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Magnetic after-effects in dilute transition metal alloys

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MAGNETIC AFTER-EFFECTS IN
DILUTE TRANSITION METAL ALLOYS

BY
ROBERT HENRY GRAHAM, 1944

A
THESIS
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(advisor)
ABSTRACT

Temperature dependent after-effects of the initial permeability in ternary dilute ferromagnetic iron-base alloys were studied in the temperature range of -50°C to +30°C. Interstitial carbon and nitrogen were the diffusing elements. Nominal percentages of the substitutional transition elements manganese, chromium, vanadium and titanium were added to determine the extent of substitutional-interstitial pair interactions. No additional temperature dependent after-effect of the initial permeability was noticed in Fe-substitutional -C alloys, while such after-effects were present in Fe-substitutional -N alloys. Magnetic after-effect data were analyzed on the basis of single Debye relaxations. Relaxation times for carbon and nitrogen diffusion in alpha-iron were calculated using activation energies of 20,100 cal/mole and 17,700 cal/mole, respectively. Magnetic after-effect data were discussed on the basis of additional strain components and electronic interactions caused by the variation of the substitutional element. It was concluded that electronic interactions cause the extra disaccommodation in Fe-substitutional -N alloys while the larger lattice distortion around carbon renders the
influence of the substitutional on the interstitial mobility ineffective.
ACKNOWLEDGMENT

The author wishes to respectfully acknowledge the competent and ever-available assistance given to him by his research advisor, Dr. Manfred Wuttig, throughout this investigation.

Recognition is also given to the Department of Metallurgical Engineering and the Alcoa Foundation for financial assistance.
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I. INTRODUCTION AND LITERATURE REVIEW

It has been proven many times that small percentages of carbon or nitrogen in iron and iron alloys have a marked effect on mechanical (1) and magnetic (2) properties of the material. Mechanical effects are observed by the application of a constant stress and subsequent analysis of the associated strain. It is found that there is an instantaneous strain followed by a time-dependent strain termed the mechanical after-effect. Similarly, the application of a magnetic field causes an instantaneous change of the induction followed by a time-dependent induction change termed the magnetic after-effect. Snoek (3)(4)(5), in 1941, gave the first explanation of mechanical and magnetic after-effects on an atomic basis. He assumed the basis of both types of after-effect to be the non-cubical surrounding of the sites on which the interstitials can reside.

In the absence of an external stress, the unit cell of bcc iron as shown in fig. 1 contains three crystallographically and energetically equivalent interstitial sites (points x, y, and z). In this condition, and if interstitial-interstitial interactions can be neglected, which is valid for low concentration solid solutions of carbon or nitrogen in iron, then interstitials will be equally
Figure 1

Iron bcc unit cell with three energetically and crystallographically equivalent interstitial octahedral sites.
○ IRON ATOMS
○ INTERSTITIAL ATOMS
distributed among the octahedral sites. However, upon the application of a non-hydrostatic stress, the dimensions of the unit cell will change and destroy cubic symmetry. The lack of cubic symmetry destroys the crystallographic and energetic equivalence of the interstitial sites so that in equilibrium, the distribution of interstitials is no longer homogeneous.

Consider an iron single crystal under a constant [100] dilatory stress. As the ionic radii of carbon and nitrogen are larger than the radius of a sphere inscribed in an octahedral site (6), a strain energy argument would predict that interstitials would, in equilibrium, preferentially reside on x-sites. As the constant stress is removed, the mobile interstitials will equally redistribute themselves among the x-, y- and z-sites, which will result in an elastic and an anelastic strain recovery. (Fig. 2) The anelastic strain is the result of the contraction of the x-sites no longer occupied by interstitials and is positive for dilatory stress and negative for compressive stress. The anelastic strain reaches a maximum as the equilibrium distribution of interstitials among x-, y- and z-sites is reached.

