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RESISTOMETRIC STUDY OF FE-BASED ALLOYS NITRIDE D BY CONSTANT ACTIVITY AGING

by

MING M. YANG

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

DOCTOR OF PHILOSOPHY

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MAY 1981
ABSTRACT

RESISTOMETRIC STUDY OF Fe-BASED ALLOYS
NITRIDED BY CONSTANT ACTIVITY AGING

by

MING M. YANG

Constant activity nitriding experiments were performed in Fe-V and Fe-Mo alloys. The nitriding was accomplished aging the alloys in a $\text{NH}_3/\text{H}_2$ atmosphere at temperature between 400°C and 600°C, during which fine substitutional-interstitial clusters are formed. These coherent clusters are small platelets lying on 100 ferrite matrix planes.

During the nitriding process, these clusters form first near the surface of the sample. For the Fe-V alloys, nitriding proceeds by the advance of a interface bounding region with and without clusters. This results in a hardness profile which is discontinuous at the interface. The rate of the hardness front movement in Fe-V can be predicted by internal oxidation equation. For the Fe-Mo alloys, a distinct interface is not observed, and the hardness varies in a continuous fashion through the cross section of the sample. No particular model has been developed for those alloys.

The resistivity rises during the nitriding for both Fe-V and Fe-Mo alloys. In Fe-V alloys, the nitried region and unnitried region are separated by a sharp boundary. Thus, the resistivity can be calculated by analogize this system to a pair of resistor connected in parallel. The resistivity at full saturation of
nitrogen were explained mainly by formation of the coherent clusters in the alloys. It is a function of density, size distribution and average size of the clusters. From the resistivity maxima upon full saturation at different nitriding temperatures, we can understand the size distribution and average size of the clusters are function of nitriding temperature, while density of the clusters and total volume of the strain field are function of concentration of alloy elements and nitriding temperature.

The static displacement around clusters has been estimated, from resistivity data, and equal 0.68\(\AA\) for a full nitried Fe-3.0at.\%Mo.
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To

My Mother and Father
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CHAPTER I

INTRODUCTION

A. General

1. Background

Nitrogen hardening of steels was first reported in a patent on "nitriding iron and steel" granted to Adolph W. Machlet in 1913 and was developed for alloy steels by Dr. Adolph Fry in Germany in 1921. Within a few years nitriding became a leading case-hardening process and the so-called "nitralloy" steels, derived from Fry's work, achieved universal acceptance. Since then, many studies on heat treatment and the process of nitriding have been performed.

In recent years, Jack and co-workers have shown that great control of the nitriding process is possible and that, under appropriate conditions, a metastable precipitation sequence may be produced. This has been termed "constant activity aging". In this process, nitrogen atoms from dissociation of gaseous NH\textsubscript{3} (or N\textsubscript{2}) at the gas-solid interface diffuse into the Fe matrix. The activity (or concentration) of N is established at a constant value at the surface of the iron alloy.

The thermodynamic principle of the constant activity aging nitriding process may be explained using the following relations:

\[ \text{NH}_3 (g) \overset{K_1}{\longrightarrow} \text{N (in } \alpha - \text{Fe}) + \frac{3}{2} \text{H}_2 (g) \quad (1) \]

or

\[ \frac{1}{2} \text{N}_2 (g) \overset{K_2}{\longrightarrow} \text{N (in } \alpha - \text{Fe}) \quad (2) \]
$K_1$ is the equilibrium constant for reaction (1), $K_2$ is the equilibrium constant for reaction (2), and

$$K_1 = \frac{[N\%]^3/2}{P_{NH_3} P_{H_2}}$$  \hspace{1cm} (3)$$

$$K_2 = \frac{[N\%]}{P_{N_2} k_2}$$  \hspace{1cm} (4)$$

$[N\%]$ is the N concentration in the Fe - based alloy and $P_{H_2}$, $P_{N_2}$ and $P_{NH_3}$ are the partial pressures of hydrogen, nitrogen and ammonia, respectively. The equilibrium constant $K_1$ is about 200 to 1000 times larger than $K_2$ at the nitriding temperature (400° C - 600° C). From equations (3) and (4), if pure nitrogen is used instead of the NH$_3$/H$_2$ gas mixture, a very large pressure of molecular nitrogen would be required to have the same nitrogen concentration in iron. Therefore, it is convenient to use an NH$_3$/H$_2$ gas mixture rather than nitrogen gas at high pressure.

Assuming Henry's Law, $a_N = \gamma_N [N\%]$, where $a_N$ is the activity of nitrogen and $\gamma_N$ is the activity coefficient, then, from equation (3),

$$K_1 = \frac{a_N P_{H_2}}{\gamma_N P_{NH_3}}^{\frac{3}{2}} ,$$

and, therefore,

$$a_N = \frac{\gamma_N k_1 P_{NH_3}}{P_{H_2}^{\frac{x}{2}}} .$$  \hspace{1cm} (5)$$
For a constant temperature and alloying element solute concentration, the values of $\gamma_N$ and $K_1$ will be constant. Therefore, by fixing the $\text{NH}_3/\text{H}_2$ ratio, the activity (or the $[\text{NH}_3]$) is a constant at the sample surface.

In the environment of the $\text{NH}_3/\text{H}_2$ gas mixture, nitrogen is removed from thermodynamic solution in the alloy by interaction with the substitutional solute to form nitrides and immediately replenished from the gas atomosphere until it again reaches the equilibrium value. This process continues until all the substitutional solute is associated with $N$. The resulting hardness increase upon nitriding is the result of interaction of the substitutional alloying element in iron with nitrogen in solid solution. Nitrogen ($D=10^{-7}$ cm/sec$^2$)$^6$ diffuses much faster than the substitutional alloying ($D=10^{-15}$ cm/sec$^2$)$^7,8,9$ elements at the nitriding temperature ($400^\circ\text{C} - 600^\circ\text{C}$). Thus, the nitrogen interacts with the substitutional alloying element, which only moves short distances relative to the nitrogen, and local heterogeneous regions are created in the material.

The chemical decomposition of both substitutional and interstitial solute atoms from the iron matrix by formation of nuclei through composition fluctuation of solutes is a homogeneous precipitation process which reduces the free energy of the supersaturated solid solution. This precipitation sequence includes the following three steps:$^{10,11,12}$

1. Metastable chemical cluster formation
2. Intermediate precipitation
3. Equilibrium precipitation

The three precipitation stages are now discussed.
(1) Metastable chemical cluster formation. At this stage solute atoms begin to associate to form solute-rich regions. During this early stage of clustering, it is possible to observe changes of physical or mechanical properties even though the clusters can only be observed using high magnification transmission electron microscopy. They can be indentified with the solute rich, coherent zones called Guiner-Preston zones. The formation of G.P. zones in classical age-hardened alloys has been frequently studied.\(^{(13,14)}\)

For constant activity aging, a high concentration of vacancies, such as occurs in classical age hardening aluminum-copper alloys, is neither created nor required. At intermediate nitriding temperatures \(400{\degree}\text{C} - 600{\degree}\text{C}\), substitutional solute atoms can move a sufficient distance to create a fluctuation of concentration and form zones inside the iron matrix. At an appropriate nitriding condition, the substitutional solute atoms and interstitial N atoms interact to form disc-shaped substitutional-interstitial clusters in the iron matrix (see Fig. 1) During the cluster stage the solute atoms occupy the same kind of sites as they do in the original solid solution, i.e. nitrogen occupies octahedral interstices and alloying element atoms stay on b.c.c. metal lattice sites. The cluster is coherent with the Fe matrix. This coherence creates large elastic strain and local distortion in the matrix around the cluster. At this stage, x-ray and electron diffraction patterns usually show sidebands.\(^{(11)}\) The value of lattice parameter of the alloy remains the same, in principle, as for the random solid solution.\(^{(15)}\)
Figure 1. Schematic representation of substitutional-interstitial cluster in Fe-M-N. M is substitutional solute atom.
(2) Intermediate precipitation. The arrangement of atoms within clusters begins to order until it is no more just a perturbation of matrix concentration but has a definite structure. During prolonged heating after cluster formation, the solutes continue ordering and the precipitates coarsen, until the strain field becomes too great to be accommodated by only bending of the lattice planes. The complete coherency breaks down and dislocations form on the interface.\(^{16,17}\) The platelets of metastable coherent phase gradually become semicoherent.

(3) Equilibrium precipitation. The final stage of precipitation is the heterogeneous nucleation of equilibrium nitride at grain boundaries and the transformation of the microstructure by discontinuous precipitation. When discontinuous precipitation starts, homogeneous precipitation completely stops and the intermediate precipitates are completely consumed by equilibrium precipitates.

2. Condition for G.P. zone formation in nitried Fe-based alloys

(1) Choice of alloying elements

The alloying elements in Fe strongly affect nitriding conditions by increasing (e.g., Si, Co, Ni, Al) or decreasing (e.g., Mo, Mn, V, Cr, Nb, W, Ti) the activity coefficient of nitrogen in Fe.\(^{18,19}\) Those elements which decrease the nitrogen activity coefficient can increase the concentration of nitrogen and promote supersaturation inside the Fe matrix, leading to G.P. zone formation.

