Precipitation Hardening in Fe-Ni Base Austenitic Alloys

by

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ABSTRACT

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The precipitation of metastable Ni_3X phases in the austenitic Fe-Ni-base alloys has been investigated by using various combinations of hardening elements, including Ti, Ta, Al, and Nb. The theoretical background on the formation of the Ll_2 type, γ' , and D0_{22} type, γ'' , transition precipitates has been summarized based on three controlling factors: atomic size, compressibility, and electron/atom ratio. A model for their appearance is proposed from an analysis of static concentration waves ordering the fcc lattice. It is established experimentally that the ordered structure of metastable precipitates will change from the triangularly ordered γ' , to the rectangularly ordered γ'' , as the atomic ratio $(\text{Ti}+\text{Al})/(\text{Ta}+\text{Nb})$ decreases. The concurrent precipitation of γ' and γ'' occurs at 750°C when the ratio is between 1.5 and 1.9.

The aging behavior of these alloys was studied over the temperature range of 500°C to 900°C . Typical hardness curves show a substantial hardening effect due to precipitation. An excellent combination of strength and fracture toughness can be developed by employing double aging techniques. It is found by transmission electron microscopy (TEM) that the growth of these coherent intermediate precipitates follows the

power law with the aging time t : $t^{1/3}$ for the spherical γ' particles; and $t^{1/2}$ for the disc-shaped γ'' . The equilibrium β phase is observed to be able to nucleate on the surface of imbedded carbides.

The addition of 5 wt pct Cr to the age-hardened alloys provides a non-magnetic austenite which is stable against the formation of mechanically induced martensite. It has been shown that the Cr addition retards the aging kinetics of the precipitation reactions, and also suppresses intergranular embrittlement caused by the high temperature solution anneal. The aging kinetics are also found to be influenced by solution annealing treatments.

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I. INTRODUCTION

The study of the precipitation reaction in alloy systems is important from both a scientific and a technical standpoint, since it involves not only the physics of the solid state phase transformation but also the enhancement of the mechanical properties of materials. Precipitation hardening is relatively pronounced in most face-centered cubic (fcc) alloys, such as nickel, aluminum, copper, and austenitic steel, in which no other solid state phase transformation, such as the martensite reaction, takes place; but it is not at all limited to them. A great deal of research in past years has focused on two-fold questions of how to develop the high density of uniformly-distributed, fine particles out of the alloy solution matrix, and how these particles interact and resist dislocation motion under applied forces. Various general models and some universal theories have been proposed to explain the phenomena observed in alloy systems, and have been successfully verified by experiment. As one would expect, though, each kind of alloy system has its own special characteristics. Thus, in addition to providing further support for existing theories, an investigation of a specific precipitation-hardening system may lead to the discovery of new areas of study, and may help in understanding precipitation reactions and using them to develop alloys of better properties.

A well-known example of a precipitation-hardened steel alloy is the austenitic Fe-Ni base superalloys.¹⁻⁵ These are traditionally strengthened by a $L1_2$ type, ordered fcc precipitate, designated γ' , which was originally identified in Ni-base alloys.^{6,7} The optimum age-hardening alloy contains titanium and aluminum as the hardening elements

and can reach 130 ksi (900 MPa) yield strength at room temperature after isothermal heat treatment to peak hardness. Due to their good creep resistance at moderately elevated temperature, these alloys have been widely used in the manufacture of turbine components.^{8,9} But the useful combination of corrosion resistance, ease of fabrication, high strength, and non-magnetic properties offered by these alloys at low temperature was not fully utilized in the past, largely because of competition from other types of low-cost austenitic steels which achieve a similar strength level after heavy cold work.^{10,11} Recently, however, demand for higher strength, non-magnetic materials has risen due to a need for improved alloys for use in applications such as retaining rings for large electric power generators.¹² The precipitation-hardened Fe-Ni base austenitic alloys are reasonable candidates for these new applications.

The major sources of strengthening by coherent, ordered precipitates are ordering and misfit hardening. The former results from the creation of an antiphase boundary as the dislocation cuts through the precipitate; the latter comes from the elastic strain field which arises due to the difference in lattice parameter between the precipitate and matrix phases. The principal source of strengthening in γ' -bearing alloys is generally believed to be order hardening^{13,14} since the misfit between precipitates and matrix is small. This also explains the spherical shape of γ' particles. On the other hand, some investigators⁶ have argued that the strengthening effect of the coherency strains of the γ' precipitate is also important. By critical hypothesis and experiment, Decker and Mihalisin¹⁷ isolated and measured the effects of coherency strains on nickel-aluminum-ternary element alloys

(see Fig. 1). The maximum response to aging for a given volume fraction of precipitate was a function of the misfit between the matrix and the γ' , the lattice parameter of which can be altered by changing the hardening element. A similar effect of coherency strains has not been reported in Fe-Ni-base alloys.

The maximum hardening achievable with a particular γ' precipitate is related to the attainable precipitate volume fraction and hence tends to increase as the solute content is raised or as the aging temperature is lowered. However, if the solute content (e.g. Ti in Fe-Ni-Ti alloys) is made too high a cellular precipitation reaction will lead to the formation of the equilibrium hcp η -Ni₃Ti along grain boundaries^{4,15,16} with a consequent loss in both strength and ductility. The degree of precipitation may be increased without catastrophic intrusion of the cellular η -phase by lowering the aging temperature, but in this case the kinetics of hardening may become too slow to be practical. A heat treatment technique which helps to avoid both these problems and permits the achievement of higher strengths is the "double-aging" treatment studied by Blower and Mayer² and widely used in the processing of superalloys. In this approach the alloy is given a hardening treatment which involves an aging at relatively high temperature followed by a second aging at lower temperature. The high temperature treatment initiates the precipitation reaction and begins hardening, which is completed during the low temperature treatment. The precise mechanisms of "double-aging" are not well understood, and are investigated further in this work. Previous experience has, however, shown that "double-aging" leads to alloy strength comparable to or exceeding the best achievable at the lower of the two aging temperatures in reasonable aging times.

Cellular precipitation of the equilibrium η -phase initiates at grain boundaries and may be retarded by chemical modifications of the alloy which weaken the catalytic effect of the grain boundary. Boron, sometimes in combination with other elements, is used for this purpose.

The recent development of INCONEL 718¹⁸ and similar Ni-base super-alloys has generated interest in the precipitation reactions which occur when niobium replaces titanium or aluminum as the hardening addition. The major hardening phase in these alloys is a metastable Ni_3Nb phase, which has a DO_{22} ordered, bct structure;^{19,20,21} this phase is designated γ'' to distinguish it from fcc γ' . The cryogenic to intermediate temperature tensile properties of the alloy are remarkably good considering the relatively low volume fraction of the strengthening phase,²² (≈ 20 vol. %). The Nb-rich γ'' precipitation has been successfully introduced into Cu-Ni-²³ and Co-Ni-²⁴ base alloys, but has previously not been found to be a major precipitate in the Fe-Ni-base alloys. Litch and Chaturvedi²⁵ studied the precipitation reactions in Fe-30Ni alloys containing up to 5 wt pct Nb, and found that the main precipitation reaction resulted in the formation of hexagonal Laves phase Fe_2Nb , although a small amount of Ni_3Nb phases also precipitated. The γ'' precipitation in Fe-Ni-base alloys was observed by some French investigators^{26,27} who used tantalum as the hardening element. They also found that the precipitate phase could change from γ'' to γ' , as the Co/Ni ratio of the alloy increased to a critical value. The γ'' -hardened alloys did show significant high hardness after the aging treatment, although no detailed microstructural analysis was reported.

