold work peak, described in section 2. An outline of the various theories will be given in this section.
3.2.1. Theory of Köster Bangert and Hahn.

Köster et al (1954) were the first to suggest that the cold work peak arises due to the interaction between impurity atoms and dislocations. According to this theory damping is produced as a result of the migration of the solute atoms (at or near the core of the dislocations) to adjacent sites, as the dislocations glide under the influence of the cyclic applied stress. Neither the exact positions of the dislocation sites between which the impurity atoms jump, nor the mechanism of the jumps is specified. Several developments based on this theory will now be discussed.

(a) Relationship between the Snoek peak height and cold work peak height.

Following the work of Entwistle (1962), let

\[ N_d = \text{number of available sites at the dislocations for a given volume} \]

\[ n_d = \text{number of occupied sites at the dislocations} \]

\[ N_1 = \text{number of interstitial sites available apart from those at the dislocations} \]

\[ n_1 = \text{number of sites filled out of the available } N_1 \]

Then, neglecting the change in thermal entropies at the two types of sites (Inman & Tipler, 1958),

\[ \frac{n_d}{(N_d - n_d)} = \left[ \frac{n_1}{(N_1 - n_1)} \right] \exp \left( \frac{E_B}{kT} \right) \quad (26) \]

where \( E_B \) = binding energy of the solute atoms to the dislocations

\( k = \text{Boltzmann constant} \)

This equation can now be used making further assumptions that:

(i) Concentration (in atomic fraction) of the impurity atoms is small compared to unity.

\[ i.e., \ n_d \ll N_d \text{ and } n_1 \ll N_1 \quad (27) \]

(ii) The two types of sites are conserved,

\[ i.e., \ \frac{N_d}{N_1} = \text{constant.} \quad (28) \]
(iii) Contribution to the cold work peak height by an impurity atom at a dislocation site is equal to the contribution to the Snoek peak by an impurity atom at a lattice site, i.e.,

\[
\frac{n_d}{n_l} = \frac{\delta_p}{\delta_{SN}}
\]  

(29)

where \( \delta_p \) = cold work peak height
\( \delta_{SN} \) = Snoek peak height.

The validity of this equation (29) demands that there be no change in the distribution of impurity atoms amongst the two types of sites while measurements of cold work peak height and Snoek peak height are being made. This, in turn, makes it necessary to quench the specimen from the cold work peak temperature after that peak has been measured, in order to measure Snoek peak height. Under these conditions one can take temperature \( T \) in equation (26) as the cold work peak temperature. If, however, peak heights characteristic of temperatures higher than the cold work peak temperature are needed, one has to quench the specimen from those temperatures to the cold work peak temperature, measure the cold work peak height as quickly as possible and then quench the specimen to the Snoek peak temperature to measure the Snoek peak height.

The validity of the above assumptions can only be tested by comparing the predictions based on these assumptions, with experimental results.

Using relations (27), (29) and equation (26), we have,

\[
\frac{\delta_p}{\delta_{SN}} = \left( \frac{n_d}{n_l} \right) \exp\left( \frac{E_p}{kT} \right)
\]  

(30)

If experiments are performed to measure the Snoek peak height and the cold work peak height, taking the necessary precautions as already outlined, \( \frac{\delta_p}{\delta_{SN}} \) can be determined for different concentrations of the impurity atoms, at a constant temperature \( T \). Then, \( \frac{\delta_p}{\delta_{SN}} \) is a constant, because the right hand side of equation (30) is a constant under these conditions (from equation 28).

\[
\text{i.e., } \delta_p \propto \delta_{SN}
\]  

(31)

(true only for small concentrations)

This, therefore explains the plots of \( \delta_p \) against \( \delta_{SN} \) for small values of the
peak heights (Figures 8 and 11).

The relation (27) does not hold good when the impurity concentration is comparable to unity, i.e., near saturation concentration. When all the dislocation sites are filled, it naturally follows that an increase in concentration only increases the Snoek peak height and not the cold work peak height. However, increase in cold work increases the number of available sites at the dislocations, thus pushing the saturation value upwards (Fig. 8). The cold work peak height may still go up, if the concentration is high enough to produce new dislocations due to homogeneous precipitation (Fig. 11).

(b) Ageing behaviour:

Ageing at temperature above the cold work peak temperature initially increases the cold work peak height (stage 1), which reaches a maximum and then begins to decay (stage 2). In practice, however, one of these two stages may be absent. During stage 1, impurity atoms diffuse to dislocations and therefore \( n_d \) increases during this time, thus increasing the cold work peak height. This will continue till the equilibrium distribution of impurity atoms between the dislocation sites and lattice sites is reached.

Stage 2 may occur due to one or more of the following reasons: (i) Impurities at the dislocations may form stable precipitates, thus decreasing the number of impurity atoms contributing to the cold work peak height. (ii) If the temperature is high enough, annealing may occur, the value of \( n_d \) will decrease; equation (28) will no longer hold good and the cold work peak height will decrease according to equation (30). (iii) If the impurity is gaseous the impurity atoms may diffuse out of the specimen. This will decrease \( N_1 \) as well as \( n_d \) and therefore decrease both the Snoek peak height and the cold work peak height (Sturges and Miodownik, 1969). (iv) If ageing is done at a high temperature, thermal unpinning (i.e. redistribution of impurity atoms between dislocation sites characteristic of the temperature) may take place leading to a fall in cold work peak height. In this case, however, the Snoek peak height will increase (Kö, 1948; Gibala, 1967). These
various possibilities are tabulated in Table V.

Table V. Ageing behaviour of cold work peak and Snoek peak based on Köster's Theory.

<table>
<thead>
<tr>
<th>Cold work peak height</th>
<th>Snoek peak height</th>
<th>Reason for the behaviour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increases initially and reaches a maximum</td>
<td>Decreases initially, and attains a constant value</td>
<td>Drift of impurity atoms to dislocations</td>
</tr>
<tr>
<td>Decreases</td>
<td>Decreases or remains constant</td>
<td>Precipitate forms on the dislocations</td>
</tr>
<tr>
<td>Decreases</td>
<td>Increases</td>
<td>Recovery takes place</td>
</tr>
<tr>
<td>Decreases (if impurity is gaseous)</td>
<td>Decreases</td>
<td>Impurity atoms diffuse out of the specimen</td>
</tr>
<tr>
<td>Peak height increases as the ageing temperature is decreased</td>
<td>Peak height is smaller for lower ageing temperature</td>
<td>Thermal unpinning of dislocations</td>
</tr>
</tbody>
</table>

(c) Determination of $E_B$

Equation (30) can be written as,

$$\ln(\frac{\delta_p}{\delta_{SN}}) = \ln\left(\frac{N_d}{N_1}\right) + \frac{E_B}{kT}$$  \hspace{1cm} (32)

But, from equation (28), $\frac{N_d}{N_1} = \text{constant}$ and therefore a plot of $\ln(\frac{\delta_p}{\delta_{SN}})$ vs $1/T$ gives a straight line of slope $= \frac{E_B}{k}$. The intercept on the $1/T = 0$ axis is equal to $\ln(\frac{N_d}{N_1})$. For carbon in iron, Kamber et al
(1961) found the value of $E_B = 0.5$ e.v./atom (11.5 k cals/mole). Assuming that there is one atom site per Burgers vector distance of dislocation, they calculated the dislocation density from the value of $\ln\left(\frac{N_d}{N_l}\right)$ obtained from the plot. The value is in good agreement with that determined by other methods.

(d) Peak broadening.

As the nature of the dislocation sites is not specified in Köster's theory, it is hard to draw any definite conclusions about the behaviour of the peak broadening with respect to different parameters. Peak broadening can, for example, be attributed to the fact that the contribution to the cold work peak height comes from atoms situated on dislocation sites which are not in fact identical. Peak broadening can be due to difference in the binding energies of the impurity atoms at various sites surrounding dislocations. Distribution of impurity atoms at these sites is such that the maximum number of sites are filled nearest to the dislocation, the ratio of the occupied sites to the unoccupied sites falling off as we move away from the dislocation line. This would imply that the observed peak is an envelope of a set of peaks due to impurity atoms at these nonidentical sites. According to Wert and Marx (1953), the peak temperature is higher for the peaks corresponding to more tightly bound atoms, i.e., those nearest to the dislocations. The experimentally observed peak should fall sharply on the high temperature side of the peak and logarithmic decrement vs 1/T plot should be asymmetrical. Fig. 2 (Gibala, 1967) shows that the Fe-H cold work peak is in fact symmetrical (at least near the peak temperature), and the results of Sturges and Miodownik (1969) show that the peak is approximately symmetrical (Fig. 6). Also we would expect the peak broadening to be very sensitive to changes in the impurity concentration. Fig. 3(b) (Gibala, 1967) shows that this is not true.

(e) The Effect of Changes in solute concentration and cold work on the Peak Temperature.

The original Köster hypothesis does not offer any plausible explanation for the observed variation of peak temperature with changes in
cold work and in concentration, but special variations have been developed
which are slightly better in this respect.

3.2.2. Theory of Yamafuji and Bauer.

According to this theory, impurity atoms at the dislocations diffuse
along the dislocations as the dislocations bow out under the application of
the external stress (Yamafuji & Bauer, 1965). Important features of the
theory will now be considered below.

In Fig. 22, A and B are the major pinning points, assumed to be
immobile, as the dislocation bows out. I₁, I₂, ..., Iₙ₋₁ are minor
pinning points, which always lie on the dislocation, but their distribution
along the dislocation can change, as the dislocation bows out, and it is
proposed that these minor pinning points are the impurity atoms responsible
for the appearance of the cold work peak. The major pinning points are
either points of intersection of the dislocations or impurity atoms of a
different species, or precipitates, which are immobile at the temperature
at which the peak is observed. The logarithmic decrement as a function
of ωτ' is given by,

\[ \delta = \left[ \frac{8 \Lambda M b^2 l_o^2}{(\pi \beta)} \right] (\sigma_o^-/\sigma_o^-)^n \left[ \frac{\omega \tau'/(1 + \omega^2 \tau^2)}{1 + \omega^2 \tau^2} \right] \]

with

\[ \sigma_o^- = \left[ \frac{24 n b \kappa T}{(b / l_o)} \right] \frac{1}{2} \]

and

\[ \tau' = 2 l_o^2 / (n^2 d_p) \]

where \( \tau' \) = relaxation time,
\( \omega \) = angular frequency of the applied stress,
\( \Lambda \) = dislocation density,
\( M \) = shear modulus,
\( b \) = Burgers vector,
\( l_o \) = dislocation loop length, (AB in Fig. 22),
\( \beta \) = dislocation line tension along the
dislocation,
\( \sigma_o^- \) = amplitude of the applied stress
\( n \) = number of pinning points per dislocation loop
Fig. 21. A single relaxation peak.

Fig. 22. Movement of a dislocation loop and impurity atoms under the application of an alternating stress, according to the theory of Yamafuji & Bauer.
(n-1 minor pinning points and one
major pinning point),
k = Boltzmann constant,
$$D_p = $$ pipe diffusion coefficient of the minor
pinning points along the dislocation
at temperature $T^°K$.

The peak height $\delta_p$ is given by,
$$\delta_p \propto \frac{1}{2} \left[ \frac{\beta M p M_b}{(4 \pi n)^{2/3}} \right] \left( \sigma_0 / \sigma_c \right)^4$$  \hspace{1cm} (36)

Discussion of the theory of Yamafuji and Bauer.

Relations (33) to (36) do not define the peak completely, because these
equations are only approximate. In relation (33), for instance, the
approximation sign hides the fact that the peak is not a single relaxation
peak. An exact solution of the problem predicts a slightly broadened peak.
Also, the above relations hold good only for $\sigma_0 < 3 \sigma_c$. If $\sigma_0 < \sigma_c$ then
the peak does not appear. As can be seen from relation (33) $\delta_p$ is
proportional to $\sigma_c^{1/4}$, which means that the peak height is strongly amplitude
dependent.

If we substitute for $\sigma_c$ from relation (34) into relation (36), we have,
$$\delta_p \propto \frac{1}{2} \left[ \frac{\beta M p M_b}{(4 \pi n)^{2/3}} \right] \left( \sigma_0 / \sigma_c \right)^4$$  \hspace{1cm} (37)

An increase in cold work increases $\Lambda$ and decreases the value of $\sigma_c$, but
the decrease in $\sigma_c$ has a much larger effect on the peak height, as the
peak height is proportional to $\sigma_c^{1/8}$. Thus, assuming $\sigma_c$ to be set solely by
dislocation intersections the peak height will decrease with an increase
in cold work. However, when the major pinning points are immobile atoms or
precipitates, cold work will not have any effect on the value of $\sigma_c$, although
the dislocation density will increase with increase in cold work, and under
these conditions the peak height will be proportional to the dislocation
density.

The relation (37) suggests that the peak height $\delta_p$ should be
proportional to $1/n^2$. As the concentration of the impurity atoms increases,
n will increase and therefore the peak height will decrease, with increasing
solute content.

In practice none of these conclusions seem to apply to any
experimentally observed cold work peaks.

3.2.3. Theory of Murata, Tamura and Brittain (1961).

According to this theory, relaxation occurs as a result of the growth and dissolution of critical sized precipitates in the stress field of oscillating dislocations.

If the equilibrium position of the dislocation is denoted by \( O \), a set of rectangular cartesian coordinates can be chosen in such a way that the origin falls at \( O \) with the \( XZ \) plane along the slip plane and the \( Z \) axis parallel to the core of the dislocation (Fig. 23). The equilibrium position of the atmosphere of impurity atoms under consideration is at \( x = 0, y = -y_0 \).

Under the application of the periodic external stress, the dislocation moves in the slip plane along \( \pm \alpha \) direction. Let \( x_d \) be its position at any instant of time \( t \). Due to the interaction between the dislocation and the impurity atoms, the new position of the impurity atom atmosphere becomes \( (x, y) \). If \( C \) is the density of impurity atoms at time \( t \), then conservation of the impurity atoms necessitates,

\[
\frac{\partial C}{\partial t} = r \sqrt{2C} + \left( \frac{r}{kT} \right) \left[ \frac{\partial C}{\partial x} \frac{\partial V}{\partial x} + \frac{\partial C}{\partial y} \frac{\partial V}{\partial y} \right]
\]

where, \( V \), the interaction potential is given by,

\[
V = A \frac{y}{\sqrt{(x - x_d)^2 + y^2}}
\]

and

\[
\Gamma = \text{rate of jump of an atom in the impurity atom atmosphere}
\]

\[
A = \text{attraction coefficient between the dislocation and the solute atom}
\]

\[
k = \text{Boltzmann constant.}
\]

An equation similar to equation (38) may be written, for the case where there is external force acting:

\[
\frac{\partial C_0}{\partial t} = r \sqrt{2C_0} + \left( \frac{r}{kT} \right) \left[ \frac{\partial C_0}{\partial x} \frac{\partial V_0}{\partial x} + \frac{\partial C_0}{\partial y} \frac{\partial V_0}{\partial y} \right]
\]

where \( V_0 = A \frac{y}{(x^2 + y^2)} \)

and \( C_0 = \text{equilibrium concentration of the impurity atoms in the impurity atmosphere.} \)

Relating the position of the dislocation \( x_d \) when the stress \( \sigma \) is applied, by
Fig. 23. Equilibrium position of a precipitate relative to an edge dislocation.

O - Equilibrium position of the dislocation

XZ - slip plane

P - Equilibrium position of the precipitate.
using Cottrell's (1953) equation:

$$\sigma \propto \beta x_d / y_o^3$$ (42)

where $\beta$ = strength of locking.

Assuming that $x$ and $x_d$ to be very small compared to $y_o$ and

$$\Delta \sigma / \Delta x = -C_o / a \quad (a = \text{atomic spacing})$$

it can be shown that:

$$\delta = \left\{ \lambda M C_o / \left[ k T b \pi (L_1^2 + L_2^2) \right] \right\} \left[ \omega \tau / (1 + \omega^2 \tau^2) \right]$$ (43)

where $\tau = \tau_o / \left[ (1/L_1^2 + 1/L_2^2) \pi^2 \right]$

and

$$\gamma = \gamma_o \exp(-Q/kT)$$ (45)

$M$ = shear modulus

$\lambda$ = constant

$\tau_o$ = relaxation time

$Q$ = activation energy for an atomic jump from the atmosphere of impurity atoms to the matrix

$L_1$ and $L_2$ are the dimensions of the atmosphere of the impurity atoms

Equation (43) represents an internal friction peak.

A further assumption as to the nature of the atmosphere of impurity atoms, namely the atoms in the atmosphere to be in the form of precipitates, allows a calculation of the value of $Q$ by the following procedure. The free energy $F$ of the precipitate is calculated as a function of the radius $\rho$ of the precipitate and the displacement $x_d$ of the dislocation from its equilibrium position:

$$F(\rho, x_d) = 4\pi (\rho \mu)^2 F_s - \frac{4\pi}{3} (\rho \mu)^3 \left[ F_v + A y_o / (x_d^2 + y_o^2) \right]$$ (46)

where $\mu = C_o = \text{number of impurity atoms per unit volume of the precipitate}$

$\rho$ = radius of the precipitate

$F_s$ = surface energy per atom in the precipitate

$F_v$ = formation energy per atom in the precipitate.

A plot of the free energy against the precipitate radius is shown in Fig. 24,
Fig. 24. Plot of the free energy of a precipitate as a function of its radius (Mura et al, 1961).
for the extreme values of $x_d = 0$ and $x_d = \infty$.

The critical precipitate radius is a minimum ($= \rho_1$) when $x_d = 0$, i.e., when the dislocation is at the equilibrium position. Therefore as the dislocation moves away from its equilibrium position, precipitates of critical size begin to dissolve. On the other hand, as the dislocation begins to move towards its equilibrium position, those precipitates whose radii are otherwise just below the critical value will now begin to grow. Thus as a result of the oscillating dislocation, the precipitates of critical size will grow and redissolve alternately. The activation energy is obviously the free energy for the precipitate of critical size, i.e.,

$$Q = \frac{16}{3}nF^3_s \left[ F_v + \frac{\Delta y_0}{(x_d^2 + y_0^2)} \right]$$  \hspace{1cm} (47)

Some of the interesting features of this theory will now be discussed.

**Effect of change in concentration on the peak height.**

This model is worked out on the basis of a single dislocation interacting with a single precipitate. Therefore, we expect the peak height to increase as the number of dislocations or the number of precipitates is increased. These effects are, therefore, similar to those of Koster's theory, except that there is an additional stage, namely precipitation. This may require a preliminary ageing time for the cold work peak to be developed fully.

**Peak broadening.**

Instead of a single precipitate, if a number of precipitates are assumed to be present, with slightly different values of $L_1$ and $L_2$, then $T$ will have a spread in its value around a mean, which in turn, produces peak broadening. However, the behaviour of the peak broadening with respect to changes in concentration and changes in the dislocation density is not evident. The effect is indirect through changes in the distribution of various parameters connected with the precipitates, such as the size of the precipitates and the geometrical positioning of the precipitates relative to the dislocations.
According to equation (43), the peak height \( \delta_p \) is given by:

\[
\delta_p = \frac{1}{2} \left[ \frac{L_{\text{MC}_o} A}{(kT_p a\beta)} \right] \left[ \left( L_1^{-2} + L_2^{-2} \right) n^2 \right]^{-1}
\]

where \( T_p \) = peak temperature.

Equation (48) shows that the peak temperature should be inversely proportional to the peak height.

(d) Effect of change in concentration.

It is important to remember that \( C_o \) is not the lattice concentration of the impurity atoms, but the number of atoms per unit volume of the precipitate and this may not be related to the lattice concentration. Thus it is difficult to predict the effect of a change in concentration, in the absence of a knowledge of the variation in the parameters connected with the precipitates.

(e) Effect of a change in cold work.

As the theory is developed on the basis of a single dislocation model, effects of distribution of dislocation loops cannot be predicted; however, as a first approximation, the peak height may be assumed to be proportional to the dislocation density. Thus the peak height is expected to increase with cold work on the basis of this theory.

3.2.4. Theory of Schoeck.

In contrast to the other theories, wherein relaxation is assumed to occur due to the reorientation of the impurity atoms or precipitates near a dislocation, this theory assumes that the relaxation occurs as a result of the movement of the dislocations, which drag an atmosphere of impurity atoms along with them.

According to this theory, dislocations are pinned by major pinning points, which are points of intersection of dislocations, atoms or precipitates, which are immobile at the cold work peak temperature. The impurity atoms which are responsible for the occurrence of the cold work peak are called as minor pinning points and are mobile at the cold work peak temperature. The minor pinning points are dragged along with the dislocations as the dislocations move from their positions of equilibrium.
The applied stress during an internal friction experiment is so small that the dislocations are unable to tear themselves away from the minor pinning points. The impurity atoms moving with the dislocations have to pass through energetically unfavourable positions and the activation energy for the cold work peak is equal to the energy required to activate the movement of the minor pinning points, situated on the moving dislocations.

If \( F \) is the force acting on a minor pinning point which is on a dislocation, then the velocity of this pinning point is given by Einstein's equation,

\[
v = \frac{D}{kT} F
\]

where \( v \) = velocity of the minor pinning points

\( D \) = diffusion coefficient of the minor pinning points at temperature \( T \)°K

\( k \) = Boltzmann constant

The force on the atom can therefore be expressed as,

\[
F = \frac{(kT/D)}{v}
\]

The force \( F_1 \) per unit length of the dislocation is given by,

\[
F_1 = nF = n(kT/D) v
\]

where \( n \) = number of minor pinning points per unit length of the dislocation.