Two solutes were chosen for investigation in this study, molybdenum and vanadium. Fe-Mo-N alloys have been shown to readily proceed
through the three stages of precipitation \cite{20,21} and thus samples may be produced in the various stages or heat-treated to follow the entire sequence. Fe-V-N, on the other hand, tenaciously remains in the initial clustered state until subjected to prolonged aging at temperatures well above the nitriding temperature. Thus more detailed study of this stage is, in principal, possible.

Our interest is in dilute Fe-Mo (up to 3 at.%) and Fe-V (up to 3 at.%) alloy. Higher concentration alloys either enter two phase regions or spontaneously fracture due to embrittlement caused by the resulting high concentration of N upon fully nitriding such alloys. The b.c.c. phase in these alloys is stable up to 1500°C except for a narrow γ loop between 900°C - 1400°C. Nitriding temperatures of 400°C - 600°C allow controlled study of the homogeneous precipitation behavior in nitrided ferritic Fe based alloys.

(2) Nitriding condition

At low temperature, the solute elements are virtually unable to move in the ferrite matrix. Therefore, only iron nitrides $\alpha' - \text{Fe}_{16}N_2$ and $\gamma - \text{Fe}_4N$ can be precipitated from nitrogen-supersaturated solid solutions. In contrast, at high temperature, the solute elements can diffuse readily through the matrix and alloy nitrides will be precipitated directly. Only at intermediate temperatures (400°C - 600°C), where substitutional solute atoms move over only short distances in the same time that nitrogen can move over large distances, is the situation appropriate for formation of small G.P. zones.

Substitutional-interstitial G.P. zones can be regarded in the same way as metastable precipitates which have higher than equilibrium
solute solubilities; their formation requires the zone solvus to be exceeded (Fig. 2). At the same time, the nitrogen potential should not exceed the iron nitride solvus. The conditions for G.P. zone formation are shown in (Fig. 3).\(^{(22)}\)

3. Application

For industrial applications, high strength is usually required. However, enhancement of strength by selected variations in steel chemistry and processing is usually accompanied by a sacrifice in metal formability. Internal nitridation which increases strength by the formation of alloy nitrides, offers a potential method for producing high strength parts whereby complex parts are formed then strengthened after forming.\(^{(23)}\)

Interest in the nitriding of alloy steels has always centered around some valuable properties unique to this case-hardening process: high surface hardness and wear resistance, a minimum of distortion, resistance to tempering, a beneficial effect on fatigue properties, and a marked resistance to corrosion in some common media.\(^{(2)}\) In addition, nitriding can be done at lower temperatures and thus can be done at less cost than carburizing which enhances the attractiveness of this process.

The research on mechanical properties of alloys subjected to constant activity aging was performed by Jack and co-worker on nitried Fe-V,\(^{(53)}\) Cuddy and Podgurski on nitried Fe-Ti and Fe-Nb alloys\(^{(54)}\) and Hook on nitried Fe-Ti-Mn alloys.\(^{(23)}\) In general, the yield strength is typically increased over that of the unnitried alloy by a factor
Figure 2. (a) Schematic phase diagram for Fe-Mo alloys nitrided at 500°C in 6%NH₃:94%H₂. Line XY shows increasing nitrogen content. Dashed line shows G.P. zone solvus.

(b) Section of ternary Fe-Mo-N system along XY.²²

Figure 3. Conditions for G.P. zone formation.²²
of 10 even through only a few tenths of a percent of 'precipitate' were present. Yield around tensile strength, toughness, weldability and fatigue characteristics were found to be good provided excess N was removed. The strengthening is attributed to coherency strains due to fine 'precipitates' during the early stages followed by the looping of dislocations around particles after sufficient particle size coarsening. The stress necessary to push the dislocation through the matrix increases inversely with interparticle spacing which in turn decrease with zone density. Thus, to elucidate the nature of the local atomic arrangements of nitrided iron-base alloys during the metastable stages of homogeneous precipitation and understand the parameters which effect elastic strain and density of the zones is the principal objective of this study.

B. Previous Work

During the constant activity nitriding of b.c.c. Fe-based alloys in NH₃/H₂ gas mixtures between 400°C and 600°C, fine coherent G.P. zones were first observed by Speirs, (10) and then confirmed by other workers. (24,25,26) These coherent G.P. zones are small platelets lying on {100} ferrite matrix planes. (10,19,12,25) Mixed substitutional-interstitial solute atom zones were proposed by Speirs and co-workers. (18) There model of G.P. zones has been directly verified by Driver et al. (24) who also suggested that the Fe-Mo-N zones obtained by constant activity nitriding may be hydrogen-reduced at 580°C to virtually negligible nitrogen concentrations, leaving disc-shaped zones of pure substitutional
Mo and Fe on \{100\} ferrite planes. Driver and Papazian\(^{(25)}\) used images from zones close to the Fe-Mo nitrided foil surface to determine the sign of the strain field. Dark field micrographs showed asymmetric images with dark contrast on the side of positive \( \mathbf{g} \) vector, indicating that the zones were of interstitial rather than vacancy character.

The dimensions, shape and number density of the platelets has been measured from combined transmission electron and field ion microscopy by Brenner and Goodman,\(^{(19)}\) and Driver and Papazian\(^{(25)}\) in the Fe-3at.\% Mo system. In this alloy, the studies indicate that zones have diameters of about 100\( \AA \) and thicknesses below 20 \( \AA \). Some discrepancy occurred with regard to density of the zones. Brenner and Goodman obtained a density in fully nitrided Fe-3at.\% Mo of 10\(^{18}\)/cm\(^3\) while Driver and Papazian got 3 \times 10\(^{17}\)/cm\(^3\). A reasonable explanation of the difference could be that different nitriding conditions were used in those two studies. The size of chemical clusters in the Fe-V system has been measured separately by Phillips\(^{(27)}\) and Pope et al.\(^{(24)}\) Both studies determined that the zones are approximately 10 \( \AA \) thick and 60 \( \AA \) in diameter, which is smaller than clusters in the Fe-Mo system.

Chemical composition of zones during the early stages of precipitation has been studied by several workers. Brenner and Goodman\(^{(19)}\) determined from atom probe data cluster compositions in the Fe-Mo-N system close to Fe\(_2\)Mo\(_3\)N\(_2\). Driver and Papazian\(^{(25)}\) concluded from their studies, which used hydrogen reduction, that the ratio of Mo:N in zones depends on the nitriding conditions and varies between 2 and 3. Huffman and Podgurski\(^{(28)}\) concluded from gravimetric studies that the Mo:N ratio in Fe-2.9at.\% Mo samples for a variety of nitrogena-
tion and reduction treatments at 500°C and 600°C was close to 1:1. They could not detect any Mössbauer absorption peaks that could reasonably be attributed to Fe contained in a nitride phase. On the basis of these observations, they concluded that, in their samples, Fe constituted less than 10% of the metal atoms in the nitride and that the nitride was very close to the stoichiometric composition MoN.

Recently, Wagner and Brenner (29) performed various nitriding treatments from 500°C to 600°C, and concluded from field ion microscopy and atom probe methods that the first stage of precipitation corresponds to \((\text{Fe,Mo})_{16}N_2\). This is equivalent to the \(\alpha' - \text{Fe}_{16}N_2\) in binary Fe-N systems (30) with about 20% of the Fe atoms substituted by Mo atoms.

The presence of small coherent metastable chemical clusters is also supported by lattice parameter measurements using x-ray diffraction. (11,15) According to short-range order theory, the lattice parameters of a solid solution are essentially invariant with respect to the distribution and arrangement of its solute atoms. A matrix containing G.P. zones is a solid solution in which non-random local atomic arrangements exist, but the lattice parameter is the same as for a random solid solution having the same solute concentration. Therefore, the lattice parameter of an Fe-M-N system is given by:

\[
\alpha_0 (\text{Fe-M-N}) = \alpha_0 (\text{Fe}) + \Delta a (M) + \Delta a (N) \quad (6)
\]

where \(M\) is the substitutional alloy element and \(\alpha_0 (\text{Fe-M-N})\) and \(\alpha_0 (\text{Fe})\) are lattice parameter for Fe-M-N system and \(\alpha - \text{Fe}\) respectively.
$\Delta a(M)$ and $\Delta a(N)$ are the increases caused by solution of the substitutional solute and nitrogen respectively. Krawitz(11) has shown by performing lattice parameter measurements of nitried Fe-Mo and Fe-V alloys that during constant activity nitriding all the N atoms essentially stay in the solid solution at the early stage of homogeneous precipitation. He also concluded that diffuse sidebands on the high-angle side of the Bragg reflections due to concentration and lattice spacing modulation due to the solute and nitrogen in the ferrite matrix during the early stage of precipitation and that streaks on x-ray rotation photographs come from the intermediate precipitate Mo$_2$N in the case of Fe-Mo-N.