Further systematic studies are required to provide a complete understanding and background for the development and design of practical γ'' -hardened Fe-Ni base alloys.

The present work was undertaken to deepen our understanding of the formation mechanism of the metastable precipitates, γ' and γ'' , in Fe-Ni base austenites, and to apply this understanding in the development of new high strength non-magnetic alloys (> 150 ksi (1035 MPa) yield). In the following classical alloy chemistry theories are summarized, and a model based on ordering theory is proposed to interpret the γ' and γ'' precipitations. A criterion which predicts the transition between γ' and γ'' is obtained experimentally through controlled additions of Ti, Ta, Al, and Nb to an Fe-Ni matrix, and the precipitate morphology and resulting alloy properties are determined. The effect of solution annealing temperature and chromium addition, which enhances the corrosion resistance and the austenite stability is also evaluated.

II. THEORETICAL REVIEW

A. CRYSTAL STRUCTURE OF γ' AND γ''

Figure 2 shows the atomic arrangement of the crystallographic unit cells and close-packed planes of the γ' , $L1_2$ type, and the γ'' , DO_{22} type, phases. The open circles represent the nickel (Ni) atoms, while the marked circles are those of the hardening elements (X). Neglecting the slight distortion which occurs along the c-axis of γ'' due to asymmetry, both crystals can be regarded as ordered fcc structures; these structures can be formed by stacking identical close-packed, ordered $\{111\}$ layers of composition Ni_3X . In the γ' phase, the X-atoms are located at the corners of equilateral triangles and the stacking sequence is $abcabc\dots$. On the other hand γ'' phase has the stacking sequence $abcdef\dots$ of close-packed planes with a rectangular ordering. The two crystal structures may interchange by the $\frac{1}{2} \langle 110 \rangle$ translation of alternative (001) planes which contain X atoms.

The most convenient method is to describe the ordered crystal structure in mathematical form is to represent the atomic distribution as a sum of static concentration waves. In the case of a binary or quasi-binary substitutional solution, the occupation probability $n(\vec{r})$ of finding a solute atom at the site $\vec{r}$ of the crystal lattice can always be expanded in a Fourier series, or a superposition of static concentration waves:

$$n(\vec{r}) = c + \frac{1}{2} \sum_j \left[Q(\vec{k}_j) e^{i\vec{k}_j \cdot \vec{r}} + Q^*(\vec{k}_j) e^{-i\vec{k}_j \cdot \vec{r}} \right] \quad (1)$$

where $\exp(i\vec{k}_j \cdot \vec{r})$ is a static concentration wave, $\vec{k}_j$ is a non-zero wave vector defined in the first Brillouin zone of the disordered alloy,

$\vec{r}$ is a lattice vector, the index j denotes the wave vectors in the first Brillouin zone, $Q(k_j)$ is the amplitude of the j th static concentration wave and c is the atomic fraction of the solute element.

For the γ' phase,

$$n(\vec{r}) = n(x,y,z) = \frac{1}{4} + \frac{1}{4} (e^{i2\pi x} + e^{i2\pi y} + e^{i2\pi z}) \quad (2)$$

and for the γ'' phase,

$$n(\vec{r}) = n(x,y,z) = \frac{1}{4} + \frac{1}{4} e^{i2\pi(2x+z)} + \frac{1}{2} \cos \pi(2x+z) \quad (3)$$

The functions (2) and (3) take only two values on fcc lattice sites;

$n=1$ represents an X atom, and $n=0$ represents a Ni atom.

B. ALLOY CHEMISTRY THEORY

Since the early 1940's, investigators have recognized that useful generalizations can be found which identify the phases present in various alloys and form the basis for a reasonable approach to predicting the effect of individual alloying elements on the occurrence and structure of precipitation phases. The rules derived as a result of extensive observation by many investigators of alloy chemistry,²⁸ are based on three controlling factors: electron/atom ratio, atomic size, and compressibility. Specific factors governing the appearance of γ' and γ'' phases may be summarized as follows:

1. Atomic Size

Hagel and Beattie^{29,30} proposed that coherent precipitation of metastable phases will be inhibited when the lattice misfit between the matrix and the precipitate exceeds ≈ 1.0 pct. This requirement was

demonstrated by Quist et al³¹ who examined the precipitation of metastable Ni_3Nb phases in the Ni-Nb system. The transitional phase was not observed in binary Ni-Nb alloys containing up to 12.5 wt pct Nb under normal conditions of quenching and aging. The results were at first interpreted as an anomaly, since the existence of γ'' phase in commercial Ni-base alloys such as INCONEL 718 (containing only about 3.5 at. pct Nb) suggested a bonding behavior in the Ni-Nb binary system that would promote precipitation of γ'' . It was then suggested that this lack of coherent γ'' in the simple binary system could be accounted in terms of the differences in the lattice constants between the matrix and γ'' precipitates. The lattice constant for pure nickel is 3.524 Å, which is ≈ 3.0 pct smaller than the values for metastable γ'' precipitates ($a = 3.626$ Å, $c/2 = 3.708$ Å). However, the interfacial matching is well within 1.0 pct of INCONEL 718 where it is observed that the presence of ≈ 20 pct each of Cr and Fe, together with small quantities of other alloying elements, expands the a_0 of the matrix to 3.604 Å.³² This observation strongly indicates that proper lattice matching is necessary for the formation of metastable phases.

The atomic size difference between the solute and the solvent has been known to play a significant role in determining phases in alloys. It is also the basis of the famous Hume-Rothery rule³³ that terminal solubility is restricted when the ratio of the atomic radii exceeds about 14%. The applicability of the role of atomic size difference in determining ordered atomic arrangements in complex structure is well documented. Although most of the intermetallic phases which have been investigated are thermodynamically stable, equilibrium phases, existing data for the metastable γ' phase has been interpreted to give the

ratio of atomic radii $R_X/R_{Ni} \approx 1.17$. Since the compressibility of the Ni atom is relatively low due to the filling of the 3d shell, the radius of X atoms, which compose, together with the Ni atoms, the close-packed layers, is evidently restricted. Figure 3 shows the Goldschmidt atomic radii of the elements as measured by the distance between atoms at room temperature for the most common crystal form modified for close packing, 12-fold coordination.³⁵ The scale at the right hand side of Fig. 3 shows the ratio of radii of the atoms relative to that of nickel, and the dotted line marks the value of the favorable size factor (≈ 1.17) for the formation of γ' or γ'' phases. It is found that only four elements, Ti, Ta, Nb, and Al, prefer to form metastable phases Ni_3X ; the other three elements having similar atomic radii, i.e., Ag, Au, Te, are excluded because of their positive chemical bonding energy with nickel. This last point will be discussed in some detail later.