For metals with B.C.C. structure, it can be shown that,

\[
n = \frac{9\pi R_0^2 C_d}{(4\sqrt{3} b^3)}
\]

where \( C_d \) = average concentration in atomic fraction of the species of atoms, which act as minor pinning points, inside a cylinder of radius \( R_0 \) surrounding the dislocation

\( b \) = Burgers vector.

From equations (50) and (51) we can write,

\[
F_1 = \alpha v
\]

where \( \alpha = \frac{9\pi R_0^2 C_d kT}{(4\sqrt{3} D b^5)} \)

\( F_1 \) is also the magnitude of the restoring force exerted on the dislocation.
of unit length by the minor pinning points (Newton's third law of motion). In addition to this force, the dislocation is also acted on by another restoring force due to the curvature of the dislocation as it bows out of its equilibrium position. \( F_2 \), the force per unit length of the dislocation due to such a curvature is given by,

\[
F_2 = \beta / r
\]

where \( r \) = the radius of curvature

\( \beta = \) dislocation line tension.

The total restoring force = \( F_1 + F_2 \) is balanced by the force due to the externally applied stress, \( \sigma \):

i.e., \( \sigma v + \beta / r = \sigma - b \) \( \tag{54} \)

Referring to Fig. 25, we can write,

\[
v = \frac{\partial x}{\partial t}
\]

and

\[
r = - \frac{\partial^2 x}{\partial y^2}
\]

Substituting these values in equation (54), we obtain,

\[
\sigma \left( \frac{\partial x}{\partial t} \right) - \beta \left( \frac{\partial^2 x}{\partial y^2} \right) = \sigma - b \tag{55}
\]

If \( \sigma \) is a periodic stress,

\[
\sigma = \sigma_0 \exp(i\omega t)
\]

where \( i = \sqrt{-1} \)

\( \sigma_0 = \) amplitude of the stress

\( \omega = \) angular frequency of the stress,

equation (55) would represent a differential equation of periodic motion. If \( \bar{x} \) is the mean of the maximum displacement of each point on the dislocation, then it can be shown that equation (55) may be written as,

\[
\alpha \left( \frac{\partial \bar{x}}{\partial t} \right) + 8\beta \bar{x} / l^2 = \sigma - b \tag{57}
\]

where \( l = \) the length of the dislocation between two major pinning points.

The solution of this equation is

\[
\bar{x} = \sigma_0 b \frac{\left[ (8 \beta / l^2) - i\omega \right] / \left[ (64 \beta^2 / l^4) + \omega^2 \sigma^2 \right]}{2}
\]

To calculate the strain produced in the specimen due to the displacement of the dislocations, unit volume of the specimen is considered. If the distribution of the loop lengths, \( l \), is such that \( \rho(l)dl \) is the
Fig. 25. Movements of a dislocation loop in response to an alternating stress, according to Schoeck's model.

Fig. 26. Plot of the integral in Schoeck's theory as a function of $\omega T$. 

\[

\frac{\exp(-2\omega T^2)}{1 + (\omega T)^2} \int_0^\infty dx

\]

$0$ $0.07$ $0.2$ $0.4$ $0.6$ $\omega T$

$2.2$ $2$ $1$
number of dislocations having loop length between 1 and 1+ \( dl \), then
\[
\int_0^\infty \rho(l)dl = A \tag{59}
\]
and
\[
\varepsilon_d = \gamma \int_0^\infty \rho(l)l dl \tag{60}
\]
where \( \Lambda \) = dislocation density
\( \varepsilon_d \) = strain produced due to the displacement of the dislocations
\( \gamma \) is a geometric factor \( \sim \) 0.1 to 0.01.

The logarithmic decrement \( \delta \) is given by,
\[
\delta = (\pi M/\sigma_o) \left| \text{imaginary part of } \varepsilon_d \right| \tag{61}
\]
where \( M \) = shear modulus.

Substituting for \( \frac{1}{x} \) and \( \varepsilon_d \) from equations (58) and (60) in equation (61) we have,
\[
\delta = (\pi M/\Lambda \Lambda \Lambda \Lambda /8\beta) \int_0^\infty \left[ \tilde{\rho}(z)z^5 \omega \Gamma/(1 + \omega^2 \Gamma^2 z^4) \right] dz \tag{62}
\]
where
\[
\Gamma = \frac{9\pi R_0^2 c_k T_0^2}{32 \sqrt{3} D_b^3} \tag{63}
\]
\[
\tilde{\rho}(z) = \frac{1}{A} \rho(1)/A \tag{64}
\]
\[
z = l/l_0 \tag{65}
\]
\( l_0 \) = mean loop length.

Substituting an approximate value of
\[
\beta = Mb^2/2 \tag{66}
\]
equations (62) and (63) become,
\[
\delta = (\pi y A l_0^2/4) \int_0^\infty \left[ \tilde{\rho}(z) z^5 \omega \Gamma/(1 + \omega^2 \Gamma^2 z^4) \right] dz \tag{67}
\]
and
\[
\Gamma = 9\pi R_0^2 c_k T_0^2/(16 \sqrt{3} M b^5) \tag{68}
\]
Assuming a distribution function for the dislocation loop length such that \( \tilde{\rho}(z) = \exp(-z) \), numerical calculation of the integral in the equation (67) can be performed for different values of \( \omega \Gamma \) (Fig 26).

The integral has a maximum value of 2.2 when \( \omega \Gamma = 0.07 \). Equation (67) represents a broadened peak, the broadening being due to a distribution in the dislocation loop lengths. A few of the major features of this theory will be outlined below; but a thorough discussion of the implications of the theory will be given in section 8.
(a) Effect of change in Concentration.

The height of the cold work peak, on the basis of Schoeck's model, can be obtained from equation (67):

\[ \delta_p = \pi \gamma A \left[ \frac{I_o}{I_{\text{max}}} \right]^2 \]  
(69)

This equation implies that the peak height should not be affected by the impurity concentration. However, the theory is developed on the assumption that all the dislocation loops contribute to the cold work peak damping and at low concentrations this assumption is not valid (Schoeck, 1970) and the peak height increases with concentration, for low concentrations, reaching the saturation value, given by equation (69). Examples of such a behaviour are shown in Figures 5 and 8; in Fig. 5 saturation peak height is not reached because the concentration is too low.

The variation of the peak temperature with concentration can be predicted using equation (68). Following the work of Gibala (1967), if we substitute,

\[ D = D_o \exp\left(\frac{Q_D}{RT}\right) \]  
(70)

(where \( Q_D \) = activation energy for lattice diffusion)

in equation (68) we obtain,

\[ \omega T' = k_1 C_d T \exp(\frac{Q_D}{RT}) \]  
(71)

where

\[ k_1 = 9 \pi R^2 k l^2 w / (16 \sqrt{3} M b^5 D_o) \]  
(72)

Using the fact that the peak height is proportional to the concentration of hydrogen, i.e.,

\[ \delta_p = k C_d \]  
(73)

equation (71) can be reduced to

\[ \ln(\delta_{p_T}) = \ln \left[ \frac{\omega T_p}{(k_1 C_d)^{\frac{Q_D}{RT}}} \right] \]  
(74)

The suffix \( p \) in the above equation indicates that the corresponding values are measured at the peak temperature. The value of \( \omega T_p \) is

* The author is grateful to Dr. Schoeck for pointing out that equation (67) is valid only when all the dislocation loops contribute to the cold work peak damping.
independent of the peak height and the peak temperature and therefore, a plot of \( \ln \left( \frac{T_p}{T_{p0}} \right) \) vs \( 1/T_p \) should be a straight line with slope equal to \(-Q/R\). Gibala (1968) has used such a procedure (Fig 27) to measure the activation energy for diffusion and the values obtained by this method are in good agreement with those obtained by others from other methods.

(b) Effect of change in cold work.

If we consider the points of intersection of dislocations as the major pinning points, then an increase in cold work increases the dislocation density and the number of dislocation loops. Thus a higher concentration of impurity atoms are needed to reach the maximum peak height predicted by equation (62), when the cold work is increased. This effect is shown in Fig. 8.

Equation (68) shows that,

\[
1^2 \frac{T_p}{T_{p0}} \exp \left( \frac{-Q}{R \cdot T_p} \right) = \text{constant},
\]

for a given concentration of impurity atoms. Therefore, as the value of \( T_{p0} \) is increased, the peak temperature will increase; i.e., as the cold work is decreased, the peak temperature will increase. Obviously, time has to elapse before this is observed.

The expected effects of changes in cold work and in concentration on the peak height and on the peak temperature are summarised in Table VI.

**Table VI. Effects of change in Concentration and in Cold Work (Schoeck's theory) on the Cold Work Peak.**

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Peak height</th>
<th>Peak temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increase in concentration</td>
<td>Increases initially reaching a maximum at a critical concentration</td>
<td>Increases when the peak height is increasing.</td>
</tr>
<tr>
<td>Increase in cold work</td>
<td>Increases</td>
<td>Decreases</td>
</tr>
</tbody>
</table>
Fig. 27. Relationship between the cold work peak height $\delta_p$ and the peak temperature $T_p$, for iron-hydrogen and iron-nitrogen cold work peaks (Gibala, 1968).

(a) Fe - H, 90% deformation
(b) Fe - H, 38% deformation
(c) Fe - N, 11% deformation
(d) Fe - N, 11% deformation + ageing at 350°C for one hour.
(c) Peak Broadening

As the peak broadening is attributed to a spread in the value of the dislocation loop lengths, we expect the broadening to be affected by (i) a change in the amount of cold work and (ii) the presence of immobile impurities or precipitates. Gibala's (1967) work (Fig 3a) confirms that an increase in the cold work increases the peak broadening. Further discussion of the peak broadening is given in section 8.

3.2.5. Schoeck's Theory for Small Displacements of Dislocations.

When the amplitude of oscillation of dislocations is less than \( b \), the Burgers vector, application of Einstein's equation (equation 49) is not justified. In this case the internal friction of the material may be attributed to the distribution of the impurity atoms forming the atmosphere around the dislocations, due to the displacement of the dislocations. Schoeck (1963) has shown that the material obeys standard linear solid equation and that the internal friction in this case is given by

\[
Q^{-1} = \left\{ \gamma b^2 \left[ 2 \sum (n_i a_i) + 8b^2 / L_0^2 \right] \right\} \left[ \mathcal{O}/(1 - \mathcal{O}) \right] \left[ \omega \tau / (1 + \omega^2 \tau^2) \right]
\]

where \( \mathcal{O} = \left[ \sum (n_i a_i^2) / (kT) \right] / \left[ 2 \sum (n_i a_i) + 8b^2 / L_0^2 \right] \)

and \( \tau = \tau_0 / (1 - \mathcal{O}) \)

\( \tau_0 \) = the time for an atomic jump of an impurity atom near a dislocation

\( a_i \) and \( d_i \) are the coefficients associated with the variation of the interaction energy \( U_i(x) \) of an impurity atom situated at a site \( i \), due to the displacement \( x \) of the dislocation from its equilibrium position; \( U_i(x) \) is given by,

\[
U_i(x) = U_i(0) + a_i x + d_i x^2 + ............
\]

The dependence of the internal friction on the structural parameters, in this case is complicated and does not render itself to direct theoretical investigation. No attempt has been made to compare this theory with any experimental work so far.

3.2.6. Modification of Schoeck's theory by Ino and Sugeno (1967).

Some modifications to Schoeck's theory, introduced by Ino and Sugeno

\[
\text{Ino and Sugeno (1967)}
\]
(1967) are intended to take into account the internal stresses due to precipitates and other interacting dislocations.

The essence of the development of this theory is considered by reference to Fig. 28, \( A_PB \) is the position of the dislocation when the external stress is absent and \( APB \) is the position of the dislocation when a stress \( \sigma \) is acting on it. If \( f(x, y) \) = force acting on the dislocation at \( P \), due to the internal stresses, then equation (55) of Schoeck's theory has to be modified to

\[
\alpha \left( \frac{\partial^2 x}{\partial t^2} \right) - \beta \left( \frac{\partial^2 x}{\partial y^2} \right) - f(x, y) = \sigma - b
\]  

(75)

When the external stress is removed the dislocation goes to its equilibrium position \( A_PB \), the point \( P(x, y) \) goes to \( P(x_0, y) \). At any point on \( A_PB \) the curvature is such that the force due to the curvature is balanced by the force due to internal stresses at that point due to other dislocations and precipitates. Thus,

\[
-\beta \left( \frac{\partial^2 x_0}{\partial y^2} \right) - f(x_0, y) = 0
\]  

(76)

From equations (75) and (76), we have,

\[
\alpha \left[ \frac{\partial (x - x_0)}{\partial x} \right] - \beta \left[ \frac{\partial^2 (x - x_0)}{\partial y^2} \right] - \left[ f(x, y) - f(x_0, y) \right] = \sigma - b
\]  

(77)

(using \( \partial x_0/\partial t = 0 \)).

Expansion of \( f(x, y) \) in the vicinity of \( x = x_0 \), using Taylor's theorem,

\[
f(x, y) - f(x_0, y) = a(y) (x - x_0)
\]

where \( a(y) = \left[ \frac{\partial f(x, y)}{\partial x} \right] x = x_0 \)

Substituting this in equation (77) and replacing \( x - x_0 \) by \( x' \), we have,

\[
\alpha \left( \frac{\partial x'}{\partial t} \right) - \beta \left( \frac{\partial^2 x'}{\partial y^2} \right) - a(y)x' = \sigma - b
\]  

(78)

If \( \bar{x}' \) is the average of the maximum displacements of all the points on the dislocation and \( \bar{a} \) is the average value of \( a(y) \) then,

\[
\alpha \left( \frac{\partial \bar{x}'}{\partial t} \right) + \left[ \frac{\partial^2 \bar{x}'}{\partial y^2} \right] \bar{x}' = \sigma - b
\]  

(79)

[\( \bar{g} \) is a numerical constant]

This equation is similar to equation (57) and the displacement is, therefore given by,
Fig. 28. Displacements of a dislocation loop under the influence of an external stress, according to the model of Ino & Sugeno.
Comparing this equation with equation (58), we see that, the equations become identical if $\theta_\beta/1^2$ of equation (58) is replaced by $(\theta_\beta/1^2) - \bar{a}$.

Thus, proceeding on the same lines as Schoeck's theory, we can show that,

$$Q^{-1} = \frac{\sum_{i=1}^{N} \Delta_m \omega T/(1 + \omega^2 \tau^2)}{N}$$  \hspace{1cm} (81)

with

$$\Delta_m = M_b^2/(\theta_\beta/1^2 - \bar{a})$$  \hspace{1cm} (82)

$$\tau = a/(\theta_\beta/1^2 - \bar{a})$$  \hspace{1cm} (83)

$$\Lambda = \frac{N}{\sum_{i=1}^{N} \tau}$$  \hspace{1cm} (84)

where $\Lambda$ is the dislocation density and the summation is carried out over all the dislocation loops ($N = \text{number of dislocation loops per unit volume}$).

Here, discrete values of $\tau$ are assumed, as against a continuous variation of $\tau$ in Schoeck's theory.

Implications of The Theory of Ino and Sugeno.

This theory reduces to Schoeck's theory if $\bar{a}$ is assumed to be $= 0$, and that the variation in $\tau$ is continuous. Further conclusions are made complicated by the fact that the peak broadening is due to a distribution not only in values of $\tau$, but also in $\bar{a}$. An attempt is made, here below, to find out the significance of the introduction of $\bar{a}$ to the theory.

(a) Cold work peak in specimens with tangled dislocations.

If there is a large number of tangled dislocations, we may expect a strong interaction between dislocations, and we may assume that the force gradient $\bar{a}$ is mainly due to dislocation interaction. If $\bar{a}$ is positive, then $\Delta_m$ will increase as $\tau$ increases ($\bar{a}$ is always less than $\theta_\beta/1^2$, otherwise the dislocation is unstable). However as can be seen from equations (81) and (82) those dislocations having values of $\bar{a}$ nearly equal to $\theta_\beta/1^2$ will have maximum effect on the cold work peak. A high proportion of tangled dislocations will therefore have a marked effect on the peak height. Thus, a change in the structure of tangled dislocations may be one reason for the enormous difference in peak height observed.
experimentally, for specimens deformed at different temperatures (Fig. 10).

(b) Effect of precipitates.

In this case the force gradient $\bar{a}$ is mainly due to the precipitates, the value of $\bar{a}$ depending on the size and distance between the precipitates. The activation energy in this case is given by,

$$Q = Q_D + E_B + nE_I$$

where $Q_D$ = activation energy for diffusion for the impurity atoms,

$E_B$ = binding energy between the dislocations and the impurity atoms,

$E_I$ = binding energy between an impurity atom and $n$ of its neighbours in the cluster.

This in fact implies that there will be a distribution in $Q$ due to the position of the precipitates relative to dislocations (due to change in $E_B$) and due to a variation in the number of impurity atoms in a cluster (i.e., change in $n$). Thus, this theory is a hybrid of Schoeck's theory and the theory of Mura, Tamura and Brittain (section 3.2.3).
4. Interaction Between Dislocations And Impurity Atoms.

Remarkable success has been achieved in understanding the nature of the interactions between dislocations and impurity atoms on a qualitative basis, during the past few years and numerical values for a number of important parameters which affect the nature and extent of the interactions are available in literature. Due to the various types of interactions that operate simultaneously, analytical solutions are almost always approximations to real situations. Furthermore, in any experimental work, one can never isolate dislocations and impurity atoms from the surroundings of other defects which themselves affect the interaction between dislocations and impurity atoms.

Only a few aspects of the interactions, that are of immediate applicability to the present work are considered here. Numerical values calculated from theoretical considerations are compared with the experimental values, taking carbon in $\alpha$-iron as an example. The results are also used in connection with the interaction of hydrogen with dislocations, in Section 8.

4.1. Static Dislocations.

Dislocations are never truly stationary except at 0°K, but in many cases, especially at low temperatures, the relationships developed here can be applied with a great degree of success.

4.1.1. Binding of Point Defects to Dislocations.

When an interstitial impurity atom whose volume is greater than the interstice, is inserted into the lattice work has to be done against the elastic force developed, while the atoms surrounding the interstice are moved to accommodate the impurity atom. However, less work is needed to perform the same operation, in the presence of the hydrostatic components of an edge dislocation. In a linear, isotropic, elastic solid, $E$, the additional energy difference is given by (Bullough & Newman, 1963; Cottrell, 1948).
with

\[ E_i = A \left( \sin \psi \right)/r \quad (86) \]

and

\[ A = \frac{4}{3} \left[ (1 + \nu)/(1 - \nu) \right] \frac{M b \delta r_i^2}{c_i} \quad (87) \]

where \( r_i \) = radius of the interstice (i.e., half the smallest dimension of the interstice)

\[ r_i(1 + \delta) \] = radius of the interstitial atom, which is assumed to be spherical

\( M \) = shear modulus

\( \nu \) = Poisson's ratio

\( b \) = Burger's vector

\((r, \psi)\) are the coordinates of the impurity atom relative to the dislocation, \( \psi \) being measured from the slip direction.

In an isotropic, linear, elastic solid, shear stresses cannot interact with spherically symmetric dilations and therefore, a screw dislocation, which produces only shear stresses, cannot interact with an impurity atom in the above model. However, such interactions do exist due to one or more of the following reasons:

1. The solid may be either nonlinear or anisotropic.
2. The impurity atom may be nonspherical (Cochardt et al., 1955).
3. A centre of dilation exerts a torque (Couch & Swartz, 1962) on a screw dislocation and this may change the orientation of the screw dislocation, producing an edge component, which in turn can interact with the impurity atom.
4. Shear stresses can interact with pairs of atoms and this enables screw dislocations to interact with impurity atoms in solutions strong enough to produce a considerable number of atom pairs (Zener, 1947).

Further modifications needed for an accurate estimation of the elastic interaction between a dislocation and an impurity atom include:

(a) changes in the elastic modulii due to the presence of the impurity atom (Fleischer, 1961);
(b) bent dislocations;
(c) effects due to the concentration gradients.
Equation (86) is not valid at the core of the dislocation, where the elastic continuum theory does not hold good. However, experimental results show that the theory can be successfully applied even upto about 2 Å from the dislocation.

Electrical interactions between dislocations and the impurity atoms have been reviewed by Nabarro (1967), but are assumed to have negligible effect on the binding energy in the present work.

For carbon in B.C.C. iron the calculated values of some of these parameters are:

\[ A = 3 \times 10^{-20} \text{erg-cm} \]
\[ E_1 = 1.5 \times 10^{-12} \text{ergs (} \approx 1 \text{ e.v.)} \]

(for \( r = 2 \AA \) and \( \sin \theta = 1 \))

Cochardt (1955) estimated, for both edge and screw dislocations, the binding energy \( E_B \) for carbon atoms in B.C.C. iron to be \( 1.1 \times 10^{-12} \text{ ergs (} \approx 0.75 \text{ e.v.}) \). Cottrell (1953) considers,

\[ A = 1.4 \times 10^{-20} \text{erg-cm} \]
\[ E_B = 0.75 \times 10^{-12} \text{ergs (} 0.5 \text{ e.v.)} \]

4.1.2. Saturation Effects.

As a result of the dislocation - impurity atom interaction, given sufficient time, impurity atoms drift towards dislocations to form an atmosphere round them. The equilibrium concentration of impurity atoms is given by

\[ C = C_L \exp(E_B/kT) \quad (88) \]

where \( C = \) concentration at a point where the impurity atom has a binding energy \( E_B \)

\( C_L = \) concentration of the impurity atoms far away from the dislocations

\( T = \) temperature on the absolute scale

\( k = \) Boltzmann constant

However, two types of saturation effects may stop this equilibrium concentration from being attained. (1) The strain produced by a dislocation can be relieved by a finite concentration of impurity atoms
and this effect, in turn, decreases the interaction energy. Thus after reaching a certain critical concentration, any increase in concentration will not decrease the total energy of the system. This critical concentration is the saturation concentration. (2) When all the available dislocation sites are filled, no increase in concentration is possible thereafter. Two conditions have to be satisfied for this to happen.

\[(a) \quad C_L \gg \Lambda b^2 \quad \text{(89)}\]
\[(b) \quad C_L \gg \exp\left(-\frac{E_B^m}{kT}\right) \quad \text{(90)}\]

where \(\Lambda = \text{dislocation density}\)

and \(E_B^m = \text{binding energy of an atom at a distance of} \quad r_0 = 2R \text{ from the dislocation.}\)

(Cottrell, 1953).