Similar to the strains caused by mechanical stress applications are dimensional changes caused by the application of a magnetic field. This change is termed magnetostriction. In a ferromagnetic material such as iron or
Figure 2

Strain versus time for an anelastic specimen. Load is applied at $t_1$ and removed at $t_2$. 
its alloys, there is a spontaneous magnetization and magnetostriction present even without an externally applied magnetic field. This spontaneous magnetization and magnetostriction is caused by the coupling between unpaired electrons in the outermost shells of neighboring atoms \(^\text{(7)}\). The spontaneous magnetostriction gives rise to a distortion of the iron lattice such that the interstitial sites lying on the axes parallel to the spontaneous magnetostriction become larger than the other interstitial sites. The larger sites are more accommodating to the interstitial solute atoms.

A ferromagnetic material is composed of small regions called domains \(^\text{(8)}\), each being spontaneously magnetized to saturation in a particular direction. The boundary between adjacent domains is termed a Bloch Wall. The mobility of the domain wall at low externally applied fields will determine the initial permeability.

The magnitude of the initial permeability in dilute Fe-C,N alloys will depend on the time elapsed after the demagnetization. Immediately after demagnetization, interstitials which may be represented as dipoles are randomly oriented (fig. 3a) and the initial permeability is high. With increasing time, the interstitial dipoles will accommodate with the direction of the local spontaneous magnetization (fig. 3b). The redistribution of the interstitial dipoles will stabilize the new Bloch Wall configuration,
Figure 3

Distribution of interstitial dipoles
a) immediately after demagnetization
b) as $t \rightarrow \infty$. 
(a) Domain Wall

(b) Interstitial Dipole
i.e., the Bloch Wall mobility decreases, and thus the permeability decreases. The time decrease of the initial permeability is termed disaccommodation.

The time change in permeability is strongly temperature dependent (fig. 4a) and a plot of the difference in permeabilities over a finite time versus temperature will show a definite maximum (fig. 4b). The same is true for differences of the reciprocal of permeability (reluctivity) versus temperature. With reference to fig. 4a, the difference between permeability values at $t_1$ and $t_2$ for low temperatures will be very small due to the low thermal activation for interstitial redistribution. At very high temperatures the change of the initial permeability will be complete before the time interval starts. Consequently, the difference between permeabilities at $t_1$ and $t_2$ is again small. At intermediate temperatures, a large change in permeability within the $t_2-t_1$ interval is noticed. Therefore, a plot of permeability difference versus temperature shows a definite maximum as shown in fig. 4b.

Now consider an interstitial atom located next to a substitutional atom placed in the regular iron lattice. There will be two additional factors affecting the mobility and equilibrium distribution of interstitials. First, an additional strain component caused by introducing a substitutional element with ionic radius different from that of iron;
Figure 4

a) Permeability versus time for varying temperatures

b) Temperature dependence of permeability change within a finite $t_2 - t_1$ time interval.
$T_1 > T_2 > T_3 > T_4 > T_5$

(a) Permeability $\mu$ vs. Time

(b) Permeability Diff. $\Delta \mu$ vs. Temperature
and second, a change in the energy barrier around interstitial sites caused by an adjacent substitutional with valence different from that of iron. A combination of both of the above can cause a change in the mobility of selected interstitials which will show up as additional peaks in a plot of reluctivity difference versus temperature.

In this investigation the effect of substitutional alloying elements on the diffusion of carbon or nitrogen in alpha-iron were studied. Magnetic disaccommodation techniques were applied to obtain relaxation times. Because changes in the electronic configurations of substitutional elements are thought to have marked effect on the diffusional process (9), substitutional elements were selected so that the number of electrons in the 3d band were systematically varied. Consequently, dilute iron-carbon and iron-nitrogen alloys containing manganese, chromium, vanadium and titanium were investigated.
II. EXPERIMENTAL PROCEDURE

The initial magnetic permeability, $\mu_i$, was determined by measuring the mutual inductance of a coil containing the sample as a core, using a self-balancing a.c. bridge (10). The earth's magnetic field was reduced from 475 mOe to less than 1 mOe by using high permeability iron-nickel alloy attenuating cylinders and end plates. The measuring cylinder (fig. 5) was placed in a Dewar flask partially filled with liquid nitrogen and then back heated to the desired temperature. The temperature controller and measuring system are shown in fig. 5. Temperatures were held to within $\pm0.05^\circ C$ and were measured with a copper-copper constantan thermocouple in contact with the sample.