Because of its high interfacial energy, the equilibrium nitride precipitate requires a large activation energy for nucleation. Jack(20,21) proposed a homogeneous precipitation sequence in nitried Fe-based alloys between $400^\circ C$ - $600^\circ C$. It starts with the formation of substitutional-interstitial clusters which then order to form $\alpha'' - Fe_{16}N_2$-type G.P. zone in which some of the iron atoms are replaced by Mo atoms. The $\alpha''$ phase then transforms to f.c.c. Mo$_2$N which is a second intermediate phase before the final equilibrium phase, Fe$_3$Mo$_3$N, occurs. Wagner and Brenner(29) conclude from their research that the first stage is b.c.t. (Fe,Mo)$_{16}$N$_2$ platelets that then transform to semicoherent Fe$_3$Mo$_3$N$_2$ before equilibrium f.c.c. (Mo,Fe)$_2$N or tetragonal (Mo,Fe)N is formed. Some discrepancies exist between the conclusions of those two groups. In the Fe-V system, there is not enough evidence to decide whether the first stage of homogeneous precipitation consists of very thin VN platelets or of Fe-V-N disc-shaped cluster.(26) However,
prolonged heating of nitrided Fe-V samples at high temperature results in precipitation of f.c.c. VN in the ferrite with the Baker-Nutting orientation:

\[(001)_\alpha \parallel (001)_{VN} ; \quad [100]_\alpha \parallel [110]_{VN}\]

It directly transforms from a disordered vanadium-nitrogen cluster to f.c.c. VN by an ordering process without forming an identifiable intermediate precipitate.

C. Resistivity

One of the most characteristic and important features of a metal is electric resistivity which is the impedance of the free electron flow. It is dependent on temperature and pressure as well as the chemical and physical state of the metal. The chemical state refers to the presence of impurity or alloy atoms in the matrix and depends upon the number and distribution of such atoms, i.e., whether they are in random solid solution, long-range ordered or present in clusters or as compounds. The physical state depends on the previous history of the metal including, for instance, any cold work, irradiation or annealing treatment to which it has been subjected. The sensitivity of the resistivity to the chemical state of solid solutions has led to its widespread use in the study of precipitation in alloy crystals.\(^{(31,32)}\)

The electrical resistivity of a metal is generated by the conduction electrons scattering from any disturbances in the periodic lattice potential.
According to Mathiessen's rule, the total resistivity can be separated into a temperature-dependent part and a temperature-independent part:

$$\rho = \rho_T + \rho_r$$

$\rho_T$ is the temperature-dependent component which is caused by the interaction of the conduction electron with the thermal vibrations of the lattice. The temperature-independent component $\rho_r$ is the so-called "intrinsic residual resistivity" which is raised by presence of impurity solutes, lattice strain and defects in the metal.

For systems of binary homogeneous random dilute solid solutions, the impurity resistivity, according to Nordheim's rule,\(^{(33)}\) can be written as

$$\rho_r = kX (1 - X) \ . \tag{7}$$

Where $X$ is the solute concentration and $K$ is a constant dependent on the base metal and impurity level. This rule, which originally was applied to substitutional solutes has been extended to interstitial solutes.\(^{(34)}\)

The effect of solutes on the electrical resistivity of a metal has two sources: (i) the valence electron difference and (ii) the size difference between solute and solvent atoms. In a substitutional alloy, the effect of charge difference usually predominates.\(^{(35)}\) In an interstitial solution for which the interstitial atom does not replace an atom of the host crystal, there should be no large effect of charge-
misfit (36) but the elastic strain field produced through displacement
of neighboring solute atoms by the interstitial atom around can have
a large effect. (36,37) It has been proposed (36) that
the increase in resistivity due to the presence of interstitials
is proportional to the mean-square static displacement.

$$\frac{\rho_S}{<u^2_S>} = \frac{\rho_T}{<u^2_T>}$$  \hspace{1cm} (8)

where $\rho$ is electrical resistivity and $<u^2>$ is the mean square displace-
ment, $S$ and $T$ refer to static and thermal effects, respectively.
General agreement has been reached for Fe-C martensite (36) and V-(N,0). (38)

The effect of clustering on electric resistivity is more complicated
than that due to point defects. The resistivity is a function of number,
size distribution and even shape of the clusters and all factors will be
a function of aging time. Typical resistivity behavior with time during
the pre-precipitation stage shows an intial increase followed by a maximum,
then a decrease to a final value which can be even lower than the original
starting resistivity. This happens in Al-Cu, (39) Al-Zn, (39,40) and
Al-Ag (39) alloys during the quench aging process. The original "abnormal"
increase has been studied by many people, but the most plausible explana-
tion is given by Mott (41) who suggested that the maximum may be associated
with a matching of cluster size and electron wavelength. In general,
the resistivity of an Fe-based dilute alloy in a unit volume can be
written as

$$\rho_{(Fe-M)} = n_S \Delta \rho_S$$  \hspace{1cm} (9)
Here, $n_S$ is the total number of solutes, $\Delta \rho_S$ the contribution of an isolated solute atom to resistivity. Panseri and Federighi suggested a phenomenological equation of resistivity due to isolated atoms and spherical zones in a unit volume.\(^{(40)}\) By analogy, we can write an equation for a nitrided wire.

$$\rho(\text{Fe-M-N}) = n_S \Delta \rho_S + n_N \Delta \rho_N + Z[\Delta \rho_Z(z) - c_S z \Delta \rho_S - c_N z \Delta \rho_N] \quad (10)$$

Here, it is assumed that all the clusters are uniformly distributed and are of the same size, each consisting of $z$ atoms. $\Delta \rho_Z(z)$ is the contribution to the resistivity of one zone of $z$ atoms, $Z$ the number of zones which have $z$ atoms, $n_N$ the total number of nitrogen atoms, $\Delta \rho_N$ the contribution of an isolated solute atoms to the resistivity, and $c_S$ and $c_N$ are the fraction of solute and nitrogen inside the zones, respectively. Letting

$$\phi(z) \equiv \Delta \rho_Z(z) - c_S z \Delta \rho_S - c_N z \Delta \rho_N$$

Eq. (10) becomes

$$\rho(\text{Fe-M-N}) = n_S \Delta \rho_S + n_N \Delta \rho_N + Z\phi(z) \quad (11)$$

Where the function $\phi(z)$ is the contribution to the resistivity of a zone of $z$ atoms corrected for the depletion of the matrix. For small $z$, the function increases quickly to a maximum value at a critical radius, $z$. After the maximum, the function decreases to another critical radius, $z_2$, at which the $\phi(z)$ value drops to zero. For values of $z$ greater than, $z_2$, the value of $\phi$ is negative. Further, by assuming that clusters have a size distribution described by $g(z)$, where
\[
\int_0^\infty g(z)dz = 1 \quad \frac{Z(z)}{Z} = g(z)
\]

Equation (11) can be written as:

\[
\int (Fe-M-N) = n_S \Delta \rho_S + n_N \Delta \rho_N + Z \int_0^\infty \phi(z) g(z) dz \quad (12)
\]

Hillel, Edwards and Wilkes\(^{(42)}\) have used numerical methods to evaluate the \(\Delta \rho_Z(z)\) for Al-Zn, Cu-Be, and Al-Cu alloys, but due to the large amount of computer time needed to complete the calculation, they were limited to cluster less than 10,000 atoms. In this study, we are interested in using equation (12) to explain the resistivity data related with early stage of precipitation. Numerically evaluating the resistivity will not be in the scope of the present study.
CHAPTER II
EXPERIMENTAL PROCEDURES

A. Nitriding Apparatus

The nitriding of samples was performed in a horizontal Lindberg 54000 series 3-zone tube furnace with a 4' x 2" O.D. x 1 3/4" I.D. high purity McDanel 998 alumina tube. The temperature of the furnace was calibrated by using a potentiometer with an alumel and chromel thermocouple inside the alumina tube with open ends. A typical temperature calibration curve is shown in Fig. 4. The central portion of the furnace has a uniform temperature region about 15 in. long. The deviation in temperature at 1000°C is less than 2°C. A Lindberg type 2200 solid-state digital temperature controller was used.

A schematic diagram of the nitriding system is shown in Fig. 5. Anhydrous ammonia and pre-purified hydrogen are mixed in a Matheson 7300 gas proportioner after passing through a gas purifier. The gas proportioner meters the flow of the NH₃ and H₂ gases and mixes them thoroughly in a special mixing tube to produce homogeneous two component mixtures. The hydrogen gas flow rate curve was calibrated at room temperature using a bubble meter with an accuracy better than 1%. The method is described in more detail elsewhere. (44) A typical H₂ flow rate calibration curve is shown in Fig. 6.