Condition (a) ensures that there are sufficient number of impurity atoms available for saturation to occur and condition (b) implies that all the available sites at the dislocations are filled.

When saturation occurs due to the filling of all the available sites at the core of the dislocations, a row of impurity atoms lie parallel to the dislocations at a distance of \(r_0 (\sqrt{2}R)\) away from them and a "condensed" atmosphere is said to be formed. If saturation occurs due to stress relief effects, only a diffuse atmosphere will be formed.

Louat (1956) has pointed out that equation (88) can only be applied to concentrations (in atomic fraction) that are small compared to unity and therefore, equation (90), which is derived from this is invalid when saturation occurs. Using the theory developed by Louat (1956), Beshers (1958) showed that the impurity atoms are distributed according to Fermi-Dirac statistics, rather than Maxwell-Boltzman statistics, at the dislocations when the concentration approaches saturation.

For carbon in B.C.C. iron, saturation occurs at \(C_L = 10^{-3}\) for \(\Lambda = 10^{12}\, \text{cm}^{-2}\) and at \(C_L = 10^{-7}\) for \(\Lambda = 10^{8}\, \text{cm}^{-2}\) according to the above equations at temperature \(T = 300^\circ\text{K}\), but the experimentally measured
values of the lattice concentration corresponding to saturation of the dislocations is higher, especially, when carbon precipitation is found to occur.

4.1.3. Migration of The Impurity Atoms to Dislocations.

Migration of impurity atoms, while equilibrium concentration is being reached, was first considered on a theoretical basis by Cottrell & Bilby (1949). According to their theory, the concentration of the impurity atoms, \( C(t) \) at the dislocations at time \( t \) is given by,

\[
C(t) = C_L \cdot 2 \left( \frac{E}{2} \right)^{1/3} (ADt/kT)^{2/3}
\]

where \( D = \) diffusion coefficient of the impurity atoms at temperature \( T^0 \).

At time \( t = 0 \) the distribution is assumed to be uniform. The following effects were neglected in the theory:

1. stress relief by the impurity atoms at the dislocations
2. diffusional effects due to concentration gradients
3. saturation effects
4. interaction between the dislocations.

Harper (1951) modified this theory to take into account the effect of the impurity atoms already segregated to the dislocations and arrived at the equation:

\[
\frac{C(t)}{C_L} = 1 - \exp \left[ -2 \left( \frac{E}{2} \right)^{1/3} (ADt/kT)^{2/3} \right]
\]

Ham (1959) took into account the diffusional effects and concluded that, the Cottrell-Bilby equation was valid during the initial stages of segregation, but for longer times the theory only predicted the flow of the impurity atoms inside a circle of radius \( \gamma \) (about 40 to 60 Å for carbon in B.C.C. iron). Outside this circle the flow would be radial.

Refined calculations (Bullough & Newman, 1959), showed that the rate of segregation at later stages depends more on the rearrangement of the impurity atoms near the dislocations, rather than the net radial flow of the impurity atoms into the \( \gamma \) circle. The persistence of the \( t^{2/3} \) law during the intermediate stages was explained (Bilby, 1956) by the fact that the diffusional effects and the saturation effects tend to cancel each other.
4.2. Dislocation Unpinning.

The dislocations are said to be pinned by the impurity atoms present at the dislocations, when the temperature is such that the mobility of the atoms is very low, and the dislocations are not able to tear away from the impurity atoms. The critical stress $\sigma_0$, needed to unpin the dislocations from a 'condensed' atmosphere of impurity atoms is given by,

$$\sigma_0 = \frac{3\sqrt{3} A}{(8 r^2 b^2)}$$  \hspace{1cm} (93)

The above equation is obtained by assuming that the thermal energy of the dislocation is zero. At a temperature $T^\circ K$, the critical stress $\sigma_T$ is given by (Nabarro, 1967),

$$\frac{\sigma_T}{\sigma_0} = 1 - \exp \left[ - f \exp\left(\frac{E_p}{kT}\right) \right]$$  \hspace{1cm} (94)

where $f =$ fraction of sites occupied by the solute atoms in the matrix.

Table VII. Variation of the Yield Stress with Temperature (Cottrell & Bilby, 1949) for Carbon-Iron Alloys with B.C.C. Structure.

<table>
<thead>
<tr>
<th>Temperature, $T$ ($^\circ$K)</th>
<th>85</th>
<th>114</th>
<th>195</th>
<th>303</th>
<th>373</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield Stress, $\sigma_T$ ($\times 10^9$ dynes/cm$^2$)</td>
<td>6.07</td>
<td>4.14</td>
<td>2.83</td>
<td>1.45</td>
<td>1.1</td>
</tr>
<tr>
<td>$\sigma_T/\sigma_0$</td>
<td>0.485</td>
<td>0.33</td>
<td>0.225</td>
<td>0.115</td>
<td>0.090</td>
</tr>
</tbody>
</table>

Table VII gives the experimental ratio $\sigma_T/\sigma_0$ for different temperatures (Cottrell & Bilby, 1949) obtained for carbon in B.C.C. iron. The value of $\sigma_0$ obtained by the extrapolation of experimental results is about an order of magnitude higher than the value calculated from equation (93).

4.3. Interaction of Impurity Atoms with Moving Dislocations.

Dislocations may move (i) under the influence of an external stress and (ii) due to thermal fluctuations. When a stress, $\sigma$ is applied, the
force experienced by the dislocation is given by,

\[ \text{Force} = \sigma \cdot b \]  

(95)

However, in the presence of an atmosphere of impurity atoms, the dislocations experience a retarding force as shown in Fig. 29(a). The retarding force due to other effects and the net force are shown in Fig. 29(b) and (c). When the force is greater than \( F_c \), any increase in the velocity of the dislocation decreases the retarding force. This means that the dislocation is separated from its atmosphere when the velocity of the dislocation reaches \( v_c \). The critical stress \( \sigma_c \) necessary to achieve this is given by (Cottrell & Jaswon, 1949),

\[ \sigma_c = \frac{F_c}{b} \cdot 17 C_L N/b \]  

(96)

where \( C_L \) = lattice concentration (in atomic fraction) of the impurity

\( N = \) number of available sites for the impurity atoms/ unit volume.

For carbon in B.C.C. iron, the value of \( \sigma_c \approx 9.3 \times 10^6 \) dynes/cm\(^2\); for lattice concentration \( C_L = 3 \times 10^{-5} \).

4.4. Hydrogen Dislocation Interaction in B.C.C. Iron

Experimental evidence for the existence of dislocation hydrogen interaction in B.C.C. iron comes from internal friction experiments (Gibala, 1967; Sturges & Miodownik, 1969) and from the effects of hydrogen on the yield point phenomenon in iron and steel (Section 4.4.1.). Controversy still exists as to how much hydrogen goes to dislocations and to other type of traps relative to the amount dissolved in the lattice (Gibala, 1967; Sturges & Miodownik, 1969; Oriani, 1967 & 1970). Sturges & Miodownik and Gibala tacitly assume that the density of trapping sites other than those that occur due to the presence of dislocations to be negligible. Oriani, using the experimental results of various research workers, has calculated the total density of trapping sites to be of the order of \( 10^{20} \) per unit volume. Further calculations based on Oriani's concepts (section 8) show that trapping sites introduced by the presence of dislocations can account for the observed results to a large
Fig. 29. Retarding forces acting on a moving dislocation surrounded by an atmosphere of impurity atoms.

Fig. 30. Effect of substitutional elements on the ageing behaviour of the carbon Snoek peak in iron (Wert, 1952).
extent, but one cannot rule out the possibility of the trapping sites influencing the absolute concentrations of hydrogen at the lattice sites and the dislocation sites. However, as will be shown in section 8 this does not affect the qualitative behaviour of the cold work peak, because the ratio of the lattice concentration to the concentration at the dislocations is affected only slightly by other traps.


Rogers (1954, 1957) observed a hydrogen yield point in steel containing 0.012% C at a testing temperature of \(-150^\circ C\). The specimens were pre-strained to remove the yield point due to carbon and nitrogen and to increase the solubility of hydrogen. Hydrogen was introduced by electrolytic charging, and such hydrogen charged specimens gave a yield point at testing temperatures below \(-80^\circ C\). Adair et al (1962) confirmed the existence of a hydrogen yield point by conducting similar experiments.

Both Cracknell et al (1955) and Rogers (1956) showed that large amounts of hydrogen can remove carbon-nitrogen yield point in iron. Rogers found that the carbon-nitrogen yield point in iron could be partially removed by introducing a small amount of hydrogen. Using specimens which were not prostrained, Rogers showed that the critical temperature at which the carbon-nitrogen yield point begins to appear could be lowered by the introduction of hydrogen.

The effects summarised above clearly indicate that there is a strong interaction between hydrogen and dislocations and between hydrogen and carbon atoms in B.C.C. iron. Further discussion of these interactions are made in Section 8.
5. **Internal Friction Peaks in Iron-Nickel Alloys.**

This section gives a brief outline of the mechanism of peaks arising from stress induced ordering of interstitial impurity atoms and peaks of this category occurring in iron-nickel alloys; attempts to detect more peaks of this kind are also mentioned. Only two other peaks have been observed in these alloys and these were reported by Gladman and Pickering (1966). The first of these two, which occurs at about 170°C is due to the interaction of dislocations with carbon atoms; the second peak, which is observed at about 235°C is also due to carbon, but a complete explanation of this peak is not given. However, they conclude that this peak is associated with retained austenite.

5.1. **Peaks due to Stress Induced Ordering of Interstitial Impurities.**

In the absence of external force fields, an impurity atom occupies one of several crystallographically equivalent sites in a metal. If the impurity atom introduces asymmetric distortions in the crystal, then the application of an external stress removes the degeneracy of these equivalent sites, and interstitials originally distributed at random amongst the sites, tend to redistribute themselves in response to the difference in energy at the various sites. This phenomenon is known as stress induced ordering, and gives rise to anelasticity and hence internal friction (Zener, 1948; Nowick, 1953). A peak is observed when internal friction is plotted either against temperature or against frequency.

Geometric considerations (Nowick & Heller, 1963) show that amongst B.C.C., B.C.T., F.C.C. and H.C.P. structures, such a peak can occur only in the B.C.C. and B.C.T. structures, with interstitial atoms occupying octahedral sites. This peak is generally known as the Snoek peak and a complete theory has been given by Polder (1945).

Interaction between substitutional and interstitial atoms, if present, gives rise to local asymmetric distortions, splitting the otherwise degenerate energy states for the interstitial atoms at equivalent
crystallographic sites. Thus, addition of substitutional elements can lead to the appearance of peaks due to stress induced ordering of interstitial atoms, even in F.C.C. and H.C.P. structures, while additional peaks may be observed in the B.C.C. and B.C.T. structures, along with the usual Snoek peak. The number of additional peaks observed due to the addition of substitutional elements depends on the number of different energy levels to which the initial degenerate energy level splits. This in turn, depends on the geometric positioning of the interstitial and substitutional atoms and the interactions between the different species of atoms. Models to account for the peaks arising from the stress induced ordering of interstitials in the vicinity of substitutional atoms have been given by Dijkstra & Sladek (1953) and Gladman & Pickering (1965). Some important features of the effects of the addition of various substitutional elements are shown in Table VIII.

Table VIII. Effect of Substitutional Elements on Peaks Due to Stress Induced Ordering of Interstitial Impurities.

(Frequency of oscillation is of the order of one cycle/sec)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Crystallographic structure</th>
<th>Peak temp. (°C)</th>
<th>Mechanism proposed*</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Mn-N</td>
<td>B.C.C.</td>
<td>(1) 22</td>
<td>(1) Snoek peak</td>
<td>Dijkstra &amp; Sladek (1953)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2) 32</td>
<td>(2) Fe-Mn/N</td>
<td></td>
</tr>
<tr>
<td>Fe-Mn-N</td>
<td>B.C.C.</td>
<td>(1) 7</td>
<td>(1) Fe-Mn/N</td>
<td>Enrietto (1962)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2) 24</td>
<td>(2) Snoek peak</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(3) 35</td>
<td>(3) Mn-Fe/N</td>
<td></td>
</tr>
<tr>
<td>Fe-Mn-C-N</td>
<td>B.C.C.</td>
<td>(1) -5</td>
<td>(1) Mn-Mn/N</td>
<td>Ritchie &amp; Rawlings (1967)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2) 7</td>
<td>(2) Mn-Mn/N</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(3) 13.5</td>
<td>(3) Mn-Mn/N</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(4) 28</td>
<td>(4) Snoek peak (N)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(5) 34.5</td>
<td>(5) Fe-Mn/N</td>
<td>(Continued)</td>
</tr>
</tbody>
</table>

*Fe-Mn/N means that the peak is due to stress induced diffusion of a N atom between a site with all Fe atoms as the nearest neighbours and a site with one Mn and all other Fe atoms as the nearest neighbouring atoms.
<table>
<thead>
<tr>
<th>Alloy</th>
<th>Crystallographic structure</th>
<th>Peak temp. (°C)</th>
<th>Mechanism proposed</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Mn-C-N</td>
<td>B.C.C.</td>
<td>(6) 44 (7) 66</td>
<td>(6) Snoek peak (C) (7) ---</td>
<td>Ritchie &amp; Rawlings (1967)</td>
</tr>
<tr>
<td>Fe-V-N</td>
<td>B.C.C.</td>
<td>(1) 22 (2) 87</td>
<td>(1) Snoek peak (2) Fe-V/N</td>
<td>Dijkstra &amp; Sladek (1953)</td>
</tr>
<tr>
<td>Fe-V-N</td>
<td>B.C.C.</td>
<td>(1) 22 (2) 37 (3) 87</td>
<td>(1) Snoek peak (2) Fe-V/N (3) Abnormal peak due to the influence of nitride precipitates</td>
<td>Jamieson &amp; Kennedy (1966)</td>
</tr>
<tr>
<td>Fe-Si-N</td>
<td>B.C.C.</td>
<td>(1) 22.5 (2) 37.5 (3) 62</td>
<td>(1) Snoek peak (2) Fe-Si/N (3) ---</td>
<td>Leak, Thomas &amp; Thomas (1955)</td>
</tr>
<tr>
<td>Fe-Si-N</td>
<td>B.C.C.</td>
<td>(1) 21.5 (2) 29</td>
<td>(1) Snoek peak (2) Interaction of moving dislocations with N atoms (3) 40 (4) 54 (5) 62</td>
<td>Rawlings &amp; Robinson (1961)</td>
</tr>
<tr>
<td>Fe-Cr-N</td>
<td>B.C.C.</td>
<td>(1) 22 (2) 47</td>
<td>(1) Snoek peak (2) Fe-Cr/N</td>
<td>Dijkstra &amp; Sladek (1953)</td>
</tr>
<tr>
<td>Fe-Cr-N-C</td>
<td>B.C.C.</td>
<td>(1) -7 (2) 5 (3) 23 (4) 38 (5) 49.5</td>
<td>(1) Cr-Cr/N (2) Snoek peak (N) (3) Snoek peak (C) (4) Fe-Cr/N (5) Due to carbon atom pairs</td>
<td>Ritchie &amp; Rawlings (1967)</td>
</tr>
<tr>
<td>Alloy</td>
<td>Crystallographic structure</td>
<td>Peak temp. (^{\circ}C)</td>
<td>Mechanism proposed</td>
<td>Reference</td>
</tr>
<tr>
<td>-------</td>
<td>-----------------------------</td>
<td>-----------------</td>
<td>-------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Fe-Mo-N</td>
<td>B.C.C.</td>
<td>(1) 22</td>
<td>(1) Snoek peak</td>
<td>Dijkstra &amp; Sladek (1953)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2) 75</td>
<td>(2) Fe-Mo/N</td>
<td></td>
</tr>
<tr>
<td>Fe-V-C</td>
<td>B.C.C.</td>
<td>(1) 22</td>
<td>(1) Snoek peak</td>
<td>Jamieson &amp; Kennedy (1966)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2) 87</td>
<td>(2) Transient peak, affected by nitrogen atoms</td>
<td></td>
</tr>
<tr>
<td>Fe-Mn-S</td>
<td>F.C.C.</td>
<td>530</td>
<td>Fe-Mn/C</td>
<td>Ke &amp; Tsien (1956)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Variable peak temp</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2) -48</td>
<td>(2) H-dislocation interaction</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2) 250</td>
<td>(2) Fe-Ni/C in the F.C.C. structure</td>
<td></td>
</tr>
<tr>
<td>Ti-X-O</td>
<td>H.C.P.</td>
<td>450 - 475 (\text{Peak temp variable for different sub. elements})</td>
<td>Ti-X/O</td>
<td>Gupta &amp; Weinig (1962)</td>
</tr>
<tr>
<td>X=Fe, V, Al</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the light of the present interest in iron alloys examples have been taken mostly from Fe-N and Fe-C alloys with substitutional elements, but similar experiments on the effects of small additions of Zr, Fe and Mo on Nb-O and Nb-N alloys have been reported by Szkopiak & Ahmad (1969).
which follow earlier work by Powers & Doyle (1959).

5.2. Peaks due to Stress Induced Ordering in Iron-Nickel Alloys.

Several additional peaks due to stress induced ordering of interstitial atoms have been observed in the neighbourhood of nickel atoms in iron (Table IX), but these peaks are due to carbon in various crystal structures and no peak has been reported due to either hydrogen or nitrogen. A notable implication of Table IX is that no additional peak due to stress induced ordering of carbon in the B.C.C. structure of nickel-iron alloys is observed. Wert (1952) tried to determine whether such a peak is likely to occur, and carried out investigations on Fe-C alloys containing one of the following elements as a substitutional impurity: Mn, Cr, Mo, Ni and V. The initial height of the Snoek peak in the Fe-C alloy was found to be unaffected by the addition of those substitutional elements. The alloys were tempered at 150°C and the Snoek peak height was plotted as a function of the time of tempering (Fig 30). Except for the Fe-V-C alloy, all the alloys had the same peak

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Crystallographic structure</th>
<th>Frequency</th>
<th>Peak temperature</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Ni-C</td>
<td>B.C.T.</td>
<td>2 cps</td>
<td>155°C</td>
<td>Ke &amp; Ma (1957)</td>
</tr>
<tr>
<td>Fe-Ni-C</td>
<td>F.C.C.</td>
<td>2 cps</td>
<td>250°C</td>
<td>Ke &amp; Ma (1957)</td>
</tr>
<tr>
<td>Fe-Ni-C</td>
<td>F.C.C.</td>
<td>0.7 cps</td>
<td>230 to 240°C</td>
<td>Gladman &amp; Pickering (1966)</td>
</tr>
</tbody>
</table>

* Snoek peaks are not shown in this table.
height as the Fe-C alloy. An additional peak due to the stress induced
ordering of carbon atoms around the substitutional element might be
expected to cause the carbon Snoek peak to decay faster in alloys
containing substitutional elements, because the carbon atoms would, in
such a case, divide themselves between two kinds of sites. In addition,
internal friction measurements of these alloys from $-35^\circ C$ to $200^\circ C$
produced no additional peak, and similar measurements from $-20^\circ C$ to $80^\circ C$
by Ritchie & Rawlings (1967) also showed no additional peak in Fe-Ni-C
alloys.

The above experiments show that in the Fe-V-C alloys, the sites with
one vanadium atom as a nearest neighbour, serve as low energy sites and
thus an additional stable peak due to stress induced ordering of carbon
atoms near vanadium may be expected. However, it appears that additional
peaks due to stress induced ordering of carbon in B.C.C. iron-nickel
alloys are unlikely to occur under normal circumstances. Nevertheless,
the possibility of a transient peak of this nature occurring in freshly
dehomed specimens cannot be ruled out, the carbon atoms being forced to
go into supersaturated solid solution. It can be envisaged that the
carbon atoms which have nickel atoms as neighbours will tend to diffuse
to lower energy sites (where all the neighbours are iron atoms).


6.1.1. Annealing Furnace.

Annealing was performed in a vertical, nichrome wound muffle furnace thermally insulated with alumina powder (Fig. 31). The hot zone used is 11" long and the temperature distribution along the length of the furnace is shown in Fig. 32. The furnace can be used for annealing specimens at any temperature up to 1100°C above room temperature.

The temperature was measured and controlled by a Pt/Pt-15% Rh thermo-couple and a Transistrol controller, the hot junction of the thermocouple being at the middle of the 11" long hot zone. The accuracy of the temperature measurement by the thermocouple is within ±1°C at 1000°C.

Gases forming the atmosphere inside the furnace are passed through a molecular sieve to remove traces of moisture. Continuously flowing argon was used as the inert atmosphere in the furnace.

6.1.2. Carburising Furnace.

Carburisation of the specimens was performed in a separate furnace. Specimens were heated by sending a heavy current through the specimens in an atmosphere of acetylene. The specimens can be held at any temperature up to the melting point of the specimens from the room temperature. The pressure of acetylene atmosphere inside the furnace can be maintained between 0.01 torr to 600 torr. The amount of carbon introduced into the specimen can be varied by changing the temperature, pressure of acetylene atmosphere or the carburising time.