Demagnetization prior to each disaccommodation measurement assured a random domain wall configuration and interstitial dipole distribution. This was accomplished by gradually and continuously decreasing a 60 cycle a.c. magnetic field to below 1 mOe.

The initial permeability was calculated from the measured induction (11) according to

$$\mu_i = \frac{R_1 \times L \times 10^{-6}}{n^2 \times \mu_0 \times F} (R_C - R_O C_0)$$
Figure 5

Measuring cylinder and temperature controller system.
MEASURING THERMOCOUPLE

TEMPERATURE CONTROLLER

D.C. POWER SUPPLY

FURNACE POWER LEADS

SAMPLE

ATTENUATING CYLINDERS

DE MAGNETIZING COIL

MEASURING COIL

CONTROL THERMOCOUPLE
where: \( R_1 = \) fixed bridge resistance = 1,000 ohms
\( L = \) coil length
\( n = \) number of coil turns
\( \mu_0 = \) permeability of a vacuum
\( F = \) sample cross-sectional area
\( R \) and \( C \) = resistance and capacitance required to balance the bridge with the sample in the coil
\( R_o \) and \( C_o \) = background resistance and capacitance.

Alloy melts were prepared by inductively melting 99.9% pure iron and (nominally) 1 atomic per cent 99.9% pure titanium, vanadium, chromium or manganese in a 99.7% pure impervious recrystallized alumina crucible. Melts with (nominally) 0.5 atomic per cent titanium or vanadium were later prepared. Before heat treating, the samples were swaged, etched for 30 seconds in aqua regia, and rinsed in acetone. The sample analyses made by Kawin Co. are given in Table I.

In preparation for carbon or nitrogen introduction, samples were first decarburized by heating to 800°C for at least 10 hours in a stream of wet hydrogen, and then denitrided by heating to 800°C for at least 10 hours in vacuum (<10^{-5} torr). Samples were carburized in a closed system (approximately 1,000 cm³) by heating a mixture of 9% CH₄ - 91% H₂ to 800°C for 10 hours. The carbon content (Table I) was estimated from thermodynamic data (12). The samples
were supported in a quartz tube and after heat treatment were quenched in brine. Immediately after quenching the samples were placed in a freezer at -20°C to retard carbide formation.

Nitriding was performed at 590°C in a gas mixture of dried 5% NH₃ - 95% H₂, flowing at approximately 300 cc/min. Percentage of nitrogen present (Table I) was estimated from thermodynamic data (13). After heat treatment, samples were brine quenched and placed in a -20°C freezer. With particular reference to the Fe-V-N and Fe-Ti-N alloys the precipitation of nitrides was very rapid after quench. Even with an elapsed time of less than 3 minutes taken to quench a sample and transfer it into the measuring coil at -20°C, nitride formation drastically decreased the value of the initial permeability. Reducing the NH₃ content in the gas mixture to less than 2% did not decrease nitride formation.
TABLE I

Sample analyses for substitutional and interstitial concentrations

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>substitutional</td>
</tr>
<tr>
<td>Fe-C</td>
<td>--</td>
</tr>
<tr>
<td>Fe-Cr-C</td>
<td>0.72</td>
</tr>
<tr>
<td>Fe-Mn-C</td>
<td>0.28</td>
</tr>
<tr>
<td>Fe-V-C</td>
<td>0.94</td>
</tr>
<tr>
<td>Fe-Ti-C</td>
<td>0.70</td>
</tr>
<tr>
<td>Fe-N</td>
<td>--</td>
</tr>
<tr>
<td>Fe-Cr-N</td>
<td>0.72</td>
</tr>
<tr>
<td>Fe-Mn-N</td>
<td>0.28</td>
</tr>
<tr>
<td>Fe-V-N</td>
<td>0.45</td>
</tr>
<tr>
<td>Fe-Ti-N</td>
<td>0.16</td>
</tr>
</tbody>
</table>
III. EXPERIMENTAL RESULTS

With zero time taken as when the demagnetizing field became smaller than the measuring field, the initial permeability, $\mu_i$, was measured at 1 and 10 minutes as a function of temperature. The magnitude of the disaccommodation was expressed by the reluctivity difference $1/\mu_i(10) - 1/\mu_i(1)$.