The ammonia flow rate curve was determined by measuring the flow rate of methane. Methane is close in molecular weight, molecular structure and viscosity to ammonia. The values obtained were corrected
Figure 4. A typical furnace temperature calibration curve with temperature controller setting at 1000°C. It shows the temperature vs. distance from one end of the furnace.
Figure 5. The schematic diagram of the nitriding system.
Figure 6. A typical hydrogen flow rate calibration curve.
FLOWMETER CALIBRATION

Scale Reading (m.m.)

Flow Rate (c.c./min)

Hydrogen - 50 psig
At 25°C, 760 mm Hg.
by using viscosity and density ratio (see Appendix 1). This method has been verified by comparison of results with the ammonia in the Chemical Engineering Department at Rice University(45) within the flow rate region used by this study. A typical flow rate calibration curve is shown in Fig. 7.

The ends of the alumina tube are sealed by two 316 stainless steel plates and a silicone rubber o-ring. They are cooled by two fans. The samples are hung on a small "frame boat" made of pure Fe wire at the cold end of the inlet side of the furnace tube. The "boat" is attached to a hook at the end of a tungsten wire. The other end of the wire is enclosed in a soft iron bar. A glass tube which is sealed on the inlet plate and houses the tungsten wire and iron bar allows the specimen to be moved into or out of the hot zone at any time by a magnet from outside the furnace without breaking the seal.

The whole system can be evacuated by a mechanical pump. Two bottles containing low vapor pressure mineral oil are connected to the system at the end of the gas train to protect against diffusion of air back into the system and to maintain the system at 1 atmosphere of pressure.

B. Materials Fabrication

Both Fe-Mo and Fe-V alloys were made by mixing a 15 gm iron cylinder cut from a ½" diameter high purity iron rod purchased from Material Research Corp. with an appropriate amount of either high purity Mo or V. The Mo was from zone-refined single crystal rods
Figure 7. A typical ammonia flow rate calibration curve.
grown in the Materials Science Laboratory at Rice University. Vanadium was cut from a $\frac{1}{2}''$ diameter high purity rod purchased from Material Research Corp. Purities of the Fe and V starting materials are shown in Table I and Table II, respectively.

The starting materials were melted in a Materials Research Corporation V-4 series arc melter under a high purity argon atmosphere. To ensure homogeneity, the samples were turned over and remelted at least 10 times. Between meltings, the samples were cut into smaller pieces. Some alloys were annealed in pure hydrogen at 1100$^\circ$C for several days to promote homogeneity. The homogeneity of the alloys was confirmed using electron microprobe analysis on the metallographically polished specimens by point counting at 1 mm increments along two perpendicular directions across the cross section of each alloy button. The fluorescent intensity variation of the solute elements was less than 3% in all cases. Alloy composition was further checked by lattice parameter measurements from Debye-Scherrer powder films and compared with the data in Pearson$^{(46)}$ to obtain the solute levels for each alloy. The results are shown in Table III.

<table>
<thead>
<tr>
<th>alloy</th>
<th>Nominal wt% Solute</th>
<th>Lattice Parameter (Å)</th>
<th>at% Solute</th>
</tr>
</thead>
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<tr>
<td>Fe-Mo</td>
<td>4</td>
<td>2.8740 (5)</td>
<td>2.24 ± 0.03</td>
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<td></td>
<td>5</td>
<td>2.8766 (3)</td>
<td>3.00 ± 0.03</td>
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<td>Fe-V</td>
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<td>2.8673 (5)</td>
<td>0.95 ± 0.03</td>
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<tr>
<td></td>
<td>2</td>
<td>2.8684 (0)</td>
<td>2.00 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2.8698 (0)</td>
<td>3.40 ± 0.03</td>
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Table III. Alloy compositions determined by lattice parameter measurement.
TABLE I
CHEMICAL ANALYSIS FOR VP GRADE IRON

<table>
<thead>
<tr>
<th>Element</th>
<th>Content (wt. ppm)</th>
<th>Element</th>
<th>Content (wt. ppm)</th>
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<td>Ga</td>
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<td>Mg</td>
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<tr>
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<td>others</td>
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TABLE II
CHEMICAL ANALYSIS FOR VP GRADE VANADIUM
The alloy samples were either cold rolled into 0.42 mm thick foils or cold drawn into 0.42 mm wires. Rolled material was cut into 2 cm x 2 cm x 0.42 mm foils for transmission electron microscopy, x-ray and neutron diffraction samples and samples for hardness measurement. The wires were about 25 cm (long) x 0.42 mm (diameter) and were wound into helical coils for resistivity, lattice parameter and hardness measurements.

Recrystallization anneals were preformed at about 800°C in pure H₂ from one-half to one hour. These treatments produced completely recovered and recrystallized polycrystals having a grain size of about 50μ.

The microstructure of the recrystallized crystals was examined under an optical metallographic microscope to ensure they had been fully recovered and recrystallized. The average grain sizes were estimated at the same time using a standard grain size chart with magnification at 100 x.

Examples of the optical microstructures are shown in Fig. 8.

Figure 8. The optical microstructures of Fe-3.0at.%Mo after recrystallized at 830°C for 30 min., magnification at 100X.
C. Nitriding

1. Nitriding conditions

The nitriding treatments were performed at temperatures from 450°C to 600°C and the nitriding potential was set to exceed that of the zone solvus but lower than the value to precipitate iron nitride.

Control of the nitrogen potential was achieved by adjusting the flow rate ratio of ammonia to hydrogen in the inlet gas. The total linear flow rate was maintained at 25 cm/min, which is above the minimum flow rate of 15 cm/min (or 2.5 mm/sec) required so that the supply of fresh ammonia to the reaction surface is not rate limiting. (47)

2. Nitriding procedure

a. Start

(1) Clean the sample in methyl alcohol using an ultrasonic cleaner.

(2) Dry and weigh the sample.

(3) Hang the sample on the iron "boat"; let it stay at cold end on the inlet side.

(4) Close the system and evacuate it using a mechanical vacuum pump until the pressure is below 100 torr.

(5) Close the mechanical pump valve and fill the system with \( \text{H}_2 \) to 1 atmosphere pressure.

(6) Pump down to below 100 torr, and repeat steps 4-6 at least three times, then disconnect the pump from the system.
(7) Set the NH$_3$/H$_2$ flow rate ratio and fill the system with NH$_3$ and H$_2$ to 1 atmosphere then open the exit valve and let the flow purge the system for one-half to 1 hour.

(8) While the system is being purged, step (7), heat up the furnace to the required nitriding temperature.

(9) Use a magnet to pull the sample into the hot central zone for nitriding. The flow rate was checked from time to time and correction of the flow meter settings were made.

b. Finish

(1) Pull the sample out of the hot zone to the cold end with the magnet.

(2) Allow a few minutes for the sample to cool down, turn off the NH$_3$ flow rate and increase the H$_2$ flow rate to purge the NH$_3$ out of the furnace; this takes about 1 hour.

(3) Evacuate the system with the vacuum pump and open the system.

(4) Turn off the power to the furnace.

(5) Clean and weigh the sample.

D. Weight Measurement

Properly prepared samples come out of the furnace with a clean shiny surface. The N gain during nitriding can be determined by the
weight difference before and after nitriding. The weight measurements were performed using an electronic microbalance accurate to $10^{-6}$ gm. The foils usually weigh about 1-2 gm and the coils about 0.3 gm, so that the weight measurement should be sensitive to N concentrations as small as $10^{-2}$ at.

E. Resistometry Measurement

A low resistivity measurement Kelvin Bridge was used in this study. The circuit diagram of the Kelvin Double Bridge is shown in Fig. 9.

$X$ is the sample, $R$ is the rheostat, $A$, $B$, $a$ and $b$ are the resistance coils on the resistance box. We have:

$$\frac{X}{R} = \frac{A}{B} + \frac{d}{R} \left( \frac{b}{a + b + d} \right) \left( \frac{A}{B} - \frac{a}{b} \right)$$

(13)

In this relation, the ratios $a/b$ and $A/B$ are set to various values such that $a/b = A/B$. The position of the two contacts on the rheostat are made with a plug and a knife-edge sliding upon a bar of manganin. These are varied until a balance of the bridge is obtained, then

$$\frac{X}{R} = \frac{A}{B} \quad \text{when} \quad \frac{A}{B} = \frac{a}{b}$$

so

$$X = \left( \frac{A}{B} \right) R$$

To avoid Joule heating from current through the coil and also to maintain sufficient sensitivity, a current of about 0.5 Amp and a D-C
Figure 9. A assembly diagram of Kelvin Bridge.
voltage of 0.2 volts was found to be appropriate and was used throughout this study. A Kepco power supply and a John Fluke Mfg. Co., Inc. Model 840A electronic galvanometer with 1 namp sensitivity were used.

The specimens for resistivity measurement were helical coils 0.7 mm in diameter made from cold drawn wire 25 cm long and 0.415 mm in diameter. Those coils were recrystallized at or above 800°C to create a fine grain size (≈50μ). Two current and two potential leads were spotwelded on each side of the nitrided wire. The coil was strain free and supported by an insulated quartz rod on the holder. The resistivity was measured at −195°C by dipping the whole sample into liquid nitrogen. The temperature was monitored at the center of the sample holder by a thermocouple. A standard pure iron sample was used to calibrate the bridge system.