The following method was used to determine the carbon content of the carburised specimens.* The samples were degreased by washing in petroleum

*The author would like to thank the Materials Department of the Royal Aircraft Establishment, Farnborough, Hants, for carrying out the carbon analysis of the specimens used in this work.
Fig. 31. Schematic diagram of the annealing furnace.


Fig. 32. Temperature distribution along the axis of the furnace tube.

![Temperature distribution graph](image-url)
ether and then dried. The weighed sample was folded into lengths of about 1 to 2 cm and wrapped in a piece of pure tin foil (9 x 1 cm). The carbon was converted to carbon dioxide in an organic solvent (ethanolamine in dimethylformamide) and titrating it automatically with tetra n-butyl ammonium hydroxide, detecting the end point potentiometrically. The method was developed by the Steel Company of Wales and E.I.I. Ltd., and is marked as "Titracarb". A plot of the pressure of acetylene used in the carburising furnace vs the resulting carbon concentration of the specimen is shown in Fig. 33.

6.2. Internal Friction Apparatus.

6.2.1. Torsion Pendulum.

A torsion pendulum method is used to measure the internal friction of specimens. Details of the apparatus are shown in Fig. 34. The 17.5 cm. specimen (L) is firmly held at the upper end in a screw vice (V), which seats into the lapped taper of a thermal contact (II). The vice (V) is held pressed to the thermal seating (II) by means of a spring loaded thin walled stainless steel tube (G). A 1/8 inch diameter stainless steel extension rod (N) clamps the lower end of the specimen (L), by means of another screw vice (P), the other end of the extension rod being connected to an aluminium inertia bar (R) of diameter 1/8 inch. Weights (W, W), made of iron can be threaded on to this inertia bar at both ends. Adjusting the distance of these weights from the midpoint of the inertia bar, the frequency of oscillation can be maintained at one cycle per second. The weights are kept the same in all the experiments, so that the vertical stress on the cross-section of the specimen is unchanged. A needle (N₁) attached to the inertia bar at its midpoint dips into silicone oil contained in the dash-pot (Z). The purpose of the dash-pot is to stop lateral vibrations of the pendulum. (Experiments conducted by Hughes (1966) showed that the effect of the dash-pot on the measured values of the internal friction is negligible). Two electromagnets are situated on opposite sides of the weights (W, W) in the horizontal plane passing through the inertia bar (R). By sending a pulse of current through these two magnets
Fig. 33. Dependence of the amount of carbon introduced into a 3% nickel-iron specimen in the carburising furnace on the pressure of acetylene in the furnace.
Fig. 34. The internal friction apparatus.
simultaneously, torsional oscillations can be initiated in the specimen. The amplitude of oscillation can be changed by sending in a number of pulses of current at the appropriate time.

6.2.2. The Reading Mechanism.

A collimated source of incident light is beamed onto a concave mirror (Q) attached to the midpoint of the inertia bar (R). The reflected beam is picked up by a light spot follower (Sefram Graphispot). A pen attached to the light spot follower makes a permanent record of the amplitudes of torsional oscillation. The sensitiveness of the measurement of the amplitudes of oscillation is increased by using three plane mirrors which increase the distance travelled by the reflected beam of light. The position of the mirror M₃ (Fig. 35) may be changed to alter the sensitiveness.

6.2.3. The Cryostat.

The cryostat (Fig. 34) built by Oxford Instrument Co., consists of an evacuated torsion pendulum housing, with a glass porthole opposite the concave mirror (Q). This housing is at a pressure less than 10⁻³ torr to avoid icing conditions and convection currents, and to decrease the effect of air resistance on the measurement of the internal friction.

The coolant tank (T₁), surrounding the specimen housing and at the level of the specimen, can be filled with liquid nitrogen, through the inlet (C). Separating the specimen housing and the coolant tank is an evacuated heat exchange space (SS). This coolant tank is surrounded by a radiation shield (RD), which is cooled by another liquid nitrogen tank (T₂) at its upper end. Both the liquid nitrogen tanks are surrounded by evacuated Dewar envelope (D).

6.2.4. Magnetic Coil.

A solenoid consisting of 192 turns of 14 S.W.G. enamelled copper wire
Fig. 35. Arrangement of mirrors used for the measurement of the torsional oscillations of the specimen in the internal friction apparatus.

\( (M_1, M_2, M_3 \text{ - Plane mirrors, } Q \text{ - Concave mirror, } P \text{ - Photodyne, } S \text{ - source of light}). \)

Fig. 36. Magnetic field along the axis of the solenoid surrounding the torsion pendulum of the internal friction apparatus.

(Sturges, 1969).
is wound round the cryostat. By sending a rectified current through the coil, a magnetic field is produced along the axis of the coil, i.e. along the axis of the specimen. The magnetic field was measured by an axial Hall probe of a Gauss meter, at different points along the axis of the cryostat and for different values of the current passing through the coil. The results are shown in Fig. 36. (Sturges, 1969).

The purpose of the magnetic field is to remove the magneto-mechanical damping (Summer & Entwistle, 1959). In pure iron, depending on the specimen history, magneto-mechanical damping is often so high that any other damping effects may be completely swamped. Application of a magnetic field, however, renders the magnetic domains immobile, and the magneto-mechanical damping can thus be completely eliminated.

6.2.5. Temperature Control.

Thermocouple used in the measurement of temperature is Au-0.03 atomic % Fe/Chromel (wires of 0.012 inch diameter), supplied by Johnson, Mathey and Co. These thermocouples are sensitive and do not deteriorate for a long time, and need not be calibrated except at long intervals. Initial calibration of the thermocouples was made using the following fixed points: boiling points of helium and hydrogen, and at the melting point of ice. Periodic checks on the calibration were carried out at the melting points of ice and dry ice, and at room temperature. The temperature of the cold junction has always been the boiling point of liquid nitrogen. The thermal emf developed was measured by a sensitive mirror galvanometer with the help of a potentiometric arrangement.

When the specimen housing chamber, and the dewar space are evacuated and the heat exchange space is filled with hydrogen, the temperature of the specimen in the specimen housing chamber reaches 80°K in about two hours after the liquid nitrogen tanks T_1 and T_2 are filled by liquid nitrogen. The lower grip begins to heat up due to the leakage of heat through the extension rod (N), so a current is sent through a nichrome winding round the upper grip and the heating element is adjusted in such a way as to keep the temperature of the two grips the same while the temperature of the
total enclosure is allowed to rise. The required heating current has been determined by using two thermocouples at the upper and the lower grips. (When internal friction measurements are made, the thermocouple at the lower grip is removed and the temperature of the specimen is followed by the thermocouple at the upper grip). For measurements above 240°K, liquid nitrogen is taken out of the tank $T_2$ to increase the heating rate.


6.3.1. Specimen Preparation.

The 3% Ni-Fe (C-0.002%, N-0.002%, O-0.001%), supplied in the form of 3/8 inch diameter rods, were swaged down to about 30 thou wire with two interstage annealings at 1000°C in an inert atmosphere, in the furnace described section 6.1.1. The final anneal was also performed at 1000°C for three hours in the inert atmosphere and the specimens were either slow cooled inside the furnace in the same atmosphere, or quenched in cold water by allowing them to drop through the furnace.

In the case of carburised specimens homogenisation was carried out by holding the specimens at 1000°C for 24 hours before these were used in the internal friction experiments.

Specimens cold worked by swaging were held at room temperature for three days and charged with hydrogen by pickling them in a solution of five per cent sulphuric acid with traces of thiourea, which promotes the introduction of hydrogen into the specimens.

6.3.2. Measurement of Internal Friction.

After charging the specimen with hydrogen in the pickling solution, the adhering solution is wiped off with cotton wool. The specimen is then immersed in liquid nitrogen, to prevent hydrogen from diffusing out of the specimens. The specimen is introduced into the internal friction apparatus, which has been cooled to liquid nitrogen temperature by filling the tanks $T_1$ and $T_2$ (Fig. 34) with liquid nitrogen. The specimen housing chamber is evacuated and the specimen is held inside the apparatus for two hours to reach thermal equilibrium.
All internal friction measurements were made at the same initial amplitude of oscillation. The number of oscillations used depends on the value of damping, higher number of oscillations being used while measuring lower damping.

6.3.3. Thermal Cycling Experiments.

Concentration of hydrogen in any given hydrogenated specimen is varied by ageing it at a temperature high enough to effuse hydrogen out of the specimen. Such ageing experiments consist of heating the specimen from 80°K to a predetermined maximum ageing temperature; measurement of the internal friction is carried out at the same time. The specimen is held at this maximum ageing temperature for a preset period, before being cooled down to the liquid nitrogen temperature. The same cycle of operations is repeated several times with the same maximum ageing temperature, so that each successive cycle represents a different hydrogen concentration. To measure the background internal friction, the specimen is aged at room temperature for three days. Results from the mass spectrometric experiments (section 7) show that the concentration of hydrogen in the specimen can be varied by this method.

In section 8.1, it is shown that the diffusion coefficient of hydrogen can be determined as a function of temperature by performing thermal cycling experiments using different maximum ageing temperatures. The specimen is, therefore, reused by recharging with hydrogen to conduct similar experiments at different maximum ageing temperatures. This procedure has been adopted because internal friction is so sensitive to metallurgical variables that specimens, which have apparently undergone the same treatments, will tend to have widely different values of internal friction. Swaging may not introduce the same amount of plastic deformation at every point in the specimen, and the deformation will almost definitely be slightly different from specimen to specimen, even though the apparent reduction in the cross sectional area is the same. However, it has to be ascertained that the specimen is not damaged by charging it several times. The following observations justify the use of the specimens for recharging. (i) The
cold work peak height was nearly the same after each charging treatment. The small change in the peak height can be accounted for by the fact that the time for which the specimen is exposed to room temperature while it is being introduced into the internal friction apparatus varies slightly for each run due to inevitable differences in handling the components. Also the actual amount of hydrogen introduced into the specimen may vary due to small changes in the temperature of pickling. (ii) The back-ground internal friction is found to be the same, every time hydrogen is removed from the specimen by holding it at room temperature for three days. If hydrogen charging treatment were to introduce permanent damage, we would certainly expect this back-ground internal friction to change. (iii) Metallographic examination of the specimens does not show any damage after repeated charging treatments.


Internal friction experiments conducted in the present work have been divided into two categories: (i) study of the hydrogen cold work peak and (ii) study of the carbon peak at 216°C. (This division also gives roughly the chronological order in which the work was performed). The major portion of the work was conducted to investigate the variation of the hydrogen cold work peak temperature and peak height with respect to changes in the concentration of hydrogen. Preliminary experiments were, however, carried out to choose suitable values for various parameters, which were then not altered once they were chosen. These parameters include (a) concentration of nickel, (b) amount of cold work, (c) duration of hydrogen charge, (d) initial amplitude of oscillation and (e) magnetic field strength.

A limited number of experiments were also conducted to determine the conditions under which the peak at 216°C occurs, and to study its behaviour with respect to variation in a few of the critical parameters involved, with a view to understand the mechanism responsible for the appearance of this second peak.

6.4.1. Preliminary Experiments.

(a) Concentration of nickel: To accentuate the differences between the
hydrogen cold work peaks in iron and iron-nickel alloys, one would like to use a large percentage of nickel, but difficulties then arise due to
(i) the low solubility of hydrogen and hence small cold work peak
(ii) the presence of a large percentage of F.C.C. structure in addition to the B.C.C. Both these effects render the interpretation of the results difficult. Thus a balance between the conflicting criteria has to be struck and a concentration of 3% nickel has been decided upon as a suitable value.

(b) Amount of cold work: In fully annealed specimens the hydrogen cold work peak is not observed; the height of the cold work peak is found to increase with increases in cold work, reaching a saturation value at about 45% reduction in area. Therefore, 45% cold work has been used in the present work. (Similar saturation effects have been reported by Sturges (1969) and Gibala (1967)).

(c) Duration of hydrogen charge: Following up the earlier experimental work on the cold work peak in iron (Sturges & Miodownik, 1969), a solution of 5% sulphuric acid with traces of thiourea has been used as the pickling solution for the introduction of hydrogen into the specimens. However, in contrast to the cold work peak height in iron, the peak in 3% Ni-Fe alloy was very small at the end of two hours of hydrogen charging. Systematic increase of the charging time showed that the peak height increased in size up to 20 hours, and the rate of increase was found to be negligible thereafter. Thus 20 hours of charging time has been used for the study of the hydrogen cold work peak in 3% Ni-Fe alloys.*

The charging time had to be decreased in the case of carburised specimens to avoid corrosion effects. However, as the peak height was found to increase with the carbon content, shorter charging times were quite

* Prolonged pickling (for about 60 hours) produced a peak at about 160°K, the characteristics of which are entirely different from that of the cold work peak. This peak is probably due to the onset of microcracks due to high hydrogen concentration. A similar peak at 160°K has been observed by Hermant (1966), where metallographic examination of the specimens showed the presence of microcracks.
sufficient to give peaks of measurable height in carburised specimens.

(d) Magnetic field strength: A magnetic field of 100 oersteds was found to have no effect on the cold work peak height and only a marginal effect on the background. However, when fully annealed specimens were used, the background damping decreased by the application of the magnetic field. This clearly indicates that the difference in the behaviour is due to the change in the level of cold work. Magnetic domains are rendered immobile by internal stresses introduced during cold work, thus eliminating magnetomechanical damping. That is to say, cold work plays the same role in deformed specimens, as the magnetic field in the annealed specimens in eliminating the magnetomechanical damping (Summer & Entwistle, 1959).

6.4.2. Effects of Change in the Concentration of Hydrogen.

The two types of alloys used in the study of the hydrogen cold work peak are (i) hydrogen charged 3% Ni-Fe alloys and (ii) hydrogen charged carburised 3% Ni-Fe alloys. The detailed treatments of the specimens used are summarised in Table X. Three typical sets of results are shown in Fig. 37 (a slow cooled specimen), Fig. 38 (a water quenched specimen) and Fig. 39 (a carburised specimen). The individual curves in each set were obtained by holding the specimens at the temperatures of ageing, specified in the diagrams. The effective times of ageing were calculated by the method outlined in Section 8.1. Similar results obtained by holding these specimens at other temperatures of ageing are not illustrated; the peak heights (background removed) and the peak temperatures from these total series of experiments are summarised in Tables XI, XII and XIII. Fig. 40 shows the marked difference in the relationship between the peak temperature and the peak height for the carburised and the uncarburised specimens.

6.4.3. The Background.

The background for the quenched specimen (Fig. 38) shows some irregularities compared to slow cooled specimen (Fig. 37). However, exactly the same background values are obtained every time hydrogen is completely removed from the specimen after each recharge. As the main purpose of these experiments was to obtain hydrogen cold work peaks, no
Fig. 37. Changes in the hydrogen cold work peak in \( \% \) nickel-iron alloys (slow cooled specimen) due to ageing.
Fig. 38. Changes in the hydrogen cold work peak in 3% nickel-iron alloys (water quenched specimen) due to ageing.
Immediately after hydrogen charge
Aged 15 mins.
Aged 35 mins.
Aged 3 days

Fig. 39. Changes in the hydrogen cold work peak in carburised 3% nickel-iron alloys due to ageing.
Fig. 40. Correlation of hydrogen cold work peak temperature with peak height for 3% nickel-iron alloys.
further work was done to determine the origin of the anomalous background, which was subtracted in the normal way as for other specimens. Despite the

Table X. History of Sample Specimens.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slow cooled specimen</td>
<td>3% Ni-Fe alloy, swaged down to 30 thou from 3/8&quot; diameter rod with two interstage anneals. Annealed at 1000°C in an inert atmosphere for three hours and furnace cooled. Then cold reduced by 45%.</td>
</tr>
<tr>
<td>Water quenched specimen</td>
<td>Same as the slow cooled specimen, but water quenched from 1000°C instead of slow cooling after the final anneal.</td>
</tr>
<tr>
<td>Carburised specimen</td>
<td>After swaging down to 30 thou (as the slow cooled specimen), carburised at 950°C for five minutes in an atmosphere of acetylene (pressure 30 torr). Homogenised at 1000°C for 24 hours in an inert atmosphere and then furnace cooled.</td>
</tr>
</tbody>
</table>

differences in the background, the behaviour of the cold work peaks in the quenched specimen is similar to those in the slow cooled specimen (Fig. 40).

In the carburised specimen, the background appears to increase with temperature, but this effect can be attributed largely to the low temperature side of the peak at 216°K (Section 6.5.).

6.4.4. Conclusions.

The above experimental results on the hydrogen cold work peak in iron-nickel alloys bring out the following features.

(i) The hydrogen cold work peak height can be decreased by thermal cycling experiments (Fig. 37, 38 and 39).

(ii) The peak temperature decreases as the peak height is decreased (Fig. 40).

(iii) No significant difference between the behaviours of the hydrogen
Table XI. Peak Heights and Peak Temperatures of the Hydrogen Cold Work Peak (Slow Cooled Specimen, 3% Ni-Fe alloys).

<table>
<thead>
<tr>
<th>Maximum temp. of ageing (°K)</th>
<th>Peak height (Background removed) (± x 10^4)</th>
<th>Peak temperature (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>7.25 ± 0.1</td>
<td>145 ± 2</td>
</tr>
<tr>
<td></td>
<td>6.30 ± 0.1</td>
<td>126 ± 2</td>
</tr>
<tr>
<td></td>
<td>5.85 ± 0.1</td>
<td>122 ± 2</td>
</tr>
<tr>
<td></td>
<td>4.90 ± 0.1</td>
<td>110 ± 2</td>
</tr>
<tr>
<td>275</td>
<td>7.0 ± 0.1</td>
<td>123 ± 5</td>
</tr>
<tr>
<td></td>
<td>4.1 ± 0.3</td>
<td>115 ± 5</td>
</tr>
<tr>
<td></td>
<td>3.1 ± 0.3</td>
<td>115 ± 5</td>
</tr>
<tr>
<td>290</td>
<td>6.5 ± 0.3</td>
<td>120 ± 5</td>
</tr>
<tr>
<td></td>
<td>3.5 ± 0.1</td>
<td>101 ± 2</td>
</tr>
<tr>
<td></td>
<td>3.0 ± 0.1</td>
<td>100 ± 3</td>
</tr>
<tr>
<td>295</td>
<td>6.9 ± 0.15</td>
<td>135 ± 3</td>
</tr>
<tr>
<td></td>
<td>4.2 ± 0.1</td>
<td>117 ± 2</td>
</tr>
<tr>
<td></td>
<td>2.8 ± 0.1</td>
<td>108 ± 2</td>
</tr>
</tbody>
</table>

cold work peaks in the slow cooled and quenched specimens has been observed.

(iv) Variation of the hydrogen cold work peak temperature with changes in the peak height is markedly decreased by carburising the specimens.

6.5. The 216°K Peak.

A hitherto unreported internal friction peak at 216 ± 5°K has been identified in nickel-iron alloys containing carbon. Investigation of the behaviour of this peak has been undertaken primarily on carburised 3% Ni-Fe alloys, but a limited number of experiments have also been conducted.
### Table XII. Peak Heights and Peak Temperatures of Hydrogen Cold Work Peak (Water quenched specimen, 3% Ni-Fe alloys).

<table>
<thead>
<tr>
<th>Maximum temp. of ageing (°K)</th>
<th>Peak height (Background removed)</th>
<th>Peak temperature (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$(6 \times 10^4)$</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>$4.85 \pm 0.1$</td>
<td>$115 \pm 2$</td>
</tr>
<tr>
<td></td>
<td>$4.2 \pm 0.1$</td>
<td>$104 \pm 2$</td>
</tr>
<tr>
<td></td>
<td>$2.5 \pm 0.1$</td>
<td>$90 \pm 2$</td>
</tr>
<tr>
<td>273</td>
<td>$4.9 \pm 0.2$</td>
<td>$113 \pm 4$</td>
</tr>
<tr>
<td></td>
<td>$3.55 \pm 0.2$</td>
<td>$97 \pm 2$</td>
</tr>
<tr>
<td></td>
<td>$1.75 \pm 0.2$</td>
<td>$94 \pm 2$</td>
</tr>
<tr>
<td>295</td>
<td>$5 \pm 0.2$</td>
<td>$114 \pm 2$</td>
</tr>
<tr>
<td></td>
<td>$1.7 \pm 0.1$</td>
<td>$97 \pm 2$</td>
</tr>
<tr>
<td></td>
<td>$1.15 \pm 0.1$</td>
<td>$93 \pm 2$</td>
</tr>
</tbody>
</table>

### Table XIII. Peak Heights and Peak Temperatures of Hydrogen Cold Work Peak (Carburised Specimen, 3% Ni-Fe alloys).

<table>
<thead>
<tr>
<th>Maximum temp. of ageing (°K)</th>
<th>Peak height (Background removed)</th>
<th>Peak temperature (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$(6 \times 10^4)$</td>
<td></td>
</tr>
<tr>
<td>273</td>
<td>$4.25 \pm 0.1$</td>
<td>$126 \pm 4$</td>
</tr>
<tr>
<td></td>
<td>$2.6 \pm 0.1$</td>
<td>$124 \pm 3$</td>
</tr>
<tr>
<td></td>
<td>$0.7 \pm 0.1$</td>
<td>$123 \pm 3$</td>
</tr>
<tr>
<td>298</td>
<td>$14.2 \pm 0.2$</td>
<td>$140 \pm 2$</td>
</tr>
<tr>
<td></td>
<td>$10.3 \pm 0.2$</td>
<td>$135 \pm 5$</td>
</tr>
<tr>
<td></td>
<td>$8.5 \pm 0.2$</td>
<td>$125 \pm 5$</td>
</tr>
<tr>
<td></td>
<td>$6.5 \pm 0.2$</td>
<td>$125 \pm 5$</td>
</tr>
</tbody>
</table>
on alloys containing higher percentage of nickel to determine whether the peak exists in these alloys as well. The significance these results are discussed in section 8.8.