The relaxation data were analyzed by assuming discrete Debye relaxation times. If the overall relaxation process can be considered to be made up of several first order relaxation processes, then

$$\frac{1}{\mu_i(\infty)} - \frac{1}{\mu_i(t)} = \sum_j a_j \exp\left(-\frac{t}{\tau_j}\right)$$

where $a_j$ and $\tau_j$ are respectively the relaxation strength and relaxation time of the $j$th relaxation. Over the given temperature range $a_j$ can be considered constant. For a single relaxation

$$\Delta r = \frac{1}{\mu(t_2)} - \frac{1}{\mu(t_1)} = a_1 \left[ \exp\left(-\frac{t_1}{\tau}\right) - \exp\left(-\frac{t_2}{\tau}\right) \right],$$

and

$$\tau = \tau_0 \exp(Q/RT).$$
The temperature dependent maximum of $\Delta r$ occurs with a relaxation time

$$\tau_{\text{max.}} = \frac{t_2 - t_1}{\ln \frac{t_2}{t_1}}$$

(4)

which, for $t_1 = 1$ minute and $t_2 = 10$ minutes, equals 243 seconds. From previous work by Wert and Zener (14)(15), the diffusivity of carbon in alpha-iron is given by

$$D = 0.02 \exp(-Q/RT)$$

(5)

where

$$Q = 20,100 \text{ cal/mole-}^0\text{K}$$

The equivalent expression for nitrogen diffusion is

$$D = 0.014 \exp(-Q/RT)$$

(6)

where

$$Q = 17,700 \text{ cal/mole-}^0\text{K}$$

The diffusivity of carbon or nitrogen in alpha-iron is also given by

$$D = \frac{a^2}{36\tau}$$

(7)

where

$$a = \text{lattice constant} = 2.86 \, \text{Å}$$

$$\tau = \text{relaxation time}.$$ Combining equations (5), (6), and (7) allows calculation of the relaxation times of carbon and nitrogen as a function of
temperature. Inserting the calculated values of \( \tau \) into equation (3) gives the temperature dependence of reluctivity difference.

The normalized reluctivity difference at 1 and 10 minutes for iron-carbon alloys is plotted in fig. 6 as a function of temperature. Equation (4) above predicts a maximum disaccommodation to occur with a relaxation time of 2.43 \( \mu \) seconds. Calculation of relaxation times for carbon diffusion (14)(15) indicates the 2.43 second peak to occur at -19°C, while the experimentally determined maximum occurred at -22°C. The agreement between the two temperatures is satisfactory considering the uncertainty in the values of \( Q \) and \( \tau_0 \).

The normalized reluctivity difference at 1 and 10 minutes for iron-nitrogen alloys is plotted in fig. 7 as a function of temperature. The low temperature maximum for nitrogen diffusion was calculated to occur at -34°C and experimentally observed at -30°C for Fe-Ti-N and -31°C for Fe-Mn-N. Again, the agreement is satisfactory considering the uncertainty in the values of \( Q \) and \( \tau_0 \). An additional disaccommodation peak was found at higher temperatures in each Fe- substitutional -N sample. The additional peak for Fe-V-N occurred at +10°C for Fe-Cr-N at -14°C for Fe-Mn-N at -21°C and for Fe-Ti-N at +12°C. The resultant curve of Fe-Mn-N was decomposed into the regular Fe-N curve with maximum at -34°C and the additional disaccommodation curve
Figure 6

Normalized reluctivity difference $\Delta r$ versus temperature $\Theta$ for Fe-Mn-C, Fe-V-C and Fe-Cr-C.
Figure 7

Normalized reluctance difference $\Delta r$ versus temperature $\Theta$ for Fe-Mn-N, Fe-Ti-N, Fe-Cr-N and Fe-V-N.
with maximum at \(-21^\circ C\). Data were normalized to the peak value of the Fe-N curve at \(-34^\circ C\). The Fe-Cr-N curve was similarly decomposed into the regular Fe-N curve at \(-34^\circ C\) and the additional disaccommodation curve with maximum at \(-14^\circ C\), and then normalized to the peak value of the Fe-N curve at \(-34^\circ C\). Fe-Ti-N and Fe-V-N curves were not decomposed as the two peaks are sufficiently apart.