The resistivity was calculated from the length and radius of the wire. The radius was measured on a microprojector which gave readings down to 0.0001". This yielded an accuracy of about ± 0.5% for a 0.415 mm wire. The length was determined from measurement of the weight of the coil.

In materials with a cubic crystal structure, the resistivity is not affected by the preferred orientation in the recrystallized cold drawn wire. Actually it is the same for polycrystals and single crystals, apart from a small extra contribution in a polycrystal that may sometimes arise because of grain boundaries. The shape and size effect can be ignored because the diameter of the wire is much larger (10^6 times) than the mean free path of the conduction electrons.
in iron at \(-195^\circ\mathrm{C}\).\(^{(48,49)}\) The scattering from surfaces will not have a significant contribution to the total resistivity.

F. X-ray Techniques and Procedures

The lattice parameters of the samples were obtained using Debye-Sherrer powder pattern films. The films were taken in a 114.6 mm camera with Co $K_\alpha$ radiation and an Fe filter. A Gandolfi camera,\(^{(50)}\) which applies a second rotation axis inclined at 45° to the ordinary Debye-Scherrer camera rotation axis, was used in this study to obtain more uniform diffraction lines from nitried polycrystalline samples. The measurements were primarily made using wires and strips cut from nitried foil samples. A very clean background was obtained from using ILFORE "G" film as well as evacuation of the camera chamber by a mechanical vacuum pump to decrease the air scattering.

The lattice parameter values were obtained by using the Nelson-Riley\(^{(51)}\) extrapolation technique which fits the lattice parameter $a_0$ of each (hkl) reflection with the Nelson-Riley parameter \(2\sqrt{\cos^2\theta/\sin \theta + \cos^2 \theta/2}\). This method offers a precision as high as 1 part in 50,000.\(^{(52)}\) For some of the nitried samples only the higher angle peaks were employed in the extrapolation because it was impossible to use all of the peaks due to non-uniform intensity distribution for the low-angle peaks.

G. Transmission Electron Microscopy

Observation of the microstructure of homogeneous precipitation in the nitried materials was performed on thin foils using a Philips
EM400 transmission electron microscope. An accelerating voltage of 120 kV was used in this study.

Sample preparation was accomplished by electropolishing the samples. The nitrided foils had a starting thickness of 0.42 mm. They were thinned to 0.1 mm in an electrolyte mixture of 10% perchloric acid and 90% acetic acid at 16°C with 35 V and 0.2 amp/cm current density. To do this pre-thinning, a stainless steel tweezer was used as the anode to hold the foil and a pair of parallel stainless steel plates were used as the cathode in a 300 ml beaker. The edges of the sample were coated with stop-off enamel to protect against preferred edge attack. After pre-thinning to 0.1 mm, the foils were cut to 3 mm diameter discs by an electrical discharge spark cutter. Final thinning was done on a Tenupol jet polish unit at 45 V, 0.12 amp and medium flow rate (4-5 units) in a 7% perchloric acid and 93% acetic acid at 18°C. A photo-cell was used to stop the polish when the first hole occurred. A reasonably large thin area around the hole was created for examination in the microscope.

H. Hardness Measurement

The measurement of Vickers microhardness was achieved on metallographically polished specimens using a 200 g load. A Micromet microhardness tester was used with a square-based diamond pyramid indenter.

Both cross sections of foils and wires were examined. The 0.415 mm wires were secured and re-enforced by putting them into brass holders
and then mounted in Bakelite. The hardness profile was measured across a line on the cross section of the samples.
CHAPTER III
RESULTS AND DISCUSSION

A. General Behavior

Constant activity nitriding of Fe-Mo and Fe-V alloy was performed on thin foils or wires in a \( \text{NH}_3/H_2 \) gas atmosphere from 400°C to 600°C. The nitrogen concentration was observed to increase gradually up to saturation as nitriding proceeded. Typical nitrogen weight gain curves are shown in Fig. 10 and Fig. 11 for Fe-V and Fe-Mo alloys, respectively. The amount of nitrogen and time required to reach saturation increase with concentration of the alloying element, and both parameters are considerably greater than for pure iron. Table IV shows the amount of nitrogen present in fully nitrided samples for three different conditions. \( N_t \) is total nitrogen, in atomic percent after saturation. \( N_\alpha \) is the equilibrium solubility of nitrogen in pure \( \alpha \)-iron under the same nitriding conditions. Values for \( N_\alpha \) were calculated from the data of Podgurski and Knechtel.\(^{(55)}\) \( \Delta N_{\text{exc}} \) is the excess nitrogen calculated by assuming the ferrite matrix contains the dissolved nitrogen expected for pure iron under the same nitriding conditions and all the vanadium and molybdenum is precipitated in the stochiometric ratios. \( N/V = 1 \)\(^{(26)}\) and \( N/Mo = 2/3 \)\(^{(19,25)}\), respectively. \( \Delta N/M \) is the atomic ratio of nitrogen associated with substitutional solute to substitutional solute content, i.e., \((N_t - N_\alpha)/\%\text{Mo or } V\). The excess nitrogen \( \Delta N_{\text{exc}} \) increases with increasing alloy element concentration and decreases with increasing temperature. The excess nitrogen most likely resides in the strain
Figure 10. Typical nitrogen weight gain curves of 0.42 mm diameter Fe-V wires nitrided at 570°C in 7NH₃/3H₂.
Figure 11. Typical nitrogen weight gain curves of 0.42 mm diameter Fe-Mo wires nitrided at 500°C in 15NH₃/85H₂.
at 500°C
15NH₃/85H₂

$\% \text{N}$

NITRIDING TIME (hr.)

$\Delta$ Fe - 2.2 at. %Mo

$\circ$ Fe - 3.0 at. %Mo
<table>
<thead>
<tr>
<th>Alloy (at.%)</th>
<th>500°C, 15NH₃/85H₂</th>
<th>550°C, 7NH₃/93H₂</th>
<th>570°C, 7NH₃/93H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nₜ (at.%)</td>
<td>Nα (at.%)</td>
<td>ΔNₑxc (at.%)</td>
</tr>
<tr>
<td>Fe-1.1%</td>
<td>1.50</td>
<td>0.14</td>
<td>0.26</td>
</tr>
<tr>
<td>Fe-2.2%</td>
<td>3.25</td>
<td>0.14</td>
<td>0.91</td>
</tr>
<tr>
<td>Fe-3.3%</td>
<td>4.82</td>
<td>0.14</td>
<td>1.38</td>
</tr>
<tr>
<td>Fe-2.2%Mo</td>
<td>1.85</td>
<td>0.14</td>
<td>0.24</td>
</tr>
<tr>
<td>Fe3-3.0%Mo</td>
<td>2.42</td>
<td>0.14</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Table IV. The amount of nitrogen after fully nitriding at three different nitriding conditions. Nₜ is total nitrogen, Nα is the equilibrium solubility of nitrogen in pure iron under the same nitriding conditions. ΔNₑxc is "excess" nitrogen. ΔN is the amount of nitrogen associated with substitutional solute. M is the substitutional solute concentration of the alloy. Atomic percent is used throughout.
fields around clusters. Thus, the strain fields of the clusters are expected to change in the same sense as $\Delta N_{\text{exc}}$. This suggests that the strain fields around clusters will be increased by an increase in alloy element concentration or a lowering of nitriding temperature. It is also noted that, at $500^\circ\text{C}$, the ratio $\Delta N/V = 1.2-1.5$ and $\Delta N/Mo = 0.8$. At $550^\circ\text{C}$ and $570^\circ\text{C}$, $\Delta N/V = 1.0-1.2$. This is consistent with the previous assumption of clusters having stoichiometric ratios of $N/V = 1$ and $N/Mo = 2/3$. The values of $\Delta N/V$ and $\Delta N/Mo$ are slightly larger than stoichiometric ratios in cluster as expected, because it takes those excess nitrogen into account.

Values of lattice parameters for nitrided Fe-Mo and Fe-V alloys are shown in Fig. 12. The solid line represents the increase in lattice parameters with nitrogen for iron nitrogen solid solution obtained from data for $\alpha$-nitrogen-martensites. The average change due to N may be estimated as follows:

$$\Delta a_0(N) = 0.0070 \pm 0.0005 \text{Å per N at. pct.}$$

This value is a upper limit of lattice parameter change due to one atomic percent nitrogen in Fe-V and Fe-Mo.