2. Compressibility

The next question to be asked is why Ti and Al in Ni alloys would promote precipitation of the triangularly ordered γ' phase, while Ta and Nb additions encourage precipitation of the rectangularly ordered γ'' phase. This discrepancy is generally believed to be due to the capacity of atoms for size change or compressibility.

Dwight and Beck³⁶ conducted research on close-packed ordered structures of the binary AB_3 composition using various combinations of the Ti- and V-group elements with the Co- and Ni-group elements. For all the structures considered, the lattice contraction increased with increasing relative size of the A atom, suggesting that it is mostly the A atom that contracted. It was observed that for the same radius

ratio the lattice contraction was larger when the A atom was Ti than when it was Nb or Ta. A similar effect was also observed by van Vucht³⁷ who studied ternary $\text{Ni}_3(\text{Ti}_{1-x}\text{Ta}_x)$ and $\text{Ni}_3(\text{Ti}_{1-x}\text{Nb}_x)$ systems; the correlated data are plotted in Fig. 4. In spite of the different crystal layer stacking, the lattice constant along the ordered, close-packed direction, which is analogous to $\langle 110 \rangle$ direction of the fcc structure, expanded as Nb or Ta atoms partly replaced the Ti atoms in alloys. However, the value dropped back when either the Ta or the Nb content was so rich that the ordered structure changed from triangular to rectangular. This interesting observation initiated a qualitative argument to explain the ordered crystal structure of the metastable Ni_3X phase based on atomic compressibility. The ordered lattice prefers the maximum symmetry when directional bonds are absent, such as is found in γ' phase. Given the high symmetry of the cubic space group, the size of each atom in the lattice is defined with no free parameter left. When the X-atom is compressible as in the case of Ti, the cubic structure may be preserved by forcing the atom to fit with relatively low elastic distortion. However, when the X-atom is the less compressible Ta or Nb, the presentation of the cubic structure would require a large homogeneous distortion. The lower tetragonal symmetry of the γ'' phase allows for the clustering of the smaller Ni atoms in the close-packed layers, and the accommodation of the strain due to the larger Ta- or Nb-atoms by expansion along the tetragonal axis (Fig. 4 right hand side).

3. Electron/Atom Ratio

In addition to the qualitative effects of ordered crystal structures determined by atomic size factor, alloy chemists have found that

the influence of the electron configuration, attributed to the filling of the Brillouin zone, can provide a more quantitative method for determining structure. The electron concentration or electron/atom ratio, e/a , is defined as the average per atom of total number of electrons outside the inert gas shells.

With a systematic study of 84 examples of close-packed ordered AB_3 structures in transition metal alloys, Sinha^{38,39} proposed a simple empirical rule which states that the ordered structure of the close-packed layers should change from "triangular" to "rectangular" at $e/a \approx 8.65$. He also observed that the quasi-binary behavior of ordered AB_3 structures appeared to break down at $e/a < 7.75$ where Laves phases were identified, and at $e/a > 8.78$ where the disordered fcc structure coexisted with the C_7 type phase. The latter case occurs for the elements Ag, Au, Te which exhibit the atomic radii likely to form the metastable Ni_3X phases mentioned in the previous section. Sinha's criterion has been applied to the formation of metastable γ' and γ'' precipitations.^{27,40} The e/a ratio of Ni_3Nb or Ni_3Ta is 8.75, which favors the formation of the rectangularly ordered γ'' phase. The triangularly ordered γ' phase is always found to occur for the composition Ni_3Ti , $e/a = 8.50$ or for Ni_3Al , $e/a = 8.25$. Coexistence of the γ' and γ'' phases has been observed in Ni-based alloys containing two types of hardening elements.^{21,31} Concurrent precipitation has never been reported in Fe-Ni-base alloys, but a change of the ordered structure of the metastable precipitates could be induced by varying the chemical composition of the compound.^{27,41} However, due to the small particle size of the γ' and γ'' phases, it is difficult to accurately measure their exact compositions. Direct verification of the validity

for the γ' and γ'' precipitates of Sinha's criterion, which was derived from equilibrium phases of stoichiometric composition, is still deficient.

All theories of alloy chemistry are essentially generalized, empirical rules based on observations and studies of simple binary or quasi-binary systems. This accumulative knowledge composes an elementary background for predicting or explaining the phases which exist in complex commercial alloys. In the precipitation of metastable γ' and γ'' , they do provide some basic understanding and criterion as described above, but they never answer the fundamental question, why do these two ordered crystal structures of the transition phases prefer to form?

C. ORDERING THEORY

A question which has interested investigators for some time is the possible existence of disordered, solute rich zones which precede the formation of the ordered metastable γ' phase in age-hardening austenitic steel. Reversion studies which allow a distinction to be made between zones and intermediate precipitates, have been carried out by utilizing continuous resistivity measurements and TEM studies.^{42,43} It has been shown that the distinction between zone and γ' precipitates is arbitrary and depends only on size. There is no structural difference between them. The ordered clusters existing in the early stages of precipitation have recently been used to explain the tetragonality of pre-aged Fe-Ni-Ti martensite.^{44,45}

A model based on the Landau-Lifshitz conception^{46,47} of the order-disorder transition will be proposed as follows to explain the formation of the metastable γ' and γ'' phases.

Consider a supersaturated, disordered solid solution held at a temperature such that a reasonable diffusion rate for the atoms allows the precipitation reaction to take place. The thermodynamical equilibrium phases predicted in phase diagrams usually have widely differing crystal structures and lattice parameters. Nucleation of these phases is very difficult because of a high activation barrier due to interfacial free energy and transformation strains. The strong interaction between the solute atoms causes them to segregate sooner or later, forming a metastable phase. This phase is similar in constitution to that of equilibrium phase, but takes on a structure which crystallographically is more compatible with that of the matrix. The ordering structure of the metastable phase should be that which yields the maximum decrease in free energy with respect to the disordered form. To consider this phenomenon, the static concentration waves may be used to analyze free energy change caused by ordering.