A decrease of initial permeability showed nitride formation in Fe - 1 at. \% V - N and Fe - 1 at. \% Ti - N to be pronounced.
IV. DISCUSSION

The after-effect of the initial permeability can be caused by reorientation of defects with symmetry lower than that of the host lattice, by long range diffusion of defects over distances comparable to Bloch Wall thicknesses and by thermally activated motion of Bloch Walls (11). Considering the temperatures at which the disaccommodations take place, it is generally concluded that the reorientation mechanism is operative.

The results of this investigation indicate that (1) varying the substitutional element in ternary iron-carbon alloys does not affect the reorientation of interstitial carbon and (2) varying the substitutional element in iron-nitrogen alloys has a non-uniform affect on nitrogen reorientation.

Seeing a definite additional after-effect of initial permeability in each Fe- substitutional -N alloy raises a significant question: Was the additional after-effect caused by the additional strain component or by the electronic interactions produced by a variation of the substitutional?

The data presented here provide a qualitative basis for rationalizing the operative mechanism of the additional after-effect of initial permeability. An argument based on additional favorable strain components and electronic interactions
can be made in explaining results of iron-nitrogen studies. The additional amplitudes of the disaccommodations are much larger in chromium and vanadium than in titanium or manganese. As the ionic radii of chromium and vanadium are both smaller than that of iron, adding a substitutional chromium or vanadium increases the effective distance between lattice centers. The addition thus decreases the free energy level of the six neighboring interstitial sites, partially contributing to an additional after-effect of permeability. Noting that the ionic radii of titanium and manganese are larger than that of iron while seeing small additional disaccommodation amplitudes in these samples, points to the electronic interactions between interstitial-substitutional pairs as being the primary contributor to the additional after-effect of permeability. The oxidation state of nitrogen is ±3, while that of vanadium, titanium, manganese and chromium can be +3. Formation of a N-V, N-Ti, N-Mn or Ni-Cr pair will thus approach a ground state level and create an energy barrier surrounding the pair that decreases the mobility of the interstitial. The decreased mobility of selected interstitials leads to an additional disaccommodation peak. As the +3 oxidation state for chromium is its most stable state, the largest additional disaccommodation would be expected in Fe-Cr-N samples, as the results verify.

Similar arguments may be made to explain the lack of an additional after-effect of permeability in Fe-substitutional
-C alloys. The primary cause is believed to be the large value of ionic radius for carbon. The radius of carbon is approximately three times as large as iron. Therefore, any change in lattice dimension introduced by a substitutional will not significantly alter interstitial mobility. The oxidation state of carbon is $\pm 4$. As no substitutional investigated has its most stable state as $\pm 4$, large energy barriers around C- substitutional pairs will not be developed in this case. Electronic interactions are thereby not significant to cause additional disaccommodations.
V. CONCLUSIONS

Measurements of the initial permeability of dilute iron-base transition metal (manganese, chromium, vanadium, titanium) alloys containing carbon or nitrogen were made. Over the temperature range investigated with iron-carbon alloys, -30°C to +20°C, no evidence of an additional disaccommodation was found. Over the temperature range investigated for diffusion of interstitial nitrogen, -50°C to -30°C, a strongly temperature dependent extra disaccommodation was found.

Data were analyzed in terms of a single Debye relaxation on the basis of Wert's values of activation energies for carbon and nitrogen diffusion in bcc alpha-iron.

The extra disaccommodation in Fe-substitutional -N is attributed primarily to electronic stabilization of interstitial substitutional pairs, while the absence of an extra disaccommodation in Fe-substitutional -C alloys is explained on the basis of strain energy arguments.
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VITA

The author was born on October 30, 1944, in Independence, Missouri. He received his primary and secondary education in Kansas City, Missouri. He has received his college education from Kansas City Junior College, in Kansas City, Missouri; and the University of Missouri - Rolla. He received a Bachelor of Science Degree in Metallurgical Engineering from the University of Missouri - Rolla in June, 1966.

He has been enrolled in the Graduate School of the University of Missouri - Rolla since September, 1966, and has held a student teaching assistantship for the period September, 1966 to June, 1967, and the Alcoa Metallurgical Fellowship for the period September, 1967 to June, 1968.