6.5.1. Effects of Cold Work.

Preliminary work on the $216^\circ$K peak showed that the peak height in the carburised iron-nickel alloys increased by plastic deformation (Fig. 41). Therefore specimens with the same level of deformation (about 45% R.A.) as those used in the study of the hydrogen cold work peak have been used for studying the $216^\circ$K peak.

6.5.2. Ageing Behaviour.

The height of the $216^\circ$K peak is found to decrease by holding the specimen at room temperature. Fig. 42 shows a plot of the $216^\circ$K peak height vs the logarithm of the time of room temperature ageing for a typical carburised, cold worked 3% Ni-Fe specimen. A comparison of curves (b) and (c) in Fig. 41 also shows that the small peak at $280^\circ$K is completely removed by 40 hours of room temperature ageing.

6.5.3. Effects of Change in Carbon Concentration.

The height of the $216^\circ$K peak is found to increase linearly with carbon concentration (Fig. 43). The peak height per weight percent of carbon for this (carburised and 45% deformed 3% Ni-Fe) is calculated from the slope of the straight line in Fig. 43 to be equal to $350 \times 10^{-4}$/wt% carbon.

6.5.4. Effects of Change in Nickel Content.

For a true comparison of the $216^\circ$K peak height in alloys containing different amounts of nickel, the peak height per weight per cent of carbon is used. A plot of this parameter against the concentration of nickel content (Fig. 44) shows that the height of this peak increases almost linearly for low nickel content, reaching a maximum at about 66% nickel, decreasing thereafter for higher nickel concentrations. The heights of the peak in the carburised iron and carburised nickel alloys are negligible (Fig. 44). Although referred to generally as the $216^\circ$K peak, this may in fact be a composite peak, as indicated by the existence of an additional peak at about $240^\circ$K in freshly deformed carburised 9% and 50% Ni-Fe alloys.
Fig. 41. Effect of cold work on the 216°K peak in carburised 3% nickel-iron alloys.
Fig. 42. Ageing behaviour of the 216°K peak in carburised 3% nickel-iron alloys.
Fig. 43. Variation of the height of the 216°K peak with the concentration of carbon.

3% Ni-Fe
carburised and 45% deformed
(Immediately after cold work)
Fig. 44. Effect of change in nickel content on the height of the 216°K peak in carburised iron-nickel alloys.
The $240^\circ$K peak disappears after an ageing treatment of 14 hours at room temperature (Fig. 45); and this peak was not visible in the other alloys investigated, namely carburised 0, 3, 90, 100% Ni-Fe alloys. One cannot, however, rule out the existence of a small peak at $240^\circ$K in these alloys. Two reasons can then be given to account for the observed results. (i) A big peak at $216^\circ$K masks the small peak at $240^\circ$K. (ii) The rate of decay of the $240^\circ$K peak may be such that the peak is completely removed by the time the specimen is heated to $240^\circ$K.

6.5.5. Effects of Hydrogen on the $216^\circ$K Peak.

Introduction of hydrogen into carburised deformed specimens has a threefold effect on the logarithmic decrement.

(i) There is a decrease in the height of the $216^\circ$K peak, which is almost completely suppressed by a 15 minute ageing treatment at room temperature.

(ii) A new peak is produced at about $200^\circ$K which also disappears after a 15 minute ageing treatment at room temperature.

(iii) The hydrogen cold work peak observed at about $140^\circ$K, whose behaviour remains unchanged, follows the normal decay pattern as explained in section 6.4.2.

Fig. 46 and Fig. 47 show that the $216^\circ$K peak reappears only on removal of hydrogen from the specimen. Investigations on a carburised 50% Ni-Fe alloy showed similar effects on the introduction of hydrogen.

6.5.6. Conclusions.

These experiments clearly indicate that the $216^\circ$K peak:

(i) needs the presence of both carbon and nickel for its appearance,

(ii) is enhanced by deformation,

(iii) decays by room temperature ageing,

(iv) is suppressed by the introduction of hydrogen into the specimen.
Fig. 45. Internal friction peaks in carburised 9% nickel-iron alloys.
Fig. 46. Effect of hydrogen on the 216°K peak in carburised 3% nickel-iron alloys.
Fig. 47. Effect of hydrogen on the ageing behaviour of the 216°K peak in 3% nickel-iron alloys.

A 180° magnetic deflection mass spectrometer (Micromass 2, supplied by Vacuum Generators Limited) has been used to measure the thermal effusion rate of hydrogen from hydrogenated specimens. The temperature range covered in these experiments was the same as that used for ageing the specimens in the internal friction experiments. The rate of effusion of hydrogen at these temperatures is so low that a very sensitive instrument such as a mass spectrometer has to be used. The results from these experiments have been used to calculate the diffusion coefficient of hydrogen in iron-nickel alloys, and the values compared (in Section 8.1.) with the diffusion coefficients obtained from the internal friction experiments.

7.1. Apparatus.


Detailed description of various kinds of mass spectrometers and the experimental techniques that have been developed can be found in the introductory books on mass spectrometry (Kiser, 1967; Biemann, 1962; Bonnett & Davies, 1967). Classified references on different aspects of mass spectrometry have also been given by Waldron (1959) and Elliott (1963). The Mass Spectrometry Bulletin (Mass Spectrometry Centre, Aldermaston) can be referred to for recent advances in this field. Only the details of immediate interest to the present work are given below.

(a) Sensitivity: The sensitivity of a mass spectrometer is defined as the ratio of the ion current produced in the detector to the partial pressure of the gaseous species in question. This definition implies a linear relationship between the ion current and the partial pressure. Fig. 48 shows that this assumption is true for low pressures only and at about 10^{-2} torr ceases to hold good. The sensitivity varies from gas to gas; this leads to the concept of relative sensitivity, which is the ratio of the sensitivity of a gas to that of nitrogen. The sensitivity of the instrument used in the present work is 3 \times 10^{-5} \text{amp/torr} for nitrogen and the relative sensitivity for hydrogen is 0.7.

(b) Resolving power: There are many definitions of resolving power, but the one most commonly accepted by mass spectrosocopists in comparing instrument
Fig. 48. Relationship between the ion current recorded by the mass spectrometer and the partial pressure for some typical gases.
performances is known as the '10% valley definition'. According to this definition, if the resolving power is specified as \( X \), the valley between the two peaks of equal height \( h \), at masses \( (X - 1) \) and \( X \) will approach to \( h/10 \). Fig. 49 (a) illustrates this definition. Another useful, but not very rigorous definition is the 'unit mass resolution' or the '50% valley resolution'. The unit mass resolution is said to be \( Y \), if peaks at mass numbers \( (Y - 1) \) and \( Y \) are detectable as separate masses provided that their abundance ratio is less than 10 (Fig. 49 b). The resolution for the instrument used here is 44 on the 10% valley definition, giving unit mass separation of peaks up to 60.

(c) Pressure range: The full scale deflection of the available detector for the most sensitive range is \( 3 \times 10^{-10} \) torr and the minimum measurable pressure is \( 3 \times 10^{-12} \) torr (noise level is \( 7\% \) of the full scale deflection of the most sensitive range). The mass spectrometer can be used to measure pressures below \( 10^{-2} \) torr, but the linear pressure range extends only up to about \( 10^{-3} \) torr (Fig. 48).

(d) Mass range: A selector switch is available to obtain mass spectrometer readings at masses 2, 3 and 4. (Continuous automatic or manual scan of mass ranges 12 - 60 and 48 - 240 can be carried out by using a separate selector switch). The mass spectrometer readings can be permanently recorded on a flow chart recorder connected to the mass spectrometer detector.

7.1.2. The Sample Introduction System

The sample introduction system (Fig. 50) consists of a pyrex glass tube, which is the specimen chamber (SPC), surrounded by the liquid circulation chamber (LC), through which a suitable liquid can be circulated using the inlet (I) and the outlet (O). The temperature along the length of the specimen chamber can be measured by the thermometers \( T_1 \) and \( T_2 \). The liquid circulation chamber is surrounded by an insulating jacket B. The open end of the specimen chamber is connected to a brass flange \( F_1 \) by means of a glass metal seal, and this flange is in turn connected to the ion source of the mass spectrometer. The specimen can be introduced into the specimen space through
Fig. 49. Diagrams illustrating the definitions of the resolving power of a mass spectrometer.
Fig. 50. Schematic diagram of the sample introduction system for the mass spectrometer.

The inlet (I) and the outlet (O) of the liquid circulation chamber (LC) were connected to a glass low temperature bath (Mizeal 200), which circulated the coolant through the liquid circulation chamber at the required temperature. A mixture of ethylene glycol and water which gives a constant temperature of -40°C, has been used in the present work.

![Schematic diagram of sample introduction system for mass spectrometer](image)

Note: The diagram shows the liquid circulation chamber (LC) connected to a glass low temperature bath (Mizeal 200) with inlet (I) and outlet (O) ports. The chamber is labeled with T1 and T2, and there is a gaseous mass spectrometer (GMS) outlet (Fi). The system includes a sample port (SPC) and a detector (D).
the flange $F_1$, by disconnecting the specimen introduction system from the mass spectrometer.

The inlet (I) and the outlet (O) of the liquid circulation chamber (LC) were connected to a Grant low temperature bath (Model LBX), which circulates the coolant through the liquid circulation chamber at the required temperature. A mixture of ethylene glycol and water which gives a minimum temperature of $-15^\circ C$, has been used in the present work.


Mass spectrometers have been used to measure the rate of evolution of gases in studies of diffusion of hydrogen through steel membranes (Frank et al, 1958), the analysis of oxygen in copper (Aspinal, 1966), and the desorption and adsorption of inert gases on metal and glass surfaces under high vacuum conditions (Lock, 1959); the method used here is similar to that used by Leck. Measurements are made in a continuously evacuated system, the quantity of gas coming out of the specimen by diffusion being estimated (in arbitrary units) by integrating the pressure transients recorded by the mass spectrometer with respect to time.

7.2.1. Experimental Procedure.

Hydrogenated specimens, identical to those used in internal friction experiments, were introduced into the specimen chamber, which was previously cooled to the required ageing temperature. The change in the temperature of the specimen chamber during this operation was found to be less than one degree and the constant ageing temperature was attained within five minutes after the introduction of the specimen. The specimen chamber was evacuated to less than $10^{-3}$ torr, before recording of the mass spectrometer reading was commenced, with the mass spectrometer set to mass number two (i.e., hydrogen).

The specimen was held inside the specimen chamber at room temperature for three days, under vacuum to degas the hydrogen completely. It was then taken out of and reintroduced into the specimen chamber to perform a blank run, similar to the one conducted with the hydrogenated specimen. The difference between the readings from these two runs gives the true mass
spectrometer readings due to the hydrogen diffusing out of the specimen. Fig. 51 gives typical readings for a 3% Ni-Fe specimen, at the ageing temperature of 303°K.

7.2.2. Calculation of the Diffusion coefficient.

The amount of hydrogen V(t) come out of the specimen up to an ageing time t is given by,

\[ V(t) = k_H \int_0^t R \, dt \]

\[ R = (R_a - R_b) \]

where \( k_H \) = constant of proportionality,

\( R_a \) = mass spectrometer reading for hydrogenated specimen at time t,

\( R_b \) = mass spectrometer reading for the blank run at time t.

It can be shown (Darken & Gurry, 1953) that if the effusion of a gas is diffusion controlled, a plot of \( V(t) \) vs \( \sqrt{t} \) should be a straight line (for small values of t), which is found to be true in the present case (Fig. 52). \( V_0 \) in Fig. 52 represents the total amount of hydrogen come out of the specimen. The diffusion coefficient can be calculated (Darken & Gurry, 1953) by using the relationship:

\[ t_{1/2} = \frac{r^2}{2 \times 2.26 \times D_T} \]

where \( r \) = radius of the specimen,

\( D_T \) = diffusion coefficient of hydrogen at the ageing temperature \( T^0 \),

\( t_{1/2} \) = time required for half the amount of hydrogen to diffuse out of the specimen,

substituting the value of \( t_{1/2} \) from Fig. 52. This experiment has been repeated at the same temperature of ageing to determine the scatter, which was found to be less than 2% relative to the mean value. Values of the diffusion coefficient at various temperatures are tabulated in Table XIV, and are compared with the diffusion coefficients obtained by internal friction measurements (section 8.1; Fig. 55).
Fig. 51. Plots of mass spectrometer reading as a function of time of ageing of the specimens in the mass spectrometer.

Fig. 52. Plots of the amount of hydrogen diffused out of the specimens vs square root of time of ageing.
Table XIV. Diffusion Coefficients of Hydrogen in 3% Ni-Fe Alloys (Mass Spectrometric Experiments).

<table>
<thead>
<tr>
<th>Temperature of ageing (T°K)</th>
<th>Diffusion coefficient of hydrogen at T°K</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>2.27 x 10^{-9}</td>
</tr>
<tr>
<td>273</td>
<td>5.27 x 10^{-9}</td>
</tr>
<tr>
<td>290</td>
<td>13.8 x 10^{-9}</td>
</tr>
<tr>
<td>295</td>
<td>16.2 x 10^{-9}</td>
</tr>
<tr>
<td>303</td>
<td>28.7 x 10^{-9}</td>
</tr>
</tbody>
</table>

7.2.2. Conclusions.

The above experiments show that:

(i) hydrogen definitely leaves the specimen under the conditions of thermal ageing such as that used in the internal friction experiments; the effects of thermal ageing may therefore be attributed to changes in hydrogen concentration.*

(ii) the time dependence of the effusion of hydrogen confirms that the process is a diffusion controlled one.

* In the palladium hydrogen alloys the variation of peak height due to thermal ageing, results from hydrogen precipitation during ageing (Arons et al, 1967).
8. Discussion.

The discussion in this section relates to:

(i) The extraction of parameters connected with the diffusion of hydrogen in iron-nickel alloys from the hydrogen cold work peak measurements.

(ii) Binding energy of hydrogen to dislocations.

(iii) A critical reappraisal of the explanation of the activation energy of the cold work peak and the peak broadening.

(iv) Modification of Schoeck's theory to explain the dependence of the cold work peak height with the concentration of hydrogen.

(v) The effect of carbon.

(vi) The mechanism responsible for the 216°K.

Previous explanations of the hydrogen cold work peaks in iron are also re-interpreted.


During the thermal cycling experiments, the specimen is heated from 80°K up to the maximum ageing temperature \( T_H \) and is held at that temperature for a preset period. An effective time \( t^* \) can be calculated (Appendix A), such that ageing the specimen for a time \( t^* \) at \( T_H \) K has the same effect as that produced by the above experimental procedure. This calculation is valid if the process involved is diffusion controlled and the mass spectrometric experiments (Section 7) have already shown that this is true for the present experiments.

It may be pointed out that although this calculation assumes an initial value of \( Q \) (the activation energy for the diffusion of hydrogen), an iterative method can be used to arrive at the true value of \( t^* \), and this value is independent of the initial assumed value of \( Q \) (See section 8.1.3.).

8.1.2. Relationship between the Hydrogen Cold Work Peak Height and the Hydrogen Concentration.

Sturges & Miodownik (1969) have shown (Fig 5) that the hydrogen cold
work peak height is proportional to the concentration of hydrogen in the specimen. It is shown below that the same assumption holds good for the present case as well.

For a gaseous impurity diffusing out of a long cylindrical specimen into vacuum, the mean concentration, \( c \) in the specimen after a short time, \( t^* \) is given by (Darken & Gurrey, 1953),

\[
1 - \frac{c}{c_0} = 2.256 \sqrt{\frac{D_{TM} t^*}{r}}
\]

where \( c_0 \) = initial concentration

\( D_{TM} \) = diffusion coefficient at temperature \( T_M \) at which diffusion takes place

\( r \) = radius of the specimen.

Coupled with the experimental fact that linear relationship exists between the cold work peak height (\( \delta_P \)) and the square root of the effective time of diffusion (Fig 53 and 54), i.e.,

\[
\delta_P - \delta_{p0} = k_{TM} \sqrt{t^*}
\]

where \( \delta_{p0} \) = peak height at \( t^* = 0 \) (i.e., initial peak height)

\( k_{TM} \) = constant

we can write:

\[
\frac{1 - c/c_0}{1 - \delta_P/\delta_{p0}} = 2.256 \sqrt{\frac{D_{TM} \delta_{p0}}{(k_{TM} r)}}
\]

Using the condition that \( \delta_P = 0 \) when \( c = 0 \), the above equation may be written as,

\[
1 = 2.256 \sqrt{D_{TM} \delta_{p0}/(k_{TM} r)}
\]

Equations (99) and (100) imply:

\[
\frac{c}{c_0} = \frac{\delta_P}{\delta_{p0}}
\]

i.e., the cold work peak height is proportional to the mean concentration of hydrogen in the specimen.

8.1.3. Calculation of Diffusion Coefficients and the Activation Energy for Diffusion.

Using the plot of peak height (\( \delta_P \)) and the square root of the effective time (\( t^* \)) of diffusion, the diffusion coefficient \( D_{TM} \) can be
Fig. 53. Plots of hydrogen cold work peak height vs square root of time of ageing for furnace cooled 3% nickel-iron alloys.
Fig. 54. Plots of the hydrogen cold work peak height vs square root of the time of ageing for water quenched 3% nickel-iron alloys.
calculated. If $t^*_{1/2}$ is the effective time needed for the peak height to drop to half its initial value, then from equation (100) we have,

$$\delta p_0/2 = \delta p_0 - k_{TM} \sqrt{t^*}$$

(102)

Eliminating $k_{TM}$ between equations (100) and (102), $D_{TM}$ may be written as,

$$D_{TM} = \frac{r^2}{C(2 \times 2.256)^2 t^*_{1/2}}$$

(103)

A plot of $\log D_{TM}$ vs $1/T_M$ (Fig 55) can be used to calculate the activation energy ($Q$) for diffusion. Table XV summarises the results from such an analysis.

As mentioned in section 8.1.1., the calculation of the effective time $t^*$ requires a knowledge of $Q$. However, once a value for $Q$ is assumed, the calculation already outlined in this section may be used to calculate a new value of $Q$. The assumed value of $Q$ may then be replaced by this new value, and the same cycle of calculations is repeated. The steps involved in this iterative process are shown in Fig 56. The true value of $Q$ obtained at the end of this iterative method of

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Temperature ($T_M^*$)</th>
<th>Diffusion Coefficient ($D_{TM} \times 10^9$ cm$^2$/sec)</th>
<th>$D_0$ (cm$^2$/sec)</th>
<th>$Q$ (k cal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slow cooled</td>
<td>250</td>
<td>1.1</td>
<td>0.093</td>
<td>9.05</td>
</tr>
<tr>
<td></td>
<td>275</td>
<td>7.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>11.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>295</td>
<td>17.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water Quenched</td>
<td>250</td>
<td>2.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>273</td>
<td>7.1</td>
<td>1.16</td>
<td>10.05</td>
</tr>
<tr>
<td></td>
<td>295</td>
<td>47.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 55. Plots of logarithm of diffusion coefficient of hydrogen vs. reciprocal of temperature for 38% nickel iron alloys.
Fig. 56. Iterative method for the calculation of $Q$, the activation energy for bulk diffusion.
calculations is independent of the initial assumed value of \( Q \) (Fig 57).

The iterative method outlined above was developed by Sturges & Miodownik (1969), but, the method of calculation of \( t^* \) was restricted to linear heating rates only (Armstrong, 1958); the new method, outlined in Appendix A can be used for any heating rates. The whole iterative process has been computerised, saving a considerable amount of time and effort involved in the calculations.

8.1.4. Time for Complete Degassing of Specimens.

Now that the values of \( Q \) and \( D_0 \) (from Fig 55) are known, we can ascertain whether three days of ageing at 300°K is sufficient to degas the specimen completely. To test this, we may refer to the plot of \((1 - c/c_0)\) vs \(\sqrt{(D_Tt^*)/r}\) (Fig 58). Using \( T = 300°K, r = 0.03 \) cm and \( t^* = 3 \) days, we obtain,

\[
\sqrt{(D_{300}t^*)/r} \approx 1.7
\]

The corresponding value of \((1 - c/c_0)\) \(\ll 10^{-4}\), which means that at the end of three days, the fraction of hydrogen remaining inside the specimen is less than 0.01% of its initial value. Therefore we are justified in assuming that three days of ageing at 300°K is sufficient to remove practically all the diffusible hydrogen from the specimen.

In the case of carburised specimens, diffusion of hydrogen is much faster and a smaller time ought to be sufficient for the complete degassing of hydrogen. However, it is found that a small amount of hydrogen is retained in these specimens, and a very slow rate of diffusion of hydrogen is observed after an initial faster rate. This behaviour is further discussed in section 8.8.2.
Fig. 57. Values of $Q$, the activation energy for bulk diffusion of hydrogen in 38 nickel-iron alloys, at the end of successive cycles of operations of the iterative process.
Fig. 58. Dependence of the mean concentration (C) on the diffusion coefficient (D), time of diffusion (t) and the radius (r) for a cylindrical specimen (Darken & Gurry, 1953). (C₀ is the initial concentration, before the beginning of diffusion from the specimen to the surroundings).
8.2. Bulk Diffusion of Hydrogen.