The hardness of the materials also increases as nitriding proceeds. Fig. 13 illustrates the typical increase in mean hardness and overall nitrogen concentration of a 0.42 mm diameter Fe-Mo (3at.%) wire nitrided at $500^\circ\text{C}$ in $15\text{NH}_3/85\text{H}_2$. The maximum hardness $= 774$ (kg/mm$^2$), was reached upon saturation with 2.4at.% nitrogen after 28 hours. The microhardness behavior of Fe-V and Fe-Mo are completely different (Fig. 14 and Fig. 15)
Figure 12. Variation of $\Delta a_o(N)$ with nitrogen content for various Fe-Mo and Fe-V alloys nitried between $500^\circ C$ to $580^\circ C$. 
Figure 13. The typical increase in mean hardness and overall nitrogen concentration of a 0.42 mm diameter Fe-Mo(3.0at.%) wire nitrided in 15NH₃/85H₂ at 500°C.
Figure 14. The hardness profiles for Fe-3.3at.

%V wire nitried in 7NH₃/93H₂ at 570°C.
Figure 15. The hardness profiles for Fe-3.0at.%Mo wire nitrided in 15NH₃/85H₂ at 500°C.
Load = 200 g

--- 0 h.
× 35 min.
○ 1 h.
□ 2 h.
◇ 6 h.
△ 9 h.
♦ 11 h.
▼ 28 h.
due to differences in nitriding kinetics and morphology. A hard subscale (case) forms in Fe-V alloys during constant activity nitriding while Fe-Mo alloys form a more uniform hardness profile. The hardness of Fe-V-N in the case or subscale region immediately reaches maximum hardness while the unnitried region stays at the original hardness level of the unnitried binary alloy. The hardness front is a sharp boundary separating the nitried and unnitried regions, advancing progressively toward the center as nitriding proceeds. For Fe-Mo alloys, a gradual build-up in hardness occurs across the specimens until maximum hardness is reached; no case is formed.

The difference in nitriding behavior between Fe-V and Fe-Mo alloys can be explained by a difference in nucleation rate of substitutional-interstitial clusters. In Fe-V alloys, V and N atoms associate very quickly to fulfill the equilibrium solubility product for V-N clusters.\(^{58,59}\) The driving force for V-N cluster formation is so large that the N atoms react with V atoms until essentially all the V atoms are consumed and local equilibrium is established before the hardness front progresses. Thus, in Fe-V alloys, the hardness front coincides with the nitrogen diffusion front (Fig. 16(a)). In Fe-Mo alloys, the situation is different due to a reduced tendency for Mo atoms to interact with N. The flux of nitrogen is larger than the rate of association with Mo and diffusion front leads the hardness front (Fig. 16(b)).

The peak hardness reached upon fully nitriding of alloys. For simplification, we can assume that the relation between the microhardness \(H_v\) and yield strength, \(Y\), of the material holds;\(^{60}\)
Figure 16(a)

Schematic of the concentrations of the nitride phase, V and N

Figure 16(b)

Schematic of the concentrations of the nitride phase, Mo and N
\[ H_v = 3Y \]

The stress required to move dislocations through the zones varies inversely with interparticle spacing, \( \hat{d} \), which in turn decreases with zone density. \( \hat{d} \) is inversely proportional to the square root of alloy concentration \( \sqrt{M} \). (b) Fig. 17 shows the hardness as a function of alloying element content in Fe. It gives a straight line through the origin.

During constant activity aging between 400°C to 600°C in dilute Fe-Mo and Fe-V alloys, G.P. zones developed. Fig. 18 and Fig. 19 show thin film transmission electron micrographs of this stage. Fig. 18, after full saturation with nitrogen and at peak hardness of Fe-Mo (3.0at.%), shows G.P. zones forming on (100)\( _\alpha \) matrix-planes and pronounced streaking between matrix diffraction spots in the \( <100> _\alpha \) directions. Fig. 19 illustrates a typical microstructure of fully nitrided Fe-V (3.3at.%) alloy containing G.P. zones which are much smaller than in Fe-Mo-N and barely visible, but bright streak in diffraction pattern can be seen clearly in \( <100> _\alpha \) direction. Upon prolonged heating of those materials, G.P. zones in Fe-Mo start to coarsen and order and some of them transform to an intermediate partly coherent \( \alpha'' - Fe_{16}N_2 \) phase. Fig. 20 shows a bright field image and diffraction pattern of some \( \alpha'' - Fe_{16}N_2 \) particles. At this stage, x-ray powder diffraction film also shows an \( \alpha'' - Fe_{16}N_2 \) pattern. Subsequent heating to higher temperature causes \( \gamma - Mo_2N \) and the equilibrium precipitate, \( n - Fe_3Mo_3N \), to appear. The G.P. zones in Fe-V alloys are very stable, persisting during prolonged heating between 500°C - 570°C for more than a week. The equilibrium precipitate f.c.c. VN forms in the ferrite with the Baker-Nutting orientation
Figure 17. The microhardness as a function of alloying element content in Fe. \( \Delta H_v = H_v(\text{Fe-M-N}) - H_v(\text{Fe}) \)
Figure 18(a)  Bright field image from Fe-3.0at.%Mo (0.5 mm thick) foil nitrided in 15NH$_3$/85H$_2$ at 500°C for 96 hours. Beam along [001]$_\alpha$.

Figure 18(b)  Diffraction pattern of the sample in 18(a), it shows continuous $<100>\alpha$ streaking.
Figure 19(a) Bright filed image from Fe-3.3at.%V (0.42 mm thick) foil nitrided in 15NH₃/85H₂ at 500°C for 165 hours.

Figure 19(b) Diffraction pattern shows continuous <100> streaking.
Figure 20. The bright field image and diffraction pattern from Fe-3.0 at.%Mo alloy (0.42mm thick foil) in 15NH₃/85H₂ at 500°C. It shows partly coherent, intermediate phase with a b.c.t. α''-Fe₁₆N₂ structure. Beam along [001]₀.

Figure 21. The bright field image of Fe-1.1 at.%V nitrided in 15NH₃/85H₂ at 500°C for 165 hours and overaged for 24 hours at 900°C. Large f.c.c. VN precipitate can be seen.
upon aging at 900°C for 24 hours. Fig. 21 shows a bright field image of this phase.

B. Nitriding Kinetics

The internal nitriding process is analogous to internal oxidation in which interstitial atoms also diffuse into an alloy and react with substitutional solute atoms to precipitate a second phase. A subscale of depth x from the surface is formed. The kinetics of internal nitriding can be simplified if the following approximations can be made: (61)

a) Diffusivity of the substitutional element is negligible.

b) The reaction only occurs at the boundary separating the nitried and untreated regions.

c) The solubility of nitrogen in α-iron is very small and can be neglected.

Let \( r \) be the width of the untreated region, \( R \) the specimen thickness, \( \left[ N_M \right] \) the equilibrium solubility of nitrogen in iron (which equals \( N_\alpha \) in Table IV), \( \left[ M_K \right] \) the initial concentration of alloy element, \( D_N \) the diffusivity of nitrogen, \( n \) the ratio of nitrogen atoms to \( M \) atoms in the precipitate and \( t \) the nitriding time. The following rate equation can be used as first-order approximation: (61)

\[
\frac{1}{2}R^2 - \frac{1}{2}r^2 + r^2 \ln \left( \frac{r}{R} \right) = 2 \frac{\left[ N_M \right]}{\left[ M_K \right]} D_N t \ln \left[ \frac{M_K}{N_M} \right]
\]

(14)

Letting

\[
S = \frac{r^2}{R^2},
\]
the rate equation can be written:

\[ (1-S) + S \ln S = \frac{4 \left[ N_Z \right] D_N t}{\left[ N_Z \right] R^2} . \] (15)

As shown in Fig. 22, a plot of \((1-S) + S \ln S\) vs. \(t\) gives a linear relation for Fe-3.3at.\%V and Fe-2.2at.\%V nitrided at 570°C. \(D_N\) can be estimated from the slope if we take \(n = 1.2\) for Fe-3.3at.\%V and \(n = 1.1\) for Fe-2.2at.\%V (see Table IV). The diffusivities of nitrogen calculated from this data are \(1.04 \times 10^{-7}\) cm\(^2\)/sec and \(1.18 \times 10^{-7}\) cm\(^2\)/sec for Fe-3.3at.\%V and Fe-2.2at.\%V, respectively, in good agreement with the value of 1.08 \(\times 10^{-7}\) cm\(^2\)/sec obtained by Leslie. \(^{62}\)

We also can see in Fig. 10 that the time required to reach saturation is inversely proportional to the \(V\) concentration, which is consistent with the internal oxidation equation. Quantitative analysis gives satisfactory results if the time required to reach 90% saturation is used. \(^{63}\)

The nitrided Fe-Mo does not form a hard subscale as nitrided Fe-V like previously described. It can not be described by the internal oxidation equation and no model for such behavior has yet been developed. \(^{63}\)

C. Resistometry

A series of resistivity measurements was carried out on Fe-Mo and Fe-V sample under a variety of nitriding conditions. The results are shown in Figs. 24-27. The so-called "abnormal" increase in resistivity during the early stage of pre-precipitation in some age-hardening alloys
Figure 22. \((1-S+S \ln s) R^2\) against time for Fe-V wires nitrided in \(7\text{Ni}_3/93\text{H}_2\) at 570°C.
Figure 23. The time required to reach 90\% saturation, $t_{0.9}$, against V concentration for Fe-V wires nitried in 7NH$_3$/93H$_2$ at 570°C.