Assuming a binary substitutional solution and neglecting anharmonic effects, the free energy of a solid can be expressed as^{46,47}

$$F(\{n(\vec{r})\}) = \frac{1}{2} \sum_{\vec{r}} \sum_{\vec{r}'} V(\vec{r} - \vec{r}') n(\vec{r}) n(\vec{r}') + kT \sum_{\vec{r}} \left[n(\vec{r}) \ln n(\vec{r}) + (1 - n(\vec{r})) \ln (1 - n(\vec{r})) \right] \quad (4)$$

where summation is carried out over all lattice sites $\vec{r}$ and $\vec{r}'$ of the solid; $n(\vec{r})$ is the density function which can be expanded as in Eq. (1), and k is Boltzmann's constant. The first term in the right hand side of Eq. (4) is the interchange energy defined as

$$V(\vec{r} - \vec{r}') = V_{AA}(\vec{r} - \vec{r}') + V_{BB}(\vec{r} - \vec{r}') - 2V_{AB}(\vec{r} - \vec{r}') \quad (5)$$

where $V_{AA}(\vec{r}-\vec{r}')$, $V_{BB}(\vec{r}-\vec{r}')$, and $V_{AB}(\vec{r}-\vec{r}')$ are the pair-wise interaction energies of A-A, B-B, and A-B pairs of atoms respectively, placed at the lattice sites $\vec{r}$ and $\vec{r}'$. The second term defines the entropy change but can be omitted since it is a constant for equivalent super-cooling temperatures. For the disordered solution, $n(\vec{r}) = c$, thus,

$$F(\{c\}) = \frac{1}{2} \sum_{\vec{r}} \sum_{\vec{r}'} V(\vec{r}-\vec{r}') c^2 \quad (6)$$

For the ordered structure, substituting Eq. (1) into Eq. (4), the free energy can be expressed as

$$F(\{n(\vec{r})\}) = F(\{c\}) + \frac{N}{2} \sum_{\vec{k}_j} |Q(\vec{k}_j)|^2 V(\vec{k}_j) \quad (7)$$

where

$$V(\vec{k}_j) = \sum_{\vec{r}} V(|\vec{r}|) e^{i\vec{k}_j \cdot \vec{r}} \quad (8)$$

is the Fourier transform in reciprocal space of the interatomic potential and N is the number of lattice sites in the solid. The free energy change due to ordering is therefore

$$\Delta F = \frac{N}{2} \sum_{\vec{k}_j} |Q(\vec{k}_j)|^2 V(\vec{k}_j) . \quad (9)$$

The determination of the wave vector $\{\vec{k}_j\}$ which provides a minimum for the Fourier transformation of interchange energies $\{V(\vec{k}_j)\}$ is the next step in the solution.

A detailed determination of $\{V(\vec{k}_j)\}$ requires delicate experimental work to insure accurate measurements; however, no data has been reported for alloys with the Ni_3X compositions which are of current interest. The simplest method would be to employ a self-consistent

field approximation in which assumes that each atom only interacts with nearest lattice neighbors by a constant interchange energy V_0 . In the fcc lattice, each lattice site is surrounded by 12 nearest neighbor sites $\langle \frac{1}{2} \frac{1}{2} 0 \rangle$. Using these coordinators, Eq. (8) becomes

$$V(\vec{k}) = V(hkl) = 4V_0 (\cos \pi h \cos \pi k + \cos \pi h \cos \pi l + \cos \pi k \cos \pi l). \quad (10)$$

If $V_0 > 0$, as will be the case for preferential ordering of Ni and X atoms, the minima occur at $\vec{k} = \{(100)\}$, or $\vec{k} = \{(10 \frac{1}{2})\}$ and $\text{Min } V(\vec{k}) = -4V_0$. In the case of the metastable Ni_3X phases, the ordered structure corresponding to the $\{(100)\}$ wave vector is the γ' phase described by Eq. (2), and the γ'' phase of Eq. (3) occurs for $\vec{k} = \{(10 \frac{1}{2})\}$.

The above simple model suggests that the γ' and γ'' phases are the preferred structures for Ni_3X -type ordering in a rigid fcc lattice. However, the model does not establish a preference between the two precipitate structures. If it is assumed that the preferred structure of the metastable phase resembles that of the subsequent equilibrium phase, it follows immediately that Ti and Al will prefer to form γ' , whereas additions of Ta and Nb would promote the formation of γ'' ; since the equilibrium phases of Ni_3Ti and Ni_3Al are triangularly ordered on the close-packed planes, whereas the equilibrium Ni_3Ta and Ni_3Nb phases are rectangularly ordered.

III. EXPERIMENTAL PROCEDURE

A. MATERIALS PREPARATION AND HEAT TREATMENTS

The nominal compositions of the alloys prepared for experimental study are divided into four groups and listed in Table I. The nickel content is chosen to be about 36 wt pct so that the alloy matrix will be non-magnetic (≈ 30 wt pct Ni) after aging treatments. The first three groups of alloys are used to identify the formation criterion for the γ' and γ'' precipitates in austenitic Fe-Ni base alloys. The Ti/Ta ratio increases from alloy BI-1 to BI-5 in the first group. The second group is based on 2Ti-6Ta (BI-3), with small increments in the amount of aluminum. The third group of alloys contains Nb. In the last group alloy III and IV, which are known from the results of the previous groups to precipitate γ' and γ'' , respectively, are chosen to study the aging kinetics of precipitation reaction and alloy mechanical properties. Modification of these alloys with a 5 wt pct Cr addition produces alloy V and VI.

All compositions labeled with the symbol BI were made as 100 gm button ingots arc-melted under argon atmosphere from metals of electrolytic purity. After homogenizing for 24 hours at 1200°C, these alloys were hot forged and then cold rolled into 1.0 mm thick sheets. Solution annealing and recrystallization was carried out at 1150°C for one hour before the subsequent aging processes. The specimens were usually water quenched after each heat treatment.

The ingots labeled by Roman numerals were made as approximately 10 kg ingots by induction melting in a helium gas atmosphere. Following a homogenization procedure similar to that for the button ingots

(1200°C, 24 hours), the ingots were upset cross-forged at 1200°C into plates 30 mm thick by 70 mm wide. Various specimens of appropriate size were cut from these plates. After machining, all specimens were sealed in stainless steel bags filled with argon for the thermal treatments. They were then subjected to a one-hour solution anneal between 900° and 1150°C unless otherwise stated. The aging treatments were carried out at temperatures between 500° and 900°C for up to 10 days.

B. MECHANICAL TESTING

1. Hardness Tests

Thin plates (20 mm × 10 mm × 4 mm) were used to measure the hardness of the alloy for initial appraisal of age hardening response. Heat-treated specimens were then cleaned by wet grinding on emery papers followed by chemical polishing using a solution of 5% HF in H₂O₂. The cleaning process was repeated until the specimen surfaces were free from both oxidation and grinding scratches in order to insure true bulk property measurements. The Rockwell hardness was measured on a Wilson Rockwell hardness tester. The Rockwell C scale with a 150 lb major load was used for most of the aged specimens with an escape time of 15 seconds taken as standard. In the case of soft specimens ($R_C < 20$), a major load of 60 lb was applied to give the Rockwell A scale, the escape time was changed to 20 seconds. At least 5 indentations were made and the readings averaged for each specimen. The standard deviation of the tests was always within ± 0.05 for both scales.

2. Tensile Test

Subsize round tensile specimens of 12.7 mm gage length and 3 mm gage diameter were used. Tests were performed on a 20,000-pound capacity MTS machine. The loading direction was kept consistent with the rolling direction of the original plate. In order to compare relative strength levels and ductilities, all specimens were tested at room temperature at a strain rate of 0.04/min. The stress corresponding to 0.2% offset strain was reported as the yield strength. Elongation and reduction in area were measured by a travelling microscope with an accuracy of ± 0.01 mm. Two specimens were tested for each data point.