In sections 8.2.1. and 8.2.2., a brief discussion of the diffusional behaviour of hydrogen is investigated in order to determine the meaning of the activation energy for bulk diffusion and to consider the possibility of dislocation sites as the only trapping sites for hydrogen in steels. However, for comprehensive reviews of the experimental work and the consequent theoretical implications, reference can be made to the recent work of Oriani (1967; 1970).

As will be seen later, the experimentally determined values of $D_0$ parameter and the activation energy for diffusion, at different temperature ranges, can be related to the number of trapping sites in the material. Typical experimental results, as shown in Table XVI, give an indication of the enormous differences in the values of $D_0$ and the activation energy reported by different research workers. However, plots of $(\log D) vs 1/T$ (T is the temperature on the absolute scale) indicate that the results generally fall into two linear portions meeting each other at a critical temperature $(T_C)$ as shown in Fig 59.

In view of the above experimental facts, it will be useful if theoretical considerations can lead to the determination of:

(i) The temperature $T_C$ at which the transition from the low temperature behaviour $(T < T_C)$ to the high temperature behaviour $(T > T_C)$ takes place.

(ii) The relationships describing the straight line portions of the $(\log D) vs 1/T$ for $T < T_C$ and $T > T_C$.

(iii) The effects of changes in the density of trapping sites, trap depth and the hydrogen concentration.

Following Oriani's work, the apparent diffusion coefficient $D$ and the lattice diffusion coefficient $D_L$ are related by,

$$D = D_L \cdot \frac{n_1}{n_{x1}} \left[ n_1 + n_x(1 - \frac{n_x}{N_x}) \right]$$

for $n_1$ very small compared to $N_{x1}$,

where $n_1 =$ number of hydrogen atoms at the lattice sites/unit volume.
Fig. 59. Relationship between the diffusion coefficient and temperature (T) for hydrogen in Steels (Coc & Moreton, 1966).

(a) Ni-Cr-Mo steel
(b) Cr-Mo-V-W steel
\[ N_1 = \text{number of lattice sites/unit volume} \]
\[ n_x = \text{number of hydrogen atoms at the trapping sites/unit volume} \]

Table XVI. Diffusion Parameters of Hydrogen in Steel (Coe & Moreton, 1966).

<table>
<thead>
<tr>
<th>Material</th>
<th>Temp. range (°C)</th>
<th>( D ) (x10^{-4} \text{cm}^2/\text{sec})</th>
<th>( Q ) (kcal/mole)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-Fe</td>
<td>0-900</td>
<td>7.6</td>
<td>2.280</td>
<td>Sykes et al (1947)</td>
</tr>
<tr>
<td>a-Fe</td>
<td>400-900</td>
<td>22</td>
<td>2.900</td>
<td>Geller &amp; Sun (1950)</td>
</tr>
<tr>
<td>Pure iron</td>
<td>150-650</td>
<td>8.8±0.8</td>
<td>3.050±0.1</td>
<td>Stross &amp; Tompkins (1956)</td>
</tr>
<tr>
<td>Armco iron</td>
<td>200-774</td>
<td>9.3</td>
<td>2.700</td>
<td>Eichenauer et al (1958)</td>
</tr>
<tr>
<td>Pure iron</td>
<td>200-780</td>
<td>14±6</td>
<td>3.200±2.5</td>
<td>Johnson &amp; Hill (1960)</td>
</tr>
<tr>
<td>Carbon steel</td>
<td>50-480</td>
<td>90-180</td>
<td>6.400-6.900</td>
<td>Eschbach (1963)</td>
</tr>
<tr>
<td>Pure iron</td>
<td>25-200</td>
<td>1200±400</td>
<td>7.820±1.600</td>
<td>Johnson &amp; Hill (1960)</td>
</tr>
<tr>
<td>Ni-Cr-Mo steel</td>
<td>20-125</td>
<td>182x10^4</td>
<td>12.100</td>
<td>Hobson (1958)</td>
</tr>
<tr>
<td>Carbon steel</td>
<td>25-90</td>
<td>50</td>
<td>3.400</td>
<td>Frank (1958)</td>
</tr>
<tr>
<td>Carbon steel</td>
<td>25-90</td>
<td>190</td>
<td>6.320</td>
<td>Frank (1958)</td>
</tr>
<tr>
<td>Ni-Cr-Mo steel</td>
<td>35-160</td>
<td>2140</td>
<td>7.800±1.6</td>
<td>Coe &amp; Moreton (1966)</td>
</tr>
<tr>
<td>Ni-Cr-Mo steel</td>
<td>260-500</td>
<td>7.9</td>
<td>2.800±1.800</td>
<td>Coe &amp; Moreton (1966)</td>
</tr>
<tr>
<td>Cr-Mo-V-W steel</td>
<td>80-300</td>
<td>320</td>
<td>7.300±2.100</td>
<td>Coe &amp; Moreton (1966)</td>
</tr>
<tr>
<td>Cr-Mo-V-W steel</td>
<td>325-600</td>
<td>3.6</td>
<td>1.990±1.600</td>
<td>Coe &amp; Moreton (1966)</td>
</tr>
</tbody>
</table>

\( N_x = \text{number of trapping sites/unit volume} \)

All the trapping sites are assumed to be identical and a local equilibrium is assumed to exist between hydrogen at the lattice sites and at the trapping sites according to the relation:

\[ \frac{n_x}{N_x - n_x} = K \cdot \frac{n_1}{N_1 - n_1} \]  \hspace{1cm} (105)

where \( K \) is the equilibrium constant. Referring to the model, such as that shown in Fig 60, the trapping site \((X)\) represents an energy level \(Q_B\) loss.
Fig. 60. Model for a trapping site for hydrogen atoms in steels (Oriani, 1970).
than that of a normal lattice site (L); the trapping site is bounded by an energy barrier equal to \( Q' + Q_D \), where \( Q_D \) represents the activation energy for lattice diffusion. Assuming \( Q' = 0 \), the value of \( K \) is given by,

\[
K = \exp\left(\frac{Q_B}{RT}\right)
\]

where \( Q_B \) is the binding energy/mole of hydrogen at the trapping sites.

Two important cases will now be considered; (a) for very high hydrogen concentrations at the trapping sites, i.e., for \( \frac{n_x}{N_x} \ll 1 \), (b) for low concentrations of hydrogen at the trapping sites, i.e., for \( \frac{n_x}{N_x} \gg 1 \).

(a) When the concentration of hydrogen is high at the trapping sites.

Under this condition, \( \frac{n_x}{N_x} \ll 1 \) and equation (104) reduces to

\[
D = D_L
\]

This implies that neither the trap depth nor the trap density has any influence on the diffusion of hydrogen when a large fraction of the total number of trapping sites are filled by hydrogen. Also this does not predict a transition temperature which seems to occur in practice (Fig 59).

(b) When the concentration of hydrogen is small at the trapping sites.

Under this condition \( n_x/N_x \) is small compared to unity, and equation (104) reduces to

\[
D = D_L / \left[ 1 + (\frac{n_x}{N_x}) \exp\left(\frac{Q_B}{RT}\right) \right]
\]

This equation shows that the apparent diffusion coefficient decreases as (i) the trap density increases and (ii) the trap depth increases.

Substituting

\[
D_L = D_{oL} \exp\left( - \frac{Q_D}{RT} \right)
\]

where \( D_{oL} \) is the \( D_0 \) parameter for lattice diffusion and \( Q_D \) is the activation energy for lattice diffusion, equation (108) may be written as,

\[
D = D_{oL} N_x \exp(-Q_D/RT) / \left[ N_L + N_x \exp(Q_B/RT) \right]
\]

At sufficiently low temperatures, the first term in the denominator can be neglected in comparison with the second, and equation (110) can then be written as

\[
D = D_0 \exp\left( - \frac{Q}{RT} \right)
\]

where

\[
D_0 = D_{oL} N_x / N_L
\]
and
\[ Q = Q_D + Q_B \]  \hspace{1cm} (113)

A plot of \((\ln D) vs 1/T\) is a straight line with slope equal to \(- (Q_D + Q_B)/R\) and the intercept on the \(1/T = 0\) axis is equal to \(D_L N_L / N_x\).

At higher temperatures when
\[ N_L \gg N_x \exp(Q_B/RT) \]  \hspace{1cm} (114)
equation (110) reduces to
\[ D = D_L \]  \hspace{1cm} (115)

Thus at high temperatures, neither the trap density nor the trap depth has any effect on the diffusion behaviour. A critical temperature \(T_c\) may be defined in such a way that for \(T < T_c\), the diffusion behaviour follows equations (111), (112) and (113) and \(T > T_c\), the corresponding equation is (115). The value of \(T_c\) is given by,
\[ T_c = (Q_B/R) / \ln(N_L/N_x) \]  \hspace{1cm} (116)

Thus the sudden change in the slope of the plots shown in Fig. 59 can be explained quite satisfactorily on the basis of the hydrogen trapping theory. Recent experimental work (Coe & Moreton, 1966; Newman & Shrier, 1969) shows that the diffusional behaviour of hydrogen in steels is affected by the composition and the structure of the material which is consistent with changes in trap density. This theory can also explain the large spread in the values of \(D_0\) (Table XVI) as due to differences in the trap density. The conclusions from the discussion are summarised in Table XVII.

**Table XVII. Effects of Hydrogen Concentration at the Trapping Sites on the Diffusion Parameters of Hydrogen in Steels.**

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Low ((N_L/N_x &lt;&lt; 1))</th>
<th>High ((N_L/N_x &gt;&gt; 1))</th>
<th>All Temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>Low ((T &lt; T_c))</td>
<td>High ((T &gt; T_c))</td>
<td></td>
</tr>
<tr>
<td>(T^°)</td>
<td>(D_0 L(N_L/N_x))</td>
<td>(D_0 L)</td>
<td>(D_0 L)</td>
</tr>
<tr>
<td>(D_0)</td>
<td>(Q_B + Q_D)</td>
<td>(Q_D)</td>
<td>(Q_D)</td>
</tr>
<tr>
<td>(Q)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
8.2.2. Treatment of Dislocation Sites as the Trapping Sites.

On a qualitative basis, we can divide the trapping sites produced by the presence of dislocations into two categories:

(i) Trapping sites on the dislocations all having the same trap depth ($Q_B$).

(ii) Trapping sites around the dislocations, whose trap depth ($Q_r$) varies inversely as the distance from the dislocations.

For a theoretical investigation, a simplified model in which only the sites on the dislocations may be considered to act as trapping sites. For such a simplified model, the trap density $N_x$, and the density of lattice sites $N_L$ are given by,

\[
N_x \propto \Lambda/b \\
N_L \propto 1/b^3 = 3.7 \times 10^{22}
\]

where $\Lambda =$ dislocation density

$b =$ Burgers vector

Table XVIII shows the effect of the various parameters on the values of $T_c$ and the ratio $D_o/D_{oL}$.

Table XVIII. Effect of changes in Dislocation Density and Binding Energy of Hydrogen to Dislocations on the Diffusion Parameters.

| Binding energy ($Q_B$, kcal/mole) | Dislocation density (/cm$^2$) | Trap density ($N_x$/c.c.) | Calculated values of
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Transition temperature ($T_c$, K)</td>
</tr>
<tr>
<td>8</td>
<td>$10^8$</td>
<td>$3.3 \times 10^{15}$</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>$2 \times 10^{10}$</td>
<td>$6.7 \times 10^{17}$</td>
<td>410</td>
</tr>
<tr>
<td></td>
<td>$10^{12}$</td>
<td>$0.3 \times 10^{19}$</td>
<td>570</td>
</tr>
<tr>
<td>7</td>
<td>$10^8$</td>
<td>$3.3 \times 10^{15}$</td>
<td>220</td>
</tr>
<tr>
<td></td>
<td>$2 \times 10^{10}$</td>
<td>$6.7 \times 10^{17}$</td>
<td>360</td>
</tr>
<tr>
<td></td>
<td>$10^{12}$</td>
<td>$3.3 \times 10^{19}$</td>
<td>500</td>
</tr>
<tr>
<td>6</td>
<td>$10^8$</td>
<td>$3.3 \times 10^{15}$</td>
<td>190</td>
</tr>
<tr>
<td></td>
<td>$2 \times 10^{10}$</td>
<td>$6.7 \times 10^{17}$</td>
<td>310</td>
</tr>
<tr>
<td></td>
<td>$10^{12}$</td>
<td>$3.3 \times 10^{19}$</td>
<td>430</td>
</tr>
</tbody>
</table>
If the trapping sites around the dislocations are also taken into account, the value of $T_c$ would go up and that of $D_o/D_{oL}$ would go down. Oriani's calculations on the experimentally measured values of the diffusion coefficient show that the dislocations alone cannot account for the number of trapping sites that seem to exist in steels.

For the specimens used in the present experimental work, $T_c \gg 300^\circ$K and $D_o/D_{oL} = 1.8 \times 10^5$ (for $Q = 7.5$ k cal/mole and $\Lambda = 2 \times 10^{10}$). Thus the value of the activation energy $Q$ obtained from the diffusion coefficient measurements, represents the sum of the binding energy ($Q_B$) and the activation energy for lattice diffusion ($Q_D$), as these measurements are made well below the temperature $T_c$.

8.3. Activation Energies for Bulk Diffusion, Lattice Diffusion and for the Cold Work Peak.

According to Schoeck's theory, the relaxation time $\tau$ is given by,

$$\tau = k_1 \left( \frac{T_c}{D} \right)$$

($k_1$ is a constant). Gibala (1967) has rewritten this formula as

$$\tau = k_1 \left( \frac{T_o}{D_o} \right) \exp \left( \frac{Q_D}{RT} \right)$$

Equation (119) assumes:

(i) The peak height $\delta_p$ is proportional to the concentration of hydrogen at the dislocations ($C_d$).

(ii) The diffusion coefficient ($D$) is given by

$$D = D_o \exp \left( -\frac{Q_D}{RT} \right)$$

where $Q_D$ = activation energy for diffusion of hydrogen in the undeformed lattice.

Assumption (i) above is justified because the experimental results show that the peak height ($\delta_p$) is proportional to the mean concentration of hydrogen (Section 8.1.), which in turn is proportional to the hydrogen concentration at the dislocations (at least at low concentrations - Appendix B). However, an inspection of the model shown in Fig. 61 shows that the barrier ($Q_{Di}$) to be overcome by an atom as it follows the moving dislocation is not equal to $Q_D$ (as assumed in equation (120)), the activation energy for hydrogen diffusion in the undeformed lattice. The values of $Q_{Di}$ for atoms jumping across the i'th barrier ($i = 0, 1, 2, \ldots$; Fig. 61) are given by,
Fig. 61. Model for the potential barrier for a hydrogen atom near a dislocation.
\[ Q_{D1} = Q_D - Q_B r_o a / \left[ (2r_o + 2a + a)(r_o + a) \right] \] (121)

where \( r_o \) = core radius of the dislocations

\[ a = \text{lattice constant}. \]

The following factors, however, indicate that the number of atoms jumping across the first barrier is very large compared to atomic jumps across other barriers:

(i) The number of atoms available for the jumps is maximum nearest to a dislocation (The number varies as \( \exp \left[ Q_B r_o / (R T r) \right] \), \( r \) = distance from the dislocations, and the angular factor is discounted).

(ii) The probability of a jump for these atoms is higher because the barrier across which they jump is lower.

(iii) Change in binding energy, which is responsible for the upsetting of the equilibrium distribution of the impurity atoms and inducing the jumps, varies inversely as the square of the distance from the dislocation for small displacements of the dislocation; hence the atoms far away from the dislocation are hardly affected by the movement of the dislocations during internal friction measurements.

The effective average value of \( Q_{D1} \) over all the atomic jumps may, therefore, be replaced by \( Q_{D1} \), i.e., the height of the first barrier. Thus we may use

\[ D = D_o \exp(-Q_{D1}/RT) \] (122)

in place of equation (120), the value of the activation energy \( Q_{D1} \), obtained from the plots shown in Fig. 62 and Fig. 63 is nearly equal to \( Q_{D1} \). In section 8.2, it has been shown that the activation energy for bulk diffusion \( Q \), which is available experimentally (section 8.1.), is given by,

\[ Q = Q_B + Q_D \] (113)

* This equation assumes that \( D_o \) value is not affected in the vicinity of a dislocation; strictly speaking this assumption is not true, but the replacement of \( D_o \) by a modified value, \( D_o' \), has no effect on the value of slope of plots in Fig. 62 and 63 and hence no effect on any of the activation energies.
Fig. 62. Plot of log (peak height x peak temperature) vs reciprocal of peak temperature for the hydrogen cold work peak in 3% nickel-iron alloys (slow cooled specimen)
Fig. 63. Plot of log (peak height x peak temperature) vs reciprocal of peak temperature for the hydrogen cold work peak in 3% nickel-iron alloys (water quenched specimen).
Likewise, an experimental value of \( Q_{D_1}^- \) is also available from plots such as those shown in Fig. 62 and 63. Since equations (121) and (113) are now simultaneous equations with only two unknowns, \( Q_B \) and \( Q_D \), these can be calculated for different values of \( i \); the results are given in Tables XIX and XX, which show that reasonable values of \( Q_D \) and \( Q_B \) are obtained if \( Q_{D_1}^- \) is assumed to be equal to \( Q_{D_1}^- \).

In conclusion it may be pointed out that, from the experimental results such as those performed in the present work, one can determine the binding energy \( (Q_B) \), the activation energy for hydrogen diffusion in the undeformed lattice \( (Q_D) \), the activation energy for bulk diffusion of hydrogen \( (Q) \) and the activation energy for the cold work peak \( (Q_{D_1}^-) \).

8.4. Peak Broadening.

For a given value of the activation energy, \( Q_{D_1}^- \), Schoeck's theory predicts a peak slightly broader than the corresponding single relaxation peak (Fig. 64). Cold work peak broadening has been reported by Sturges & Miodownik (1969); and Gibala (1967) has studied the broadening parameter \( (\beta) \) as a function of the level of cold work and the concentration of hydrogen (Fig. 3). However, experimentally determined cold work peak broadening has not been compared with that predicted by Schoeck's theory, by any of the research workers. Such a comparison is made in this section using experimental results from the present work and also by re-evaluating the earlier work of Gibala.

8.4.1. Construction of the Cold Work Peak based on Schoeck's model.

From Schoeck's theory (section 3.2.4.) we have:

\[
\omega \Gamma = k_1 C_d \exp \left( \frac{Q_{D_1}^-}{k_B T} \right) \tag{123}
\]

and

\[
\delta = (\pi \sqrt{2}/4) \int_0^\infty \left[ \tilde{\phi}(z)^5 \omega \Gamma / (1 + \omega^2 z^{1/2}) \right] dz \tag{67}
\]

where \( k_1 \) is a constant.

Using the property that the value of the integral in equation (67) is equal to 2.2 and \( \omega \Gamma = \omega \Gamma_p = 0.07 \) at the peak temperature \( T_p \), we can write.*

*The temperature variation of the concentration \( (C_d) \) of hydrogen at the dislocation is assumed to be negligible, while writing equation (124). The implications of this assumption will be discussed later in this section.
Fig. 64. Comparison of a cold work peak based on Schoeck's model with the corresponding single relaxation peak. (a) Based on Schoeck's model (b) Single relaxation peak.
Table XIX. Calculated values of the Binding Energy ($Q_B$) and the Activation Energy ($Q_D$) for diffusion in the undeformed lattice from experimentally determined values of the Activation Energies for Bulk Diffusion ($Q_B$) and for the Cold Work Peak for Slow Cooled Specimens. **

<table>
<thead>
<tr>
<th>$Q_{Di}^{-}$ (Experimental) (k cal/mole)</th>
<th>$Q$ (Experimental) (k cal/mole)</th>
<th>i</th>
<th>$Q_B$ (Calculated) (k cal/mole)</th>
<th>$Q_D$ (Calculated) (k cal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>9.0</td>
<td>0***</td>
<td>5.5</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>7.1</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>7.3</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>7.4</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>7.8</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Table XX. Calculated values of the Binding Energy ($Q_B$) and the Activation Energy ($Q_D$) for Diffusion in the undeformed lattice from experimentally determined values of the Activation Energies for Bulk Diffusion ($Q_B$) and for the Cold Work Peak for Water Quenched Specimens. **

<table>
<thead>
<tr>
<th>$Q_{Di}^{-}$ (Experimental) (k cal/mole)</th>
<th>$Q$ (Experimental) (k cal/mole)</th>
<th>i</th>
<th>$Q_B$ (Calculated) (k cal/mole)</th>
<th>$Q_D$ (Calculated) (k cal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>10.1</td>
<td>0***</td>
<td>6.0</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>7.9</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>8.1</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>8.2</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>8.6</td>
<td>1.5</td>
</tr>
</tbody>
</table>

** Values of $Q_B$ and $Q_D$ are calculated assuming $Q_{Di} = Q_{Di}^{-}$ for different values of i.

*** $i = 0$ involves a jump from the first lattice position to the core of the dislocation; such a jump is unlikely to occur, because under the reasonable assumption that impurity atoms at the core of the dislocation are not parted from the dislocation as it moves, there is no room for any more atoms trying to jump onto the core of the dislocation.
\[
\tau = 0.07 \exp\left(\frac{Q_{Di}}{RT}\right) / \left[ \omega_p^2 \exp\left(\frac{Q_{Di}}{RT_p}\right) \right]
\]  

(124)

and

\[
\delta = \frac{\gamma}{2} \int_0^\infty \left[ \exp(-z) z^5 \omega^2 (1 + \omega^2 z^2)^{1/2} \right] dz
\]

(125)

The calculation of the integral is carried out using \( \delta(z) = \exp(-z) \) for the distribution function; use of other functions in place of \( \exp(-z) \) is found to have little effect on the broadening of the peak; only the constants, 0.07 and 2.2, in equations (124) and (125), have to be replaced by other constants. The properties of the cold work peak discussed in this section are unaffected by such a change.