Value $D_N=7.3 \times 10^{-8}$ cm$^2$/sec calculated from slope of the straight line by using equation (15).
Nitrided in 7NH₃/93H₂

at 570°C
Figure 24. The resistivity curves of Fe-V wires during constant activity nitriding in 15NH₃/85H₂ at 500°C.
Figure 25. The resistivity curves of Fe-V wires during constant activity nitriding in $7\text{NH}_3/9\text{H}_2$ at $550^\circ\text{C}$
Figure 26. The resistivity curves of Fe-V wires during constant activity nitriding in 7NH₃/93H₂ at 570°C.
Figure 27. The resistivity curves of Fe-Mo wires during constant activity nitriding in 15NH₃/85H₂ at 500°C and overaged at 500°C and 550°C.
is usually only a few tenths of 1 $\mu\Omega\cdot\text{cm}^{(14,40)}$, much smaller than the resistivity changes observed in the present study and thus probably of different physical origin.

The change of resistivity caused by N in this study is approximately between 1.5 to 3.5 $\mu\Omega\cdot\text{cm}$ per atomic percent nitrogen. This is smaller than the contribution by free N atoms in iron solution$^{(64)}$, indicating that the nitrogen is not randomly distributed in the $\alpha$-Fe matrix.

In the Fe-V alloys, the nitried and unnitrided regions are separated by a sharp boundary assuming that any transition region between them is of negligible width. Let us denote $\rho_s$ as the resistivity of the unnitrided region and $\rho_{1-s}$ as the resistivity of the nitrided region. This is analogous to a pair of resistors connected in parallel. Thus,

$$\rho = \frac{\rho_s \rho_{1-s}}{S\rho_{1-s} + (1-S)\rho_s} \quad (16)$$

$S$ was defined previously and $\rho$ is the overall resistivity. By assuming $\rho_s$ equals the resistivity of the original unnitrided sample and $\rho_{1-s}$ equals the resistivity of the fully nitrided sample before any over-aging occurs, we can calculate the total resistivity by knowing $S$ from hardness measurements. The result is shown in Table V for Fe-3.0at.%V. The good agreement between the experimental data and the calculated curve suggests that the clusters in this Fe-V alloy do not coarsen before full saturation occurs.

Such an analysis will not apply to Fe-Mo alloys, because they do not form a subscale. The resistivity of Fe-Mo alloys reach maxima before
| Alloy        | Time
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(at.%)</td>
<td>(hours)</td>
</tr>
<tr>
<td>Fe-3.3at.ZV</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
</tr>
<tr>
<td>Fe-2.2at.ZV</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
</tr>
</tbody>
</table>

Table V. The calculated resistivity $\rho_{cal}$ compared with observed resistivity $\rho_{obs}$. 
the samples are fully nitrided, a result consistent with the lattice parameter results and also the TEM results, which show fully nitrided Fe-Mo samples having bigger cluster sizes than corresponding Fe-V samples.

Table VI shows the resistivity maxima of samples nitrided under different conditions. $\Delta \rho_{\text{max}}$ is the resistivity of a fully nitrided wire reduced by the resistivity of pure Fe, at $-195^\circ C$.\(^{(65)}\) For a constant temperature, $\Delta \rho_{\text{max}}$ increases with the concentration of the alloy but the ratio $\Delta \rho_{\text{max}} / M$ is approximately constant. For an explanation, consider equation (12) in Chapter I. The equation gives the resistivity of a nitrided Fe-based alloy. We can rewrite the equation (12) as follows:

$$\rho(\text{Fe-M-N}) = \left[ \frac{n_S}{N_S} - Z \int_0^\infty c_S z g(z) dz \right] \Delta \rho_S + \left[ \frac{n_N}{N_N} - Z \int_0^\infty c_N z g(z) dz \right] \Delta \rho_N$$

$$+ Z \int_0^\infty \Delta \rho_Z(z) g(z) dz$$

In this equation, the first and second terms are fairly small comparing them with the third term due to the complete depletion of the solute atoms by forming clusters. We know $\Delta \rho_Z(z)$ is the resistivity contribution due to the clusters having $Z$ atoms and is not dependent on $M$. $g(z)$ is a size distribution function which is not a function of $M$. $n_S$ is the total number of the solutes per unit volume. This is proportional to the atomic percent of alloying element $M$. $n_N / M$ is also a constant (see Table I) at constant temperature. $c_S$ and $c_N$ are constant, and it must be concluded that $Z$ is proportional to $M$. Therefore, the number of clusters is a function of alloy concentration. This is quantitatively
<table>
<thead>
<tr>
<th>Alloy</th>
<th>500°C</th>
<th>15NH₃/85H₂</th>
<th>550°C</th>
<th>7NH₃/93H₂</th>
<th>570°C</th>
<th>7NH₃/93H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M at%)</td>
<td>Δρ max</td>
<td>Δρ max/M</td>
<td>Δρ max</td>
<td>Δρ max/M</td>
<td>Δρ max</td>
<td>Δρ max/M</td>
</tr>
<tr>
<td>Fe-1.1%V</td>
<td>8.19</td>
<td>7.44</td>
<td>5.54</td>
<td>5.04</td>
<td>4.96</td>
<td>4.49</td>
</tr>
<tr>
<td>Fe-2.2%V</td>
<td>16.64</td>
<td>7.56</td>
<td>11.44</td>
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<tr>
<td>Fe-3.3%V</td>
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<td>7.38</td>
<td>15.44</td>
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<tr>
<td>Fe-3.0%Mo</td>
<td>12.84</td>
<td>4.28</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Table VI. The resistivity $\Delta \rho_{\text{max}}$ is the resistivity of a fully nitrided wire reduced by the resistivity of pure Fe, at -195°C. M is the alloying element concentration. $\Delta \rho_{\text{max}}/M$ is close to a constant at constant temperature.
consistent with $\Delta N_{\text{exc}}$ increasing with alloy concentration in Table IV. Further, at any constant temperature, the size distribution $g(z)$ is the same in all different alloy concentration. This is consistent with the conclusion of hardness measurements (see Fig. 17). Both the size distribution and average size are functions of temperature. Also, if the temperature increases, both $\Delta \rho_{\text{max}}$ and $\Delta \rho_{\text{max}}/M$ will decrease. This is because the average size of the cluster increases while the number of the clusters decrease at increased temperatures. This is consistent with the results Wagner and Brenner (29) who measured the cluster size distribution and density after nitriding at different temperatures in Fe-2.0at.%Mo. Comparison shows that $\Delta \rho_{\text{max}}$ and $\Delta \rho_{\text{max}}/M$ are larger for Fe-V alloys than for Fe-Mo alloys. This indicates that the average size of clusters in Fe-Mo-N is larger than in Fe-V-N while the number of clusters in Fe-V-N is larger than in Fe-Mo-N.

The overaging behavior of nitrided samples is also shown in Fig. 19-22. The resistivity decreases in Fe-Mo wires before saturation is achieved. The overaging behavior is shown at two different temperatures. The solid line represents overaging at 500°C and 15NH$_3$/85H$_2$ and the dotted line represents overaging at 550°C and 10NH$_3$/90H$_2$. As expected, the resistivity drops faster at 550°C than at 500°C because cluster coarsening is faster at the higher temperature. Extra x-ray powder diffraction lines corresponding to the $\alpha''$-Fe$_{16}$N$_2$ structure which is semi-coherent, begin to appear for both samples after 28 hours of nitriding.

In the Fe-V alloy, x-ray powder diffraction patterns do not show extra diffraction lines, however. Iron lines appear upon overaging.
The amount of nitrogen present in the samples slowly decreases during overaging. The resistivity decrease is caused by both nitrogen loss and coarsening of the clusters. Actually, this behavior represents two aspects of one phenomenon. The excess nitrogen resides in the strain fields around the clusters, and coarsening of the clusters results in a reduction of the total strain field, i.e., the number of available sites for excess nitrogen. Thus, the nitrogen content decreases upon coarsening causing a decrease in resistivity. There appear to be no intermediate phases occurring in Fe-V-N during overaging at 500°C-570°C for a week. Rather, small clusters redissolve and large VN clusters start to grow.