3. Fracture Toughness Test

V-notched Charpy specimens of ASTM standard size (10 mm $\times$ 10 mm $\times$ 55 mm) were prepared along the longitudinal direction of the plates. Two tap holes, used to fix the strain gage knife edges during testing were machined on the surface of the notched side. The specimens were pre-cracked by fatigue to develop a crack length between 0.45 to 0.55 mm. The tests were conducted at room temperature on a 300,000-pound capacity MTS machine. Valid K_{IC} values were not obtainable due to the small thickness of the specimens, and Witt's equivalent energy method⁴⁸ was used to estimate the fracture toughness. All data reported represented the average of the results of two tests.

C. MICROSCOPY

1. Fractography

The fracture surfaces of specimens were studied in an AMR 1000 scanning electron microscope (SEM) operated at 20 kV. Because of the large

field depth of the SEM, this technique is excellent for characterizing the fracture mode.

2. Optical Metallography

Metallographic samples were cut from tested tensile and hardness specimens. Transverse sections were examined to obtain measurements of grain size and to evaluate the distribution of precipitate at the grain boundaries. After emery paper grinding, a final polishing was carried out on a rotary wheel impregnated with a 1 μm diamond compound. The samples were then etched by a solution of FeCl_3 (1 gm) + HCl (10 ml) + H_2O (20 ml). The metallograph used was a Carl Zeiss Universal Photomicroscope Ultraphoto II.

3. Transmission Electron Microscopy (TEM)

Specimen sheets 1.0 mm in thickness received selected heat-treatments for TEM studies. They were chemically thinned to about 0.05 mm in a solution of 5% HF in H_2O_2 . Thin discs of 3 mm diameter were spark cut in an EDM machine and electropolished in a twin jet-polishing machine with a chromic-acetic solution: 75 gm CrO_3 + 400 ml CH_3COOH + 21 ml H_2O . The optimum thinning condition was found at a voltage of 30V with 20 mA current. The thin foils were examined under a Philips 301 electron microscope operated at 100 kV. The identification of fine precipitation phases was carried out by means of selected area diffraction and dark field imaging methods as described in detail in the Appendix.

IV. EXPERIMENTAL RESULTS

A. FORMATION OF γ' AND γ'' PRECIPITATES

The first three groups of experimental alloys listed in Table I were subjected to isothermal holding at 750°C for 4 hours after an 1150°C solution anneal. The precipitate phases which developed were identified by using electron diffraction and dark field techniques with the [100] or [110] axes of the matrix parallel to the electron beam. Differentiation between γ' and γ'' was easily achieved with these orientations as demonstrated in the Appendix. The behavior of the alloys with respect to the precipitation of triangularly ordered γ' and rectangularly ordered γ'' is shown in Table II. The first group of alloys contained only Ti and Ta with systematically varying Ti/Ta ratios. The metastable γ'' phase was found to occur in alloys with a high Ta content. Increasing the Ti/Ta ratio caused the ordered structure of the transition precipitate to change from γ'' to γ' . Both γ' and γ'' were observed in the BI-4 alloy whose Ti/Ta atomic ratio is equal to 1.9. However the volume fraction of γ'' was very small compared to that of γ' , which suggests that the transition of $\gamma'' \rightarrow \gamma'$ probably occurs at somewhat a lower Ti/Ta ratio. The absence of the transition phase in the BI-2 alloy was believed to be due to two factors: the lower degree of supersaturation and the unfavorable aging treatment. This microscopic observation was consistent with the hardness data measured by Bourgeot and Manence⁴⁹ who observed no obvious hardness increase in Fe-Ni-Ta alloys aged at 750 °C.

The presence of Al in the alloys promoted the precipitation of the γ' phase as demonstrated in the second group of alloys. Only 0.3 at pct

Al was sufficient to cause the precipitation of γ' in the Fe-36Ni-2Ti-6Ta alloy (BI-3), in which only γ'' had been found in the absence of Al. The coexistence of almost equal amount of γ' and γ'' in BI-6 is shown in Fig. 5, where the rectangularly ordered γ'' has a plate-like morphology and the triangularly ordered γ' has a spherical shape. The atomic ratio of (Ti+Al)/Ta was approximately 1.58 in this case. Only γ' was present in the alloy when the Al addition was increased to 0.6 wt pct.

The Nb-bearing alloys of the third group showed a more complex behavior. No γ'' was ever found in the alloys containing only Ti and Nb. In lieu of the metastable phase, the Laves phase, Fe_2Nb , nucleated and grew along grain boundaries in alloy BI-8, which contained 3 wt pct Nb and 1 wt pct Ti, (Fig. 6). This result agrees with earlier reports.^{25,50} When the Ti content was increased to 2 wt pct, only the γ' precipitate was found even though the Ti/Nb atomic ratio was small (≈ 1.3). It is concluded that Nb does not promote the precipitation of the metastable Ni_3Nb phases in the above alloys under normal conditions of quenching and aging. The presence of tantalum, however, stimulates the partition of Nb in the precipitation of metastable phases. In alloys I and II, both of which contained Ta additions of no more than 1 at pct, γ' and γ'' precipitation occurred respectively, with the difference in the ordered structure of the precipitates depending on the Nb content.

All results are summarized and plotted in Fig. 7. The ordered structure of the metastable phase Ni_3X is determined in relation to the Ti+Al and Ta+Nb contents of the Fe-Ni-base alloys. The broken line represents the undersaturation limit, below which no metastable phase precipitates. The boundaries of the transition region, where the

two phases, γ' and γ'' , coexist, are approximately straight lines. The ratios of these boundaries are $(\text{Ti}+\text{Al})/(\text{Ta}+\text{Nb}) = 1.5$ and 1.9 . It is then possible, using Fig. 7, to predict which metastable precipitate will be predominant in Fe-Ni-base alloys at varying hardening element levels.

Application of Sinha's criterion to the metastable phases is still questionable, since this empirical rule is based on studies of stable equilibrium phases with stoichiometric compositions. Moreover, no accurate data on the chemistry of the metastable precipitates is available. Assuming that the relative ratio between hardening elements remains the same in the precipitates as in the matrix, and no iron participates in the metastable phases, the electronic concentration e/a of the precipitates formed in the alloys studied in the work can be estimated. The calculated results are presented in Fig. 8. It is found that the transition of ordering from triangular to rectangular takes place over a range of $8.56 < e/a < 8.59$, instead of the defined value of 8.65 reported by Sinha.