Knowing the values of \( Q_{Di} \) (from plots in Fig. 62 and 63) and the peak temperature \( T_p \), values of \( \tau \) can be calculated at any temperature \( T \) using equation (124); the corresponding values of the logarithmic decrement \( \delta \) can then be obtained from equation (125). Thus, using the experimentally determined values of the peak height and the peak temperature, the cold work peak based on Schoeck's model can be constructed. Such a construction has been used in section 8.4.2. to

(i) Compare the experimental results with those predicted from Schoeck's theory.

(ii) Determine the activation energy responsible for the cold work peak.

### 8.4.2. Comparison of Experimental Results with those obtained from Schoeck's Theory.

Gibala (1967) modified the expression for the relaxation time \( \tau \), using a temperature variation of the hydrogen concentration at the dislocations \( (C_d) \):

\[
C_d = C_L \exp\left(\frac{Q_B}{RT}\right)
\]

(126)

where \( C_L \) = concentration of hydrogen far away from the dislocations, and obtained,

\[
\tau = k_L C_L T \exp\left(\frac{Q_B + Q_D}{RT}\right)
\]

(127)

On this basis, Gibala concluded that the activation energy for the cold work peak to be equal to \( Q_B + Q_D \). Curve (c) in Fig. 65 shows the expected values of internal friction calculated from Schoeck's theory (as outlined in section 8.4.1), using \( \tau \) derived from equation (127), whereas curve (a) represents the experimental results. The overall agreement is rather poor*; the same

*Agreement at the peak temperature is only a consequence of the method of calculation of the theoretical values of internal friction.
Fig. 65. Comparison of the cold work peak based on Schoeck's model with experimental results of Gibala (1967) for hydrogen cold work peak in iron.
conclusion may be drawn from the corresponding plots for the present results (Curves (a) and (c) of Fig. 66).

This discrepancy can be explained in the following way. Gibala's use of equation (126) assumes an instantaneous redistribution of hydrogen atoms between dislocation sites and the lattice sites, while the temperature is increasing. For this to be true, hydrogen atoms will have to travel away from the dislocation, and a series of atomic jumps will have to follow before a new equilibrium distribution is reached. A good indication of how much redistribution is likely to occur can be obtained by calculating the time (t) required for an atomic jump; this time t is given by

\[ t \sim \frac{x^2}{D} \]

where \( D = D_0 \exp \left( \frac{Q}{RT} \right) \)

\( x \) = distance travelled by an atom during a jump (\( \sim 3 \AA \)).

As redistribution involves bulk diffusion, the appropriate value of \( Q \) is the activation energy for bulk diffusion. Table XXI shows that hardly any redistribution is expected to occur below the peak temperature, although an increasing amount of redistribution is likely at higher temperatures. Thus the assumption made in section 8.4.1., that the hydrogen concentration at the dislocations (\( C_d \)) does not vary appreciably up to the peak temperature, is confirmed.

Table XXI. Estimated times for single atomic jumps for hydrogen in deformed 3% nickel-iron alloy at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Time for single jump (second)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>( 3.5 \times 10^5 )</td>
</tr>
<tr>
<td>120</td>
<td>( 1.9 \times 10^2 )</td>
</tr>
<tr>
<td>125</td>
<td>( 4.3 \times 10 )</td>
</tr>
<tr>
<td>145</td>
<td>( 2.9 \times 10^{-1} )</td>
</tr>
<tr>
<td>150</td>
<td>( 1.1 \times 10^{-1} )</td>
</tr>
<tr>
<td>180</td>
<td>( 7.2 \times 10^{-4} )</td>
</tr>
</tbody>
</table>

The following conclusions may be drawn from the above analysis:
Fig. 66. Comparison of the cold work peak based on Schoeck's model with experimental results for the hydrogen cold work peak in 3% nickel-iron alloys.

Experimental values

Schoeck's model, \( Q = 1.3 \) k cal/mole

Schoeck's model, \( Q = 9.5 \) k cal/mole
(i) An activation energy for the cold work peak \((Q_{Di}^-)\) can be obtained by the plots shown in Fig. 62 and 63.

(ii) The values of the internal friction predicted by Schoeck's theory should agree with the experimental results best below the peak temperature (with activation energy \(Q_{Di}^-\)) and should then progressively deviate towards a theoretical curve with activation energy \((Q_{Di}^- + Q_B)\) above the peak temperature. Fig. 65 and 66 confirm the above results.

Above the peak temperatures, it is possible to calculate the apparent activation energy \((Q^*)\) for the cold work peak as a function temperature using Schoeck's theory. \(Q^*(T)\) will then vary from \(Q_{Di}^-\) (at \(T < T_p\)) to \(Q_{Di}^- + Q_B\) (at very high temperatures). Such a plot is a good indication of the extent of redistribution of hydrogen taking place during the measurement of internal friction (Fig. 67).

8.4.3. Re-examination of Peak Broadening.

Recalculation of the peak broadening parameter \((\beta)\) for Gibala's peak gives values of \(\beta = 0\) to 2 (assumed activation energy \(Q_{Di}^-\); Fig. 68) compared with \(\beta = 7\) (Fig. 4) for the activation energy \((Q_B + Q_{Di}^-)\) assumed by Gibala. Similar calculations on the present experimental results produce \(\beta = 12\) to 21 (Fig. 69) for activation energy \((Q_B + Q_{Di}^-)\) and \(\beta \approx 2\) (Fig. 68) for activation energy \(Q_{Di}^-\). Values of \(\beta = 0\) to 2 are consistent with the small peak broadening predicted by Schoeck's theory. A similar analysis on the high temperature side of the peaks is complicated by the fact that the measured internal friction is affected by the redistribution of hydrogen in the specimen. This can even lead to the apparent breadth of the peak on the high temperature side to be less than that of the corresponding single relaxation peak (i.e., \(\beta = 0\); Fig. 68) and in such a case the peak broadening parameter \(\beta\) is not defined.

8.5. Schoeck's model: Applicability and Modifications.

Certain restrictions laid down by Schoeck's model are reviewed in this section, and modifications are suggested for the theory to be applicable to the experimental results. The variation of the peak height with the concentration of hydrogen is also explained. In general there are a number of restrictions for the dislocations to be effective in contributing to the
III. 11.1

A Fe (Gibala's experimental results)

O 3% Ni-Fe
(scatter corresponds to ± 0.05 x 10⁻⁴ of logarithmic decrement).

Fig. 67. Effect of thermal redistribution of hydrogen on the apparent activation energy for the hydrogen cold work peak.
Fig. 68. Broadening of hydrogen cold work peak in iron and 3% nickel-iron alloys according to the new interpretation of Schoeck's model.
Fig. 69. Broadening of the hydrogen cold work peak in 3% nickel-iron alloys according to Gibala's (1967) interpretation of Schoeck's model.
cold work peak, and these restrictions may be broadly divided into two types:

(i) Restriction on loop lengths
(ii) Restrictions on the impurity concentration.

8.5.1. Critical Range of Active Dislocation Loop Lengths.

One of the conditions to be satisfied in order that a dislocation loop may give rise to cold work peak damping is that the maximum displacement of the dislocation, as it vibrates, is greater than the Burgers vector, b. If this condition is not satisfied, the use of Einstein's equation (equation (49), section 3.2.4.) in Schoeck's theory is not justified. The critical value \( l_c \) for the loop length can be obtained as follows. It is shown in section 3.2.4. that

\[
\alpha \left( \frac{\partial x}{\partial t} \right) - \beta \left( \frac{\partial^2 x}{\partial y^2} \right) = \sigma b \quad (55)
\]

The displacement \( x \) is maximum when \( y = 1/2 \), \( \sigma = \sigma_o \) and \( \partial x / \partial t = 0 \); using these conditions, we can write:

\[
x_{\text{max}} = \frac{\sigma_o b l^2}{(8\beta)}
\]

Substituting,

\[
\beta = \frac{Mb^2}{2} \quad \text{and} \quad \sigma_o = cM,
\]

where \( c \) = strain corresponding to the stress \( \sigma_o \)

\( M \) = Shear modulus

we obtain,

\[
x_{\text{max}} = \frac{c l^2}{4b}
\]

The condition to be satisfied,

\[
x_{\text{max}} > b
\]

yields,

\[
l^2 > \frac{4b^2}{c}
\]

i.e., the critical loop length \( l_c \) is given by

\[
l_c^2 = \frac{4b^2}{c}
\]

Dislocation loops shorter than \( l_c \) do not contribute to the cold work peak.

Using the values,

\[
c = c_s = 3 \times 10^{-5}
\]

\[
b = 2.9 \times 10^{-8} \text{ cm}
\]

\( (c_s = \text{surface strain of the specimen}) \)

equation (131) gives,
\[ l_c = 1.06 \times 10^{-5} \text{ cm (at the surface of the specimen).} \]

\[ l_c = 10^{-5} \text{ cm} \]

This means that dislocations on the surface of the specimen having loop lengths less than \( l_c \) do not contribute to the cold work peak damping.

The strain in the specimen is proportional to the distance from its geometric axis and therefore the value of \( l_c \) for dislocation loops at a distance \( r' \) from the axis of the specimen is given by,

\[ l_c^2 = \frac{4br}{(c r')} \quad (132) \]

where \( r = \text{radius of the specimen} \).

Thus the critical value of the loop length is inversely proportional to the square root of the distance from the axis of the specimen, approaching infinity at the axis of the specimen.

Summarising, we can conclude that there is a lower limit for the length of the dislocation loop to be effective in contributing to the cold work peak and this lower limit itself increases as we approach the axis of the specimen. As a consequence a larger number of dislocation loops would not contribute to the cold work peak.

(Dislocation loops having lengths less than the critical value, can however, contribute to damping through other mechanisms, probably giving rise to another peak (see section 3.2.5 for example) but not having the same peak temperature).

Equation (125), leading to the cold work peak height \( \delta_p \), theoretical \(^3\)

\[ \delta_p, \text{ theoretical} = 2.2 \pi \sqrt[4]{\frac{l_c^2}{2}} \quad (133) \]

is obtained by assuming that all the dislocation loops contribute to the cold work peak. However, typical values of \( \Lambda = 2 \times 10^{10} \), \( l_c = 1000 \) \( \% \) give a value for the peak height \( 500 \times 10^{-4} \), which is much higher than the experimentally observed peak heights. As shown above, not all dislocation loops contribute to the cold work peak and this accounts for most of the discrepancy; further effects also arise due to variations in the impurity concentration.

8.5.2. Dependence of the Cold Work Peak Height on the Impurity Concentration

For all the dislocation loops of length 1 to be effective in contributing to the cold work peak, two conditions regarding the impurity concentration...
The concentration of the impurity atoms responsible for the cold work peak must be above a critical value; otherwise the velocity of the moving dislocations will be so high that the impurity atoms are not able to follow the moving dislocations.

(ii) It is self evident that at least one impurity atom must be available for a moving dislocation loop to be effective.

The critical concentration referred to above can be estimated in the following way. The maximum force on a dislocation of loop length 1 due to the external stress is equal to $\sigma_o b l$. The binding between the atoms at the first lattice position (i.e., for $i = 1$ in Fig. 61) and the moving dislocation loop will be broken unless the force between the dislocation and the atoms is equal to at least $\sigma_o b l$.

For example,

$$\sigma_o b l \leq Q_x J N/(A_N b)$$

where $Q_x = Q_B r_o/(r_o + b/2)$

where $Q_x$ = binding energy of the atoms giving rise to cold work peak

$N$ = number of atoms at the first lattice positions (i.e., $i = 1$ in Fig. 61) per dislocation length = 1

$r_o$ = dislocation core radius

$Q_B$ = binding energy of the core atoms (in calories/mole)

$J$ = mechanical equivalent of heat ($4.2 \times 10^7$ ergs per calorie)

$A_N$ = Avogadro number

Rearranging equation (134) we have,

$$N \geq \frac{\sigma_o b^2 A_N l / (Q_x J)}{1}$$

(135)

The critical value $N_c$ is given by,

$$N_c = \frac{\sigma_o b^2 A_N l / (Q_x J)}{1}$$

(136)

$N$ may be calculated from the mean impurity concentration and depending on the value of $N$, one of the following types of behaviour for the dependence of the cold work peak height on the impurity concentration may be observed.

(a) When $N < N_c$: The dislocation loops of length 1 do not contribute to
the cold work peak height.

(b) When $N \gg N_c \gg 1$: In this case the value of $N$ satisfies both the conditions (i) and (ii) stated in the beginning of this section and therefore all the dislocation loops of length 1 contribute to the cold work peak height.

(c) When $1 \gg N \gg N_c$: This range of values of $N$ satisfies condition (i); however, on an average, less than one atom per dislocation loop of length 1 is available at the lattice positions adjacent to the dislocation (i.e., $l = 1$ in Fig. 61). This means that some of the dislocations of loop length 1 will have one impurity atom, whereas the others of the same loop length will have none, giving an overall average value of $N$ less than one. Thus a fraction of the dislocation loops of length 1 satisfy condition (ii) as well, and contribute to the cold work peak height. As the impurity concentration is increased, more of these dislocation loops acquire an impurity atom each and the peak height will increase.

The above analysis has to be applied to dislocations of different loop lengths (i.e., different values of $l$), to determine the total concentration dependence of the cold work peak height. A general analysis of this nature is very complicated, a simplified calculation can, however, be made because the contribution to the cold work peak height comes almost exclusively from dislocations of loop length around $l_o$. With this simplifying assumption, Schoeck's theory leads to,

$$\delta = (\pi l_o^3/8) \left[ \omega \sqrt{l_o/(1 + \omega^2 r^2)} \right] \rho (l_o)$$

(137)

where $\rho (l_o)$ = number of dislocation loops of length $l_o$ having at least one impurity atom in the lattice positions adjacent to the dislocation (i.e., $l = 1$ in Fig. 61).

and the peak height is given by,

$$\delta_p = (\pi l_o^3/8) \rho (l_o)$$

(138)

If all the dislocation loops of length $l_o$ contribute to the cold work peak (i.e., $N(l_o) \gg N_c (l_o) \gg 1$), the peak height will be independent of the impurity concentration, i.e., the peak will attain the saturation value. If only a fraction of the dislocation loops of length $l_o$ contribute to the cold work peak (i.e., $1 \gg N(l_o) \gg N_c (l_o)$) then the peak height will increase.
linearly with increase in impurity concentration, because addition of impurity atoms will render more dislocation loops of length \( l_0 \) effective, i.e., the value of \( \rho (l_0) \) in equation (138) will be increased.

8.5.3. Explanation of the Linear Dependence of the Hydrogen Cold Work Peak Height on Hydrogen Concentration.

A comparison of the experimental results between the present work (Table XXII) and that of Sturges (1969) indicates that the mean concentration of Table XXII. Comparison of the Present Experimental Conditions of Charging with those of Sturges (1969).

<table>
<thead>
<tr>
<th></th>
<th>Present Work</th>
<th>Work of Sturges</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Charging time (t)</strong></td>
<td>20 hours</td>
<td>100 minutes</td>
</tr>
<tr>
<td><strong>Radius of the specimen (r)</strong></td>
<td>27 thou</td>
<td>27 thou</td>
</tr>
<tr>
<td><strong>Diffusion coefficient of hydrogen at 300°C</strong></td>
<td>( 10^{-8} ) cm²/sec</td>
<td>( 10^{-6} ) cm²/sec</td>
</tr>
<tr>
<td><strong>Mean concentration of hydrogen</strong></td>
<td>Estimated 0.3 wt. ppm.</td>
<td>1 wt. ppm.</td>
</tr>
</tbody>
</table>

hydrogen in the specimen for the present work is 0.3 wt. ppm., if we assume that \( \sqrt{D t}/r \) can be used as a criterion for the calculation of the relative concentrations. The concentration \( C_d \) at the lattice positions adjacent to the dislocations (i.e., \( i = 1 \) in Fig. 61) is given by,

\[
C_d = C_L \exp \left( \frac{Q}{RT} \right) \approx 5 \times 10^{-3} \text{ for } C_L = 3 \text{ wt. ppm.}
\]

This is equivalent to about 3 atoms per dislocation loop of length \( l_0 \) (\( l_0 \) assumed equal to 1000 Å). The value will be much below this upper limit because:

(i) The value of \( C_L \) used in equation (139) should be much lower than the mean concentration of hydrogen (see Appendix B).

(ii) One can expect to have a large number of short dislocation loops at the grain boundaries, which take up a considerable amount of hydrogen. These
loops are too short to contribute to the cold work peak (section 8.5.1.).

If we allow for all these factors, we may expect the average number of hydrogen atoms per dislocation of length $l_0$ to be less than one. This would then account for the linear dependence of the cold work peak height on hydrogen concentration as explained in section 8.5.2.

8.6. The Effects of Carbon on the Hydrogen Cold Work Peak.

A comparison of the results of Gibala (1967) and Sturges & Miodownik (1969) with those from the present work allows the effects of carbon on the cold work peak of hydrogen to be discussed. Apparent contradictions in the behaviour of the hydrogen cold work peak, as reported by various research workers can then be explained as due to the effect of impurities other than hydrogen.

The presence of carbon can affect the hydrogen cold work peak in three ways.

(i) Changes demanded by Schöck's model due to the presence of carbon.

(ii) Changes in the distribution of hydrogen between the dislocation sites and the interstitial sites away from the dislocations, brought about by the filling up of the dislocation sites by carbon atoms.

(iii) Various indirect effects due to precipitation of carbon, interaction between hydrogen and carbon, and strain relief due to the presence of carbon atoms at the dislocation sites.

These effects will now be discussed in some detail. At the hydrogen cold work peak temperature, carbon atoms are immobile and therefore act as pinning points on the dislocations. If the concentration of carbon atoms is such that the mean distance between the carbon atoms on the dislocations is less than the mean distance between the points of intersection of dislocations, the mean loop length $l_0$ is controlled by the carbon concentration. Assuming $10^{-2}$ weight percent of carbon concentration is sufficient for the dislocations to be saturated in specimens having a dislocation density of about $2 \times 10^{10}$ per cm$^2$, the distance between carbon atoms on the dislocations, for lower concentrations at equilibrium are given in Table XXIII (columns 2 and 3).

Due to the high carbon concentration in the specimens used by Sturges & Miodownik (1967), three days of room temperature ageing after cold work
Table XXIII. Distance between Carbon Atoms on the Dislocations, assuming Equilibrium Distribution.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Concentration of carbon (wt. percent)</th>
<th>Distance between carbon atoms on the dislocations (for $\Lambda = 2 \times 10^{10} \text{/cm}^2$)</th>
<th>Mean loop length assumed by the authors.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sturges &amp; Miodownik (1969)</td>
<td>0.018</td>
<td>$b$ (i.e., dislocations saturated with carbon atoms).</td>
<td></td>
</tr>
<tr>
<td>Gibala (1967)</td>
<td>0.004</td>
<td>2 to 3 $b$</td>
<td>3000 $b$</td>
</tr>
<tr>
<td>Present work</td>
<td>0.002</td>
<td>5 $b$</td>
<td>345 $b$</td>
</tr>
</tbody>
</table>

would bring the concentration of carbon at the dislocations to near equilibrium value ($\sqrt{b}$), shown in Table XXIII. Under these conditions, the mean loop length appropriate to the Schoeck's theory is $\sqrt{b}$. Schoeck's theory for long loop lengths, as described in section 3.2.4, is therefore not applicable, because the displacements of the loops, during the measurement of internal friction, will be much smaller than $b$, the Burgers vector. The appropriate model applicable here is that for small displacements of dislocation, and the peak observed is due to atomic jumps of hydrogen in response to the oscillating dislocations as explained in section 3.2.5.

Another effect to be considered in this context is the non-availability of dislocation sites for the hydrogen atoms, as most of the sites are occupied by carbon atoms, before the introduction of hydrogen. In this situation, hydrogen forming atmospheres round the dislocations may be bound to the carbon atoms already present at the dislocations. Thus a cold work peak may occur due to the mechanisms similar to those suggested by Mura et al. (1963, section 3.2.3) or Ino & Sugeno (1967, section 3.2.6).

The concentration of carbon used in the present work is very small.
compared to that used by Sturges and Miodownik. Thus ageing at room
temperature for three days after cold work will not have much effect and one
can assume that only a very small percentage of the carbon atoms goes to the
dislocations. Three experimental facts may be produced to support this
proposition:

(i) Experimental work conducted on a specimen similar to those used by
Sturges and Miodownik (1969) showed that, in specimens used without three
days of room temperature ageing, the peak observed is very unstable.

(ii) Deliberate introduction of carbon into relatively pure specimens
showed behaviour similar to that reported by Sturges & Miodownik (see section
6.4.2.)

(iii) The height of the additional carbon peak at 216°K, for relatively
pure specimens (low carbon concentration), did not change appreciably by room
temperature ageing, whereas for carburised specimens, the peak height
decreased considerably by room temperature ageing. This supports the idea
that there is no appreciable redistribution of carbon atoms between the
dislocation sites and the interstitial sites, due to drift of carbon atoms
towards dislocations, when the carbon concentration is low.

These experimental results may also be supplemented by the theoretical
prediction of Cottrell's theory, that the rate of increase of impurity
concentration at the dislocations is proportional to the concentration in
solid solution.