A hydrogen reduction experiment was performed in Fe-Mo-N wires. The resistivity behavior and weight loss are shown in Fig. 28. Fe-Mo (3.0at.% and 2.2at.%) wires were nitrided at 500°C and 15NH₃/85H₂ for 32 hours before reducing in a pure hydrogen atmosphere at 500°C for up to 100 hours. In Fig. 28, the rate of N loss slows down after lost 0.45at.%N in both samples. This is the equilibrium amount of nitrogen in solution that does not form clusters. The value 0.45at.%N, is consistent with the values calculated from Table IV which gave 0.38at.%N for Fe-2.2at.%Mo and 0.42at.%N for Fe-3.0at.%Mo to form clusters with N/Mo = 2/3. The nitrogen continues to decrease at a slow rate during further reduction treatment. Presumably the nitrogen has diffused out of the clusters at this stage. The resistivity measurement offers unique evidence for this. During the early stage of reduction, the resistivity suddenly drops due to loss of nitrogen from the solution. Prolonged annealing in hydrogen, up to a week, results in only a slight
Figure 28. Resistivity behavior and nitrogen weight loss of Fe-Mo-N wires during hydrogen reduction at 500°C for 100 hours after nitrided in 15NH₃/85H₂ at 500°C for 32 hours.
\[ \rho \text{ (} \mu \Omega \text{-cm)} \]

- Fe-3.0 at.\% Mo
- Fe-2.2 at.\% Mo

\( \rho \)

N at.\%

TIME (hr.)

% at.\% N

0  10  20  30  40  50  60  70  80  90  100

0.0  1.0  2.0  3.0
further in resistivity change. This slight decrease in resistivity is caused by loss of interstitial nitrogen in the clusters. This results in reduced strain fields around the clusters. Fig. 29 shows the amount of resistivity decrease vs. nitrogen loss in the wire. A change of slope occurs at 0.45at.%N in both samples. The straight line portion gives a slope of 3.5μΩ-cm/at.%N.

D. Static Displacement

It was originally intended to measure the static displacement caused by introduction of nitrogen and any subsequent changes during overaging and hydrogen reduction. This was to be done using integrated intensity measurements of Bragg peaks to determine mean-square displacements employing polycrystalline foil samples. Such measurements require a sufficiently fine grain size and uniform grain orientations, i.e., non-textured samples, to yield reliable data. A sufficiently fine grain size, below 50μ, was achieved by appropriate control of the recrystallization temperature and time. However, production of samples free of texture was never fully accomplished. Several methods were tried to eliminate the recrystallization texture. These included: (a) Cyclic heat treatment - For iron alloys containing less than 1.0at.%Mo or 1.5at.%V the possibility of repeated normalization into the austenite region exists. The narrowness of the γ-loop precludes this option for higher concentrations of Mo and V. The inverse pole figure method was used to check the degree of texture after each heat treatment. Although a dramatic decrease in texture and grain size resulted after this cycling
Figure 29. The resistivity decrease vs. nitrogen content decrease during hydrogen reduction at 500°C for 100 hours after nitrided in 15NH₃/85H₂ at 500°C for 32 hours.
H₂ Reduction
at 500°C

\[ \Delta \rho (\mu, \Omega \text{ cm}) \]

\[ \Delta N_{\text{at} \%} \]

- \( \Delta \) Fe-5 Mo
- \( \circ \) Fe-4 Mo
treatment, it was not sufficient for high quality integrated intensity data. (b) Analytical method - An analytical method\textsuperscript{(66,67)} was developed that consisted of making inverse pole figure measurements on the iron-base alloy foils prior to and after nitriding. This assumes that the texture remains constant during the nitriding treatment. The inverse pole method consists of forming a ratio of integrated intensities between the actual sample and an ideally random standard. This method was found to be unsatisfactory because the texture was found to change during nitriding at 500\textdegree{}C due to grain growth. (c) Filing under liquid nitrogen - Although the filing of a nitried sample at liquid nitrogen temperature can reduce the cold work from filing through embrittlement of the material, considerable line-broadening was still observed on powder diffraction films. The amount of distortion caused by cold work will, in addition to making peak integrations less reliable, add an extra term to the static displacement which can not be separated from the part caused by clustering of N and alloy atoms. (d) Resistivity measurement - A preliminary result can be reached using the resistivity data, if it is assumed that the resistivity is completely caused by the distortion around the clusters. Calculation is based on the equation (8):

\[
\rho_{st} = \left[ \frac{\rho_{th}}{u_{th}^2} \right] u_{st}^2
\]

\[
\frac{\rho_{th}}{u_{th}^2} = 3015
\]

The effective static displacement of Fe-3.0at.%Mo can be estimated.
The results are listed in Table VII. The quantity \( \overline{u}_{st} \) is the change of resistivity due to nitrogen, i.e., it is equal to the maximum resistivity of a fully nitried sample minus the resistivity of the original iron-based binary alloy. \( u_{st} \) and \( B_{st} \) are the static displacement and Debye-Waller factor, respectively, due to elastic distortion in the matrix created by the coherency of clusters. The values calculated for \( u_{st} \) are about an order of magnitude less than the value measured by Driver and Papazian who reported an elastic displacement around the cluster in a nitried Fe-1.7at.%Mo alloy as between 0.3-0.9\( \AA \) from electron diffraction intensity data. However, the electron diffraction approach measures directly local areas, while resistivity, x-ray diffraction and neutron diffraction measure bulk volume averages. The effects on the Debye-Waller factor can be seen in Table VII. For Fe-3.0at.%Mo and Fe-2.2at.%Mo the \( B_{st} \) is too small to be measured. This is why neutron diffraction intensity does not show any significant attenuation. But a reasonable estimation of the local static displacement can be calculated by knowing the volume fraction, \( V_f \), of the zones. Let us assume \( (\overline{u}_{st})_i \) is static displacement around cluster \( i \), we can write the volume average static displacement, \( u_{st} \), as follows:

\[
\overline{u}_{st} = \frac{1}{V} \sum_i (\overline{u}_{st})_i \Delta V_i .
\]

Where the summation is over the whole material. \( \Delta V_i \) is the volume of the material and \( \Delta V_i \) is the volume of the strain field around the cluster \( i \). Assuming \( (\overline{u}_{st})_i \) attenuates very fast, \( (\overline{u}_{st})_i = 0 \) when \( r >> r_o \), (\( r_o \) is the size of the cluster, then
<table>
<thead>
<tr>
<th>Alloy (at.%</th>
<th>$\rho_{st}$</th>
<th>$u_{st}$</th>
<th>$B_{st}$</th>
<th></th>
<th>$\rho_{st}$</th>
<th>$u_{st}$</th>
<th>$B_{st}$</th>
<th></th>
<th>$\rho_{st}$</th>
<th>$u_{st}$</th>
<th>$B_{st}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-1.1ZV</td>
<td>5.40</td>
<td>0.042</td>
<td>0.141</td>
<td>2.70</td>
<td>0.030</td>
<td>0.071</td>
<td>2.15</td>
<td>0.027</td>
<td>0.056</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-2.2ZV</td>
<td>12.05</td>
<td>0.063</td>
<td>0.316</td>
<td>6.85</td>
<td>0.048</td>
<td>0.179</td>
<td>6.05</td>
<td>0.045</td>
<td>0.158</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-3.3ZV</td>
<td>18.45</td>
<td>0.078</td>
<td>0.483</td>
<td>9.60</td>
<td>0.056</td>
<td>0.251</td>
<td>7.50</td>
<td>0.050</td>
<td>0.196</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-2.2%Mo</td>
<td>3.75</td>
<td>0.035</td>
<td>0.098</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-3.0%Mo</td>
<td>5.10</td>
<td>0.041</td>
<td>0.134</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Table VII. The static displacement $u_{st}$ calculated from the resistivity $\rho_{st}$ by equation

$$\rho_{st} = (\rho_{th}/\sqrt{u_{th}^2})u_{st}^2$$

The Debye-Waller's factor $B_{st}$ is also shown in the table.
\[
\tilde{u}_{st} = \sum_i \left( \tilde{u}_{st} \right)_i \left( \frac{\Delta V_i}{V} \right) = \left< \tilde{u}_{st} \right>_i \frac{\Delta V_i}{V}
\]

\(<\tilde{u}_{st}>\) is the average static displacement around a cluster. From Driver's paper, we can have \(\sum_i \Delta V_i / V = V_f = 0.06\) which is the volume fraction of the cluster. The value estimated for a cluster in Fe-3.0at.\%Mo after being fully nitrided is then 0.68 Å which is in excellent agreement with the 0.58 Å value estimated by Driver.
CHAPTER IV
CONCLUSIONS

(1) The total volume of the strain field around the clusters is affected by alloy concentration and nitriding temperature. The volume of elastically strained material increases material with solute concentration and decreasing nitriding temperature.

(2) There is a stronger interaction between V and N atoms than between Mo and N in iron-based alloys during constant activity aging.

(3) The compositions of clusters have ratios N/Mo = 2/3 in Fe-Mo alloys and N/V = 1 in Fe-V alloys.

(4) The density of clusters is proportional to the substitutional solute concentration.

(5) The cluster size distribution $g(z)$ after full nitriding is only a function of nitriding temperature. It is not dependent on composition for dilute iron-based alloys. The average size of clusters is about the same for all solute concentrations at constant temperature.

(6) In the early stages of precipitation, coherency of the zones creates elastic strain fields for which the static displacement is about $0.68\,\text{Å}$ around the zone for a nitried Fe-3at.%Mo.

(7) Resistivity measurement is a useful tool for study of the early stage of nitriding in constant activity aged materials.
REFERENCES

45. A. F. Azuaje, Private Communication.