Two alloys, BI-7 and alloy I, of composition close to the transition boundary were aged at a somewhat lower temperature (720°C) for long periods. In addition to the γ' phase observed after 750°C aging, a few γ'' particles formed on the γ' precipitates in both cases. Figure 9 shows the microstructures of alloy I after aging at 720°C for 8, 24, 72, and 148 hours. The γ'' particles are always found to adjoin to the γ' particles along their (001) crystal planes. This coupled morphology of coherent precipitates presumably decreases the free energy by reducing the interfacial energy and the elastic misfit. The number of γ'' particles increased with time. They grow as plates perpendicular to the [001] axis. The γ'' does not appear to coarsen by consuming γ' , since the

simultaneous growth of γ' was also observed. For long aging time, the γ'' precipitates have a tendency to grow beyond the γ' precipitates on which they were first located. The late appearance of the γ'' phase can be explained by considering the difference in the diffusion kinetics of the hardening elements. This phenomenon will be explained in more detail later.

B. AGING KINETICS

1. Precipitation of γ' Phase

Referring to Fig. 7, alloy III which contained 3 wt pct Ti and 3 wt pct Ta was chosen for an extensive study of γ' precipitation. Microalloying additions (Mo-V-B) were introduced to suppress intergranular precipitation and to improve grain boundary properties. The choice of additions was based on previous studies of age-hardening austenitic alloys.^{51,52} Before any subsequent aging treatment, a solution anneal was carried out at 1000°C for 1 hour, producing an initial microstructure with a grain size of 60 μm and a low density of dislocations (Fig. 10).

a. Isothermal Aging

Typical curves of hardness vs. aging time for alloy III aged at 500-900°C are shown in Fig. 11. The results demonstrate that substantial hardening occurs at all temperatures between 625° and 800°C. The level of peak hardness and the associated aging time decrease as the aging temperature is increased. However, no hardness change is observed when the alloy is aged at 500°C for up to 168 hours. The absence of hardening at 500°C is presumably due to low diffusion rate of substitutional solutes in the austenitic lattice at this temperature,

which substantially retards the kinetics of precipitation. The metastable γ' phase is also unlikely to form at 900°C since this temperature is above the γ' solvus temperature ($\approx 870^\circ\text{C}$).^{42,43} The slight increase in hardness for long aging times at 900°C is caused by the formation of the equilibrium η phase which has a Widmanstätten morphology.

Clearly defined spherical γ' particles are observed in the early stages of precipitation. The typical micrographs illustrating the isothermal growth of γ' precipitates are shown in Fig. 12. The triangular ordering of γ' is reflected in the superlattice spots in the (001) diffraction pattern shown in the upper left-hand corner of Fig. 12(a). Lifschitz and Wagner^{53,54} suggested that, for diffusion controlled coarsening, the average particle diameter d increases with time t according to a relationship of the form:

$$d^3 - d_0^3 = kt$$

where d_0 and k are constants. Figure 13 shows that the γ' diameter at 725°C is a linear function of $t^{1/3}$ within experimental error. The particle sizes plotted in the figure are averages based on more than 200 measurements.

Tensile test data for alloy III, subjected to isothermal aging at 725°C, is presented in Fig. 14. Hardness data is also included. The results indicate the excellent combination of strength and ductility obtainable in alloy III compared with those typical of γ' -strengthened austenitic alloys. The beneficial effect comes from the nominal addition of 3 wct pct Ta. While the source of the Ta-improvement is not firmly established, Ta increases the coherency strains by expanding the

lattice constant of the γ' phase, which may explain its beneficial effect. Loss of strength and ductility is observed to occur when a cellular form of the equilibrium η phase nucleates at the grain boundaries and grows out into the matrix by a discontinuous precipitation process. Structural instabilities due to the cellular precipitation in Ni-Cr-Ti steels has been investigated metallographically by Clark and Pickering,⁵ and will not be discussed in detail here. A typical microstructure consisting of lamellae of the η phase in a matrix of recrystallized austenite is shown in Fig. 15.

b. Double Aging

To achieve higher strengths within a reasonable aging period, alloy III was aged at 725°C for 8 and 16 hours, followed by a second aging at 625°C, at which temperature the time to achieve peak isothermal hardness is too long to be practical. The results plotted in Fig. 16 show that the alloy hardness increases rapidly during the second aging, reaching a plateau at a maximum hardness greater than that obtained at 725°C. A hardness increment of 2.5 R_C is obtained in 16 hours with the second aging process. The final hardness of the alloy seems to depend on the hardness level developed in the first aging step, but the difference is not great.

The acceleration of the aging reaction by the double aging process in Ti-containing steels has been known for a long time,² but no theoretical explanation supported by direct experimental evidence has been reported. Recent investigations using resistivity measurements at the early stages of aging suggested⁵⁵ that nucleation of new γ' particles in the matrix occurred when the alloy was treated at the second, lower

aging temperature. The size distribution of the ordered γ' particles after single aging (750°C/8 hours) and double aging (+ 650°C/8 hours) has been determined by measuring the particle diameter in the dark field image of the (100) superlattice reflection. The histograms are shown in Fig. 17. The measured particle size in the single aged condition is close to the normal (Gaussian) distribution having a mean value ≈ 125 Å. The second aging does not change the mean particle size greatly, but the number of small particles (60 - 80 Å) increases significantly. There is little doubt from this observation that the independent nucleation of new γ' particles does take place at the second aging temperature. The increase in hardness associated with the double aging treatment is then expected as a consequence of the increase in volume fraction and the decrease in interparticle spacing of γ' . These new γ' particles may be the original undersized embryos of the first aging temperature which then grow during the second aging. If so, it is reasonable that only a short time is needed to reach the saturation hardness.

The selected aging treatments applied to alloy III were used to determine the mechanical properties developed in the γ' -hardening austenitic alloy. The heat treatments and resulting mechanical properties are presented in Table III. The results show that a yield strength of up to about 175 ksi (1200 MPa) is obtainable with a good residual fracture toughness.

2. Precipitation of γ'' Phase

The Ta-rich alloy IV, which is expected for form γ'' precipitates according to Fig. 7, was solution annealed at 1000°C for 1 hour and

quenched in water. This treatment seemed to suffice to dissolve all intermetallic phases and to allow the alloy to recover from residual stresses and defects produced during forging. Hence an initially clean austenitic matrix was obtained (Fig. 18).

a. Isothermal Aging

The age-hardening characteristics of alloy IV were determined for the temperature range of 500° to 900°C for aging times up to 150 hours. The aging curves shown in Fig. 19 indicate that the alloy developed higher strength at the lower aging temperatures; overaging was observed to occur rapidly at higher temperatures. The aging behavior at 900°C, which exhibited no hardness change at all, suggested that the solvus of the γ'' phase is below this temperature. Moreover, the equilibrium δ phase appeared along grain boundaries in optical micrographs of specimens aged at 900°C. Tensile test data for the alloy aged at 700°C are given in Fig. 20. It is clear that γ'' precipitates can strengthen austenitic alloys up to 170 ksi (1170 MPa) yield on single aging, while preserving good ductility.