The above arguments indicate that in the case of alloys used in the
present experiments, the distance between the carbon atoms is not the
controlling factor in determining \( l_0 \), the mean loop length. Therefore this
has been calculated by assuming a regular network of dislocations, giving
\( l_0 = 1000 \) Å as a reasonable estimate for the mean dislocation loop length for
the present work. Any interaction between hydrogen and carbon atoms is
bound to affect the behaviour of the cold work peak, but the effect of the
introduction of carbon on \( l_0 \) may be assumed to have the largest effect.

Thus it may be concluded that, for iron alloys with high carbon
concentration, Schoeck's theory for long dislocation loops discussed in
section 3.2.4, is not applicable to the hydrogen cold work peak, and the
peak temperature variation with hydrogen concentration is therefore expected to be different in such alloys; this conclusion is confirmed by experimental results.

8.7. Effect of Cooling Rate.

A comparison of the experimental results shows that the initial height of the hydrogen cold work peak in water quenched specimens is slightly less than that in the slow cooled specimens* (Fig. 37 and 38). This is consistent with the higher $D_0$ and $Q$ values for hydrogen in the water quenched specimens (Table XV). These differences may be attributed to the effects due to changes in the dislocation structure (either dislocation geometry or dislocation density or both), brought about by rapid cooling. The values of the parameters connected with hydrogen diffusion and hydrogen dislocation interaction, shown in Table XXIV are only marginally affected. The

Table XXIV. Comparison of Binding Energies to Dislocations ($Q_B$), Activation Energies for Bulk Diffusion ($Q$), for Diffusion in Undeformed Lattice ($Q_{Di}^-$), and for the Cold Work Peak ($Q_D$) for Hydrogen in Slow Cooled and Water Quenched Specimens (3% Ni-Fe).

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$Q_B$ (in k cal/mole)</th>
<th>$Q$ (in k cal/mole)</th>
<th>$Q_{Di}^-$ (in k cal/mole)</th>
<th>$Q_D$ (in k cal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slow cooled</td>
<td>7.1</td>
<td>9.0</td>
<td>1.1</td>
<td>1.9</td>
</tr>
<tr>
<td>Water Quenched</td>
<td>7.9</td>
<td>10.1</td>
<td>1.5</td>
<td>2.2</td>
</tr>
</tbody>
</table>

The significance of such slight differences really requires more detailed experimental results than are available in the present study. It seems sufficient to indicate for the present that the cooling rate is not a vital factor despite some differences in the morphology (Fig. 70).


In this section an attempt is made to determine the mechanism responsible

* The cooling rate refers to the one at the end of the final anneal at 1000°C in an inert atmosphere. Slow cooled specimens are cooled inside the furnace, and the fast cooled ones are water quenched.
Fig. 70. Microstructure of 4% deformed 3% Ni-Fe alloys.

(a) Slow cooled  (b) Water quenched.  \textit{MAG.} x 250.
for the occurrence of the 216°K peak, previously described in section 6.5.


In section 6.5.3, it has been shown that the height of the 216°K peak increases linearly with the mean carbon concentration. The room temperature ageing of this peak can be explained with the following assumptions.

(i) The peak height is proportional to the fraction of carbon atoms in solid solution, i.e.,

\[ \frac{\delta_p}{\delta_p^0} = \frac{1}{1 - W(t)} \]  

where \( \delta_p^0 \) = initial peak height
\( \delta_p \) = peak height after time \( t \) of room temperature ageing
\( W(t) \) = fraction carbon atoms drifted to the dislocations by the end of the period of ageing \( t \).

(ii) The ageing behaviour follows Harper's (1951) empirical law:

\[ W(t) = 1 - \exp(-k_H t^{2/3}) \]  

where \( k_H \) is a constant.

Eliminating \( W(t) \) from equations (140) and (141) and taking logarithms twice, we obtain,

\[ \log \ln \left( \frac{\delta_p}{\delta_p^0} \right) = \log k_H + (2/3) \log t \]  

which explains the slope of 2/3 obtained in Fig. 71 for low values of \( t \); for higher values of ageing time \( t \), Harper's equation (141) is not obeyed and consequently the value of the slope deviates from 2/3. Thus the ageing behaviour of the 216°K peak can be explained satisfactorily as due to the depletion of carbon concentration in solid solution.

8.8.2. Effects of Hydrogen on the 216°K Peak.

As explained in section 6.5.5, introduction of hydrogen removes the 216°K peak and the eventual recovery of the peak occurs long after the disappearance of the hydrogen cold work peak (Fig. 46 (a) and (e)). These effects may be explained on the basis of a strong interaction between hydrogen and carbon atoms; evidence for the existence of such an interaction may be obtained from a study of yield point phenomena in these alloys (see section 4.4.1.). This interaction between hydrogen and carbon atoms would certainly curtail the movement of carbon atoms and may even inhibit the mechanism responsible for the occurrence of the peak; in any case, the peak height is expected to
Fig. 71. Relationship between the height of the 216K peak and the time of room temperature ageing in 3% nickel-iron alloys.
The delay in the recovery of the 216°K peak after the disappearance of the hydrogen cold work peak suggests that hydrogen atoms in the vicinity of the carbon atoms do not diffuse out of the specimen as fast as those bound to the dislocations.

8.8.3. Conclusions.

Peaks due to stress induced ordering of carbon atoms in the vicinity of nickel atoms in iron-nickel alloys with both B.C.C. and B.C.T. structures have already been identified (Table IX); experiments conducted by Wert (1952) show that such a peak is unlikely to occur in these alloys with B.C.C. structure (section 5.2.). Furthermore the fact that the 216°K peak is observed both in B.C.C. and F.C.C. structures at the same temperature, rules out the possibility of this peak being a peak due to stress induced ordering of carbon atoms in the vicinity of nickel atoms in the alloys with B.C.C. structure. As the peak height increases with an increase in the carbon concentration, this peak cannot be similar to any of those reported by Bordoni (1949; Niblett, 1966), Hasiguti (1953) or Niblett & Wilks, because increase in the impurity concentration always decreases the peak height in these cases. Out of the several other mechanisms that are available in literature, some of the likely ones are peaks due to precipitates, clusters of impurity atoms or due to the stress induced ordering of interstitial atom - vacancy pairs in the vicinity of substitutional atoms. The role of cold work in increasing the height of this peak may then be one of the following, depending on the mechanism of the peak:

(i) Increase in the dislocation density.

(ii) Tearing away of dislocations from the carbon atoms, enhancing the number of carbon atoms in solid solution.

(iii) Increase in the number of vacancies.

The 216°K peak was not the main object of the investigation, and the limited number of experiments conducted here are not sufficient to understand either the full significance of the effects of hydrogen or the mechanism
responsible for the occurrence of the peak itself, despite a number of interesting properties obtained from such experiments (summarised in section 6.5.6.).

The following conclusions may be drawn from the present study of the hydrogen cold work peaks in iron alloys.

1. The height of the hydrogen cold work peak is proportional to the mean concentration of hydrogen.

2. The peak temperature increases with peak height in carbon free iron and iron-nickel alloys, but this peak temperature variation decreases markedly with the addition of carbon atoms.

3. The total behaviour of hydrogen cold work peaks in iron alloys closely follows the model proposed by Schoeck (1963). Discrepancies reported by various research workers, in the peak temperature variation can be largely attributed to differences in the carbon concentration of the various specimens used.

4. Measurements of the hydrogen cold work peak height with thermal cycling experiments have been used to calculate the hydrogen diffusion coefficients at different temperatures and yield activation energies for bulk diffusion ($9.5 \pm 1$ k cal/mole), for diffusion in undeformed lattice ($2.0 \pm 0.5$ k cal/mole), for the hydrogen cold work peak ($1.3 \pm 0.5$ k cal/mole) and the binding energy of hydrogen to dislocations ($7.5 \pm 0.5$ k cal/mole).

5. Measurements of diffusion coefficients of hydrogen using mass spectrometer confirm that the decrease in the hydrogen cold work peak height during thermal cycling experiments is due to the diffusion of hydrogen out of the specimen. The diffusion coefficients measured by this method agree with those calculated from cold work peak height measurements.

6. Detailed consideration of the mechanism for the cold work peak leads to values of the peak broadening of about 0-2, which gives further confirmation of the validity of Schoeck's theory. With this new approach to the mechanism for the cold work peak, higher values of peak broadening parameter, previously reported by Gibala have been re-interpreted, and shown to fall in the same range, 0-2.
7. The cooling rate of the specimen at the end of the final anneal is found to have little effect on the main characteristics of the hydrogen cold work peak.

8. A hitherto unreported peak has been detected at 216°K in iron-nickel-carbon alloys. The height of this peak is sensitive to nickel and carbon concentration, amount of cold work and room temperature ageing.

9. A study of the 216°K peak in hydrogen charged iron-nickel-carbon alloys indicates that there is a strong interaction between carbon and hydrogen atoms in these alloys.
10. Suggestions for Future Work.

1. The present series of experiments on the hydrogen cold work is carried out with constant cold work; it would be interesting to see if the same conclusions can be drawn from a similar study with varying amounts of cold work.

2. The present work is largely restricted to hydrogen cold work peak measurements on 3% Ni-Fe alloys; an extension of this work to alloys containing different amounts of nickel and carbon may be used to study the effects of substitutional and interstitial impurities on various parameters connected with the diffusion of hydrogen in these alloys. However, the ranges of nickel and carbon concentration are limited, due to the occurrence of F.C.C. structure at higher nickel and carbon contents.

3. Although Schoeck's theory has been explored in detail, no comparable theoretical study on the basis of Küster's model has been carried out. Such a study with reasonable assumptions as to the nature of atomic jumps, may be carried out to determine the expected variation of peak temperature with peak height. It would be interesting to compare the experimental peak broadening with that predicted by Küster's model.

4. A theoretical study of the effect of the redistribution of hydrogen while the specimen is being heated can be used to verify quantitatively the present ideas about the broadening of the hydrogen cold work peak; the present work deals with the limiting cases, namely instantaneous redistribution of hydrogen and frozen state.

5. A great deal of work remains to be done on the 216° peak; a study of this peak with respect to changes in nickel concentration, carbon concentration, cold work, heat treatment and ageing treatment may lead to a better understanding of the mechanism responsible for the occurrence of the peak.

6. It would also be interesting to measure the height of the 216°K peak, while the specimen is cooling from room temperature, to determine whether the peak is due to some sort of structural transformation rather than a relaxation process.
Appendices

Appendix A. Graphical method for the calculation of the Effective Time of Ageing.

When a specimen is to be aged at a temperature $T_M$, it has to be heated to that temperature, to begin with. A time $t^*$ at $T_M$, equivalent to the time spent at different temperatures while the specimen is being heated, can be calculated in the following manner.

It can be shown (Crank, 1956) that,

$$t^* = \int_0^{t'} D(T) \, dt$$

(Al)

where $D(T_M) = \text{diffusion coefficient at } T_M^K$

$D(T) = \text{diffusion coefficient at } T^K$

$t = \text{time at which the temperature is } T^K$

$t' = \text{total time of ageing.}$

Equation (Al) is valid only if

(i) The ageing process under consideration is diffusion controlled

(ii) The diffusion coefficient can be written as a function of time only.

For the present case of diffusion of hydrogen, we can write,

$$D(T_M) = D_0 \exp \left( -\frac{Q}{RT_M} \right)$$

and

$$D(T) = D_0 \exp \left( -\frac{Q}{RT} \right)$$

where $D_0 = \text{constant}$

$Q = \text{activation energy for bulk diffusion}$

$R = \text{universal gas constant}$

The temperature $T$ can be recorded as a function of time from experimental observations, and therefore, the diffusion coefficient can be treated as a function of time only. Thus equation (Al) is applicable to the present case; i.e.,

$$D_0 \exp \left( -\frac{Q}{RT_M} \right) \, t^* = D_0 \int_0^{t'} \exp \left( -\frac{Q}{RT} \right) \, dt$$
Fig. A1. A plot for the calculation of the effective time of ageing for a typical ageing cycle.

(Area under the curve is the effective time of ageing at $T_M$ K.)
\[ t^* = \int_0^t \exp \left[ \frac{Q}{RT_H} - \frac{Q}{RT} \right] \, dt \quad (A2) \]

Analytical solution of the above equation is impossible except in special cases (Armstrong, 1958). Temperature readings taken during the heating up of the specimen can be used to obtain a graphical solution for \( t^* \). A typical plot of \( \exp \left[ \frac{Q}{RT_H} - \frac{Q}{RT} \right] \) vs time is shown in Fig. A1. The area under the curve gives \( t^* \), the effective ageing time. Using the temperature readings taken during the ageing treatment, numerical calculation of the integral in equation (A2) can be carried out using a computer. In the present work, such a calculation is incorporated in the programme developed for the calculation of the activation energy \( Q \) for bulk diffusion (see section 8.1.3. and Fig. 56).
Appendix B. Relationship between the Moan Concentration, Concentration at the Interstitial Sites and the Concentration at the Dislocation Sites.

The presence of dislocations in a metal increases the overall solubility of impurity atoms. Under thermal equilibrium, stable concentration gradients are set up inside the metal, and there is a relationship between the lattice concentration $C_L$, the mean concentration $\bar{C}$ and the concentration at the dislocation sites $C_d$. However, it is impossible to solve this problem for a real metal because,

(i) The geometrical arrangement of the dislocations cannot be specified unambiguously, and some sort of assumptions have to be made about the arrangement of dislocations.

(ii) The nature of the dislocation impurity atom interaction is not completely understood.

(iii) Analytical solutions cannot be obtained without making some simplifying assumptions.

Nevertheless, it is worthwhile examining a method whereby approximate values may be obtained.

**Assumed Model.**

(1) The operative dislocation sites are assumed to be at a distance $r_0$ ($\approx 2 \bar{R}$) from the core of the dislocations, these being the positions corresponding to the maximum binding energy ($Q_B$); a similar model (Fig. B1) has been used by Bullough & Newman (1959).

(2) An effective radius of influence ($R_e$) around a dislocation is defined in such a way that a cylinder of this radius surrounding the dislocations covers the whole volume of the metal. From Fig. B2, it is obvious that, for a length $\Lambda$ of dislocation line per unit volume,

$$\pi R_e^2 = \Lambda$$

i.e.,

$$R_e = \frac{1}{\sqrt{\pi \Lambda}} \quad (B1)$$

This method of calculation makes $R_e$ independent of the dislocation structure.
Fig. B1. Model of the potential barriers for a hydrogen atom around an edge dislocation.
Fig. B2. Schematic diagram showing the positions of the dislocation sites and the radius of influence.
(Re – radius of influence, r₀ – dislocation core radius, Λ – dislocation density).
and depend only on the dislocation density $\Lambda$. However this would lead to overlap of the volumes of influence of different dislocations at some places, whereas at other places some volumes are not covered by any dislocations at all; the net effect on the estimated concentrations due to these errors may be assumed to be negligible. (Interaction between dislocations is taken into account to the extent that the effect of any dislocation is assumed to be zero beyond a distance $R_e$ from the core of the dislocations).

(3) The effect of other defects is assumed to be negligible.

(4) The binding energy $Q_\tau$ of impurity atoms is assumed to be inversely proportional to the distance from the dislocation and the angular variation is neglected, i.e.,

$$Q_\tau = Q_B r_0 / r \quad (B2)$$

More accurate calculations can be made taking into account the angular variation of the binding energy, but the calculations would then involve a more complicated double integration.

(5) The concentration at the dislocation sites is given by,

$$C_d / (1 - C_d) = C_L \exp(Q_B / RT) \quad (B3)$$

i.e.,

$$C_d = C_L \exp(Q_B / RT) / \left[ 1 + C_L \exp(Q_B / RT) \right] \quad (B4)$$

where $C_L =$ concentration of the impurity atoms far away from the dislocation core (i.e., the lattice concentration) $T =$ temperature on the absolute scale.

Calculations.

The number $dN_\tau$ of sites contained between cylinders of radii $r$ and $r + dr$ surrounding the dislocations is given by

$$dN_\tau = (2\pi r \, dr) \Lambda (1/b_3^3) \quad (B5)$$

assuming the distance between the sites to be $b$ (the Burgers vector). Of these, if $d_n_\tau$ is the number of filled sites, the concentration of solute atoms (in atomic fraction) $C_\tau$ is given by,
Fig. B3. Effect of changes in the dislocation density and the binding energy between the dislocations and the impurity atoms on the mean concentration ($\bar{c}$) and the concentration at the dislocation sites ($c_d$) (Numbers on the curves refer to the dislocation density).
Fig. B4. Effect of temperature variation and the mean concentration ($\bar{C}$) and the concentration at the dislocation sites ($C_d$) for impurity atoms. (Numbers on the curves refer to the binding energy in k cal/mole).
Fig. B5. Dependence of the mean concentration (\( \bar{C} \)) and the concentration at the dislocation sites (\( C_d \)) on the impurity concentration at the undeformed lattice (\( C_L \)).
An equation similar to (B4) can be written for $C_r$:

$$C_r = \frac{d n_r}{dn_r}$$

(B6)

$$C_r = \frac{C_L \exp(Q_r/RT)}{\left[1 + C_L \exp(Q_r/RT)\right]}$$

(B7)

Using equations (B5), (B6) and (B7), we can write for the total number $n_r$ of impurity atom per unit volume as,

$$n_r = \int_{r_0}^{R_0} 2\pi r dr \left(\frac{A}{b^2}\right) \frac{C_L \exp(Q_r/RT)}{\left[1 + C_L \exp(Q_r/RT)\right]}$$

(B8)

and the total number of available sites per unit volume is given by,

$$N_r = \int_{r_0}^{R_e} dN_r$$

Substituting for $dN_r$ from equation (B5), the above equation can be simplified:

$$N_r = \frac{\pi A}{b^2} \left(R_o^2 - r_o^2\right)$$

(B9)

The mean concentration $\bar{C}$ is given by,

$$\bar{C} = \frac{n_r}{N_r}$$

Using equations (B2), (B8) and (B9) this may be further simplified,

$$\bar{C} = \frac{C_L}{(R_o^2 - r_o^2)} \int_{r_0}^{R_o} r \exp(Q_B r_o/\left[RT\right]) \left[1 + C_L \exp(Q_B r_o/\left[RT\right]\right] dr$$

(B10)

with $R_e$ given by equation (B1). Thus, the ratio of mean concentration to lattice concentration may be calculated by graphical integration from a knowledge of the binding energy ($Q_B$), the dislocation density ($A$) and the temperature ($T$) for any value of $C_L$, the lattice concentration. When the solute concentration is low, so that the concentration at the dislocation sites is small compared to unity, equation (B3) can be rewritten as,

$$C_d = C_L \exp(Q_B/RT)$$

(B11)

and equation (B10) simplifies to

$$\frac{\bar{C}}{C_L} = \left(R_e^2 - r_o^2\right)^{-1} \int_{r_o}^{R_o} \left\{r \exp(Q_B r_o/\left[RT\right]\right\} dr$$

(B12)
The ratio of $\bar{C}$ to $C_L$ is independent of $C_L$ in this case, whereas the accurate value of this ratio, given by equation (B10), is dependent on $C_L$, the lattice concentration.

Figures (B3), (B4) and (B5) show the variation of the ratios $\bar{C}/C_L$ and $C_d/C_L$ for some typical values of the various parameters involved. Furthermore, figures (B4) and (B5) illustrate that the approximate equation (B11) gives vastly erroneous results, if used for near saturation concentration of the solute atoms at the dislocation sites.
Appendix C. List of Computer Programmes Developed.

(1) Least square analysis for straight lines, giving estimates of errors in slope and intercept, and correlation coefficient; graph plotting programme to draw the points and the line corresponding to the least square analysis fit.

(2) Calculation of logarithmic decrement from measured values of initial and final values of the amplitude of torsional oscillation; graph plotting programme to plot logarithmic decrement vs temperature.

(3) Programme to calculate and plot normalised logarithmic decrement as a function of $x : [ = (Q/2.303)/(1/T - 1/T_p) ]$.

(4) Calculation and tabulation of $f_2(x, \beta)/f_2(0, \beta)$ as a function of $x$ for different values of $\beta$, using the following equation:

$$f_2(x, \beta) = (2\sqrt{\pi})^{-1} \int_{-\infty}^{+\infty} \exp(-u^2) \text{sech}(x + u\beta) \, du \quad (C1)$$

(5) Calculation of $\beta$, the peak broadening parameter, as a function of temperature $(T)$, for given values of the logarithmic decrement $(\delta_p)$, the peak height $(\delta_p)$, the peak temperature $(T_p)$, and the activation energy $(Q)$, using equation (C1) and

$$\frac{\delta_p}{\delta_p} = \frac{f_2(x, \beta)}{f_2(0, \beta)}$$

$$x = (Q/R)(1/T - 1/T_p)$$

(6) Calculation and tabulation of Schoeck integral $(I)$ as a function of $\omega T$,

$$I = \int_0^\infty \tilde{p}(z) \, z^5 \omega T \left[ 1 + (\omega T)^2 z^2 \right] \, dz$$

for

$$\tilde{p}(z) = \exp(-z)$$

and

$$\tilde{p}(z) = (k/\pi^2) \exp(-k^2z^2)$$
(7) Calculation of logarithmic decrement values as a function of temperature, for the cold work peak based on Schoeck's model, for different values of the peak temperature, peak height, and activation energy.

(8) Iterative method for the calculation of the activation energy for bulk diffusion using cold work peak measurements (see Fig. 56).

(9) Calculation of the amount of hydrogen diffused out of the specimens at any given temperature, using mass spectrometer readings (see section 7.2.2.).

(10) Tabulation of the mean concentration (C) and the concentration at the dislocation sites (C_a) for impurity atoms, as a function of the dislocation density (Λ), binding energy (Q_B), temperature (T) and the lattice concentration (C_L). (See Appendix B).
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