Decomposition of the supersaturated austenite after the solution anneal and water quench was monitored by electron microscopy. A series of samples were examined after aging at 725°C for different times. The only transition phase observed was the γ'' precipitate. Disc-shaped γ'' particles were seen in the early stages of precipitation as shown in Fig. 21. The streaking of the superlattice reflections in the associated diffraction patterns is related to the shape factor of the precipitate and indicates that the c-axis of the γ'' phase is normal to the plane of the disc. Aging for longer times caused a considerable

coarsening of the γ'' particles, with growth predominantly in the plane of the disc. Figure 22 shows the microscopic image in the [001] foil orientation for various aging sequences. The γ'' precipitates remain coherent even after aging for 100 hours. No interfacial dislocations were detected. The size variation of the γ'' particles was determined as a function of aging time and is plotted in Fig. 23. The measured dimension referred is to the length of the edge-on disks with the foil in a [001] orientation. The linear plot of precipitate size as a function of (aging time)^{1/2} suggests that the coarsening follows a $t^{1/2}$ growth law, instead of $t^{1/3}$ as for the γ' particles. Figure 23 also includes the data obtained by Coza and Pineau³² in nickel-base alloys. The aspect ratio of the γ'' disc increases monotonically with time. When the disc has a diameter (d) of $\approx 60\text{\AA}$, the diameter is about twice of the thickness (h), while when $d \approx 600\text{\AA}$, $d/h \approx 10$. It is apparent that the coarsening of γ'' precipitates occurs primarily through two-dimensional growth in the plane of the disc. An inverse in aspect ratio with particle size is an expected consequence of the thermodynamic tendency for the particle to minimize its elastic energy.

On extended aging, the γ'' phase is eventually replaced by the equilibrium β phase, which has a DO_{19} type (Cu_3Ti) orthorhombic structure.⁵⁰ The γ'' precipitates are replaced by β phase through a cellular reaction analogous to that observed in γ' -hardened alloys.⁵ As reported before for other Ni-base alloys, the cellular precipitates nucleate at grain boundaries and then grow into the adjacent grain consuming the γ'' dispersion (Fig. 24). The nucleus appears to have a low-energy interface with one of the grains with which it has the orientation relationship:

$$(010)_\beta \parallel (111)_\gamma ; [100]_\beta \parallel [110]_\gamma$$

This interface is stable, and therefore not very mobile, so that the growth of β accompanying the recrystallization of the austenite will occur into the grain with which there is no well-developed orientation relationship (Fig. 25). The growth front of the cellular colony remains attached to the grain boundary, which sweeps the adjoint grain. It appears that as β begins to grow, diffusion conditions are set up which lead to side-by-side nucleation of the β lamellae, as in the pearlite reaction.

The nucleation of the β phase was also observed on the surface of large carbide particles, as seen in Fig. 26. This observation has not been reported before. No grain boundary migration accompanies the growth of the β lamellae if the carbide is embedded inside a grain. The mechanism of β growth in this case is related to the intragranular reaction of the Widmanstätten type, which is favored at higher aging temperatures. The denudation of γ'' around the thin Widmanstätten plates is very obvious. However, carbide particles are most often found along grain boundaries, in which case the nucleation of β phase on carbide surface is followed by the usual cellular reaction with migration of austenite grain boundaries (Fig. 27).

b. Double Aging

A higher hardness plateau can be obtained in alloy IV by first aging at 700°C for 8 and 16 hours, and then for longer periods at 600°C. The results are given in Fig. 28. Only 8 hours at 600°C are needed for hardness increase of $\sim 2.5 R_C$. The difference in the final hardness due to difference in the initial aging treatment is within experimental

accuracy ($\pm 0.5 R_C$). Tensile and fracture toughness tests were performed on specimens subjected to selected aging treatments. The resulting data are listed in Table IV. The second aging appears to strengthen the alloy without sacrificing its toughness. A yield strength of 180 ksi (1240 MPa) can be attained, through thermal processing alone.

The strain hardening behavior in the γ'' -strengthened alloy differs notably from that in the γ' -strengthened one. Figure 29 shows the true stress-strain curves of alloy III and IV double-aged to the yield strength level of 175 ksi (1200 MPa). There is no doubt that the strain hardening rate is higher for the γ' -strengthened alloy. The curves in Fig. 29 can be fitted by a general power law of the type.

$$\sigma = k\epsilon^n$$

where k and n are material constants. For alloy III, $n=0.113$ and $k=317$ ksi; for alloy IV, $n=0.093$ and $k=268$ ksi. A possible explanation for this difference can be based on the slightly different strengthening mechanisms associated with the two precipitation processes. The higher degree of coherency strain hardening from the γ'' particles has the result that fewer particles are needed to harden the alloy to a same yield strength level than when the precipitates are γ' . When a large number of dislocations cut through a coherent particle after yielding, the ordered particle will mechanically dissolve into the matrix.⁵⁶ The disc morphology of the γ'' particles also allows them to dissolve more easily due to the smaller cross-sectional area of the particle on the slip planes. The strain hardening rate of the γ'' -strengthened alloys is therefore relatively low.

C. EFFECTS OF Cr ADDITION

Both alloy III and IV in the full-hardened condition are mechanically unstable with respect to martensitic transformation near ambient temperature. As a consequence an induced martensite phase (α') of volume fraction $\approx 60\%$ is detected on the fracture surface of samples broken at room temperature. The bcc martensite phase (α') may cause the austenitic alloys to become sensitive to hydrogen embrittlement and stress corrosion cracking.⁵⁷ Many non-magnetic elements are known to stabilize Fe-Ni austenites. Chromium was chosen for this study since it both stabilizes austenite and provides the alloy with a good resistance to oxidation and corrosion.

Alloys V and VI are essentially modifications of alloys III and IV, respectively, which involve the addition of 5 wt pct Cr, together with a decrease in Ni content. Their age hardening curves at 625°, 700°, 725°, 750°, and 800°C are shown in Figs. 30 and 31. As expected the hardness response of these compositions resembles those obtained from the Cr-free alloys, but the precipitation kinetics are relatively slow. The increase in time required to reach peak hardness due to the Cr addition is illustrated in Fig. 32, in which the aging times to peak hardness for four alloys are plotted on a logarithmic scale against the inverse of the aging temperature. The linear relationship suggests that the precipitation reaction for the metastable phases is thermally activated. The Cr addition causes the lines to shift upward to longer aging times, but does not seem to change the slope of the lines. The activation energy for γ' and γ'' precipitation, which corresponds to the slope of the lines in Fig. 32, is estimated to be 67 and 80 kcal/°K-mole,

respectively. The somewhat greater activation energy required for the γ'' precipitation reaction is probably due to the higher elastic strains associated with the formation of γ'' particles in an austenitic matrix.

For the double aging treatment, attention was focused on the effect of the first aging temperature upon the total hardening response. The alloys were initially aged at different temperatures and then given the same second aging temperature. The final hardness plateau, as shown in Figs. 33 and 34, is determined primarily by the second aging temperature, especially when the hardness obtained in the first agings are equivalent. Selected aging treatments were performed on the alloys in order to determine their mechanical properties. The results are given in Table V. No martensite phase (α') was ever detected on the fracture surfaces, indicating that the Cr addition effectively stabilized the matrix austenite. Tensile elongations for these stable austenitic alloys are comparatively less, which is consistent with previous observations^{58,59} that indicate that the induced martensitic transformation has a beneficial effect on tensile elongation. However, fracture toughness measurements show that the induced transformation makes a negligible contribution to toughness at a given value of the yield strength.

D. SOLUTION ANNEALING

It is known that solution treatment of Ni-base superalloys in an appropriate temperature range leads to the best ductility and stress-rupture life at elevated temperatures.^{18,60} Grain growth of these alloys during solution annealing occurs at a temperature exceeding the solvus of the equilibrium precipitation phases, which is usually

higher than those of the metastable precipitates. Studies of the effect of a solution anneal on the microstructures and mechanical properties of Fe-Ni-base alloys have primarily been performed on the γ' -strengthened alloys.

To determine the effective solvus temperature for the equilibrium η phase, samples from an as-forged plate of alloy III were solution annealed from 900° to 1150°C for 1 hour in 50°C increments. The effect of these solution treatments on the as-forged structure is shown in Fig. 35. The globular-to-plate-shaped η particles observed to form along grain boundaries at 900°C were almost completely dissolved at 925°C. The grains grew rapidly at temperatures above the η solvus.

Tensile tests were then conducted on specimens solution-annealed at temperatures above 950°C, followed by the double aging treatment: 725°C for 8 hours plus 625°C for 16 hours. The results are given in Fig. 36, along with the measured grain size for each treatment. The optimum solution annealing temperature was found to be 1000°C, which produced the best combination of tensile properties with the least grain growth. The alloy strength decreased slightly with increasing annealing temperature, but more significant result was the dramatic drop in tensile ductility for anneals above 1100°C. This decrease in ductility is associated with a change in the fracture mode from ductile rupture to intergranular failure as revealed in the fractographs in Fig. 37. The intergranular fracture is believed to result from chemical contamination of the grain boundaries during thermal treatments, but the exact mechanism is not clear at this moment. It should be noted, as indicated in Fig. 36, that the specimen directly-aged from the as-forged condition has a yield strength about 20 ksi higher than the

maximum value obtained after solution annealing, and retains good ductility. The enhanced strength appears to result from the retention of induced defects and fine substructure introduced during hot forging.

The grain size of the alloy seems to be fixed by the solution-annealing temperature. Prolonged annealing does not cause any obvious growth of the austenite grains, as seen in Fig. 38, nor does it affect the mechanical properties.

Similar studies were also carried out in the Cr-modified alloy V, which was aged at 725°C for 16 hours after annealing for one hour at different temperatures. In Fig. 39, the results suggest that the optimum solution annealing temperature is still 1000°C despite the Cr addition. However, the intergranular fracture exhibited in the Cr-free alloy III annealed at high temperatures is replaced by a dramatic decrease in strength level. Large, torn dimples instead of intergranular cleavage are observed on the fracture surface (Fig. 40). A large amount of elongation and severe slip tracings on the specimen gage indicate that the alloy is underaged after high temperature anneal.

The aging behavior of the alloy V in the as-forged condition, as well as after solution-treatment at 1000° and 1150°C was investigated, using a 750°C aging temperature (Fig. 41). The initial hardnesses before aging was R_A 62, 49, 47, respectively. In both of the solution-treated cases, the alloy eventually reached the same level of peak hardness, but longer aging times were required. It can be concluded that the solution annealing temperature can vary the aging kinetics of the metastable phase precipitation. The maximum hardness of the annealed specimens was again observed to be less than that of the directly aged, as-forged ones by $\Delta R_C \sim 2.5$.

V. DISCUSSION

A. COEXISTENCE OF γ' AND γ'' PHASES

Reference to Fig. 7 shows that in the Fe-Ni base alloys the ordered structure of the metastable precipitate depends on the $(\text{Ti} + \text{Al})/(\text{Ta} + \text{Nb})$ atomic ratio, and that concurrent precipitation of γ' and γ'' occurs at 750°C when the ratio is between 1.5 and 1.9. In only a few cases has the coexistence of two metastable phases been reported in the literature,^{22,32} and no theoretical interpretation has been offered to explain the coupled γ' and γ'' precipitation. However, two mechanisms can be proposed and evaluated on the basis of the research reported here.

1. Metastable Phase Diagram

As discussed in Section II, the elements forming the metastable Ni_3X phases can be divided into two groups. One contains Ti and Al, and favors the triangularly ordered γ' ; the other contains Ta and Nb, and favors the rectangularly ordered γ'' . Thermodynamically, the phase transformation is driven by the decrease in the free energy of the alloy and the ordered structure of the precipitates is determined by a minimum free energy criterion. Therefore, the triangular ordering of γ' gives a lower free energy for the metastable phase of composition $\text{Ni}_3(\text{Ti}, \text{Al})$, while the metastable phase $\text{Ni}_3(\text{Ta}, \text{Nb})$ has a lower free energy for the rectangular ordering of γ'' . In the case in which both kinds of elements exist in an alloy system, the free energy change for γ' and γ'' formation becomes somewhat complicated. The simplest approach is to assume that the free energy of each ordering structure is a function of the $(\text{Ti} + \text{Al})/(\text{Ta} + \text{Nb})$ ratio, or the atomic fraction, of one type of

precipitate former with respect to the total content of hardening elements in Ni_3X . The triangular ordering of γ' is expected to have a minimum free energy on the Ti- or Al-rich side, but to become less strongly preferred as the fraction of Ta+Nb increases. An opposite trend is found for the rectangular ordering of γ'' . Figure 42 shows schematic free energy curves for the two metastable phases at a given aging temperature. The procedure used to determine the composition limits of the two phase region in the equilibrium phase diagram is employed here. A line tangent to two free-energy curves minimizes the free energy at each composition and gives a two-phase mixture. The coexistence of γ' and γ'' is then a trivial result of minimizing the total free energy of the alloy.

The above consideration is supported by experimental observation as shown in Fig. 9. During the coarsening of the precipitates in alloys exhibiting both precipitate structures, γ' and γ'' particles grow simultaneously even when adjacent to one another. It appears neither is strongly preferred.

2. Diffusion Kinetics

The precipitation reaction of metastable phases is known to be a thermally-activated and diffusion-controlled process. The transformation rate or the clustering speed of the solute elements depends mainly on their diffusivity coefficients at the aging temperature. The value of the diffusivity depends on several parameters, but is proportional to the inverse square root of the atomic weight. The significant difference in atomic weight between two types of precipitate formers (Al = 27, Ti = 48, vs. Nb = 93, Ta = 181 g/mole) will be reflected in the relative values of their diffusivities.

An argument based on diffusion kinetics can be used to explain the occurrence of the coupled γ' and γ'' precipitation. The alloy containing two types of precipitate formers is subjected to a proper aging temperature. During the early stage, the lighter γ' forming atoms, Al or Ti, will segregate quickly to form the triangularly ordered γ' , leaving the alloy matrix relatively enriched in the heavier elements Nb or Ta. As aging proceeds, the subsequently nucleated metastable precipitates will contain a relatively high ratio of the γ'' -forming elements Nb or Ta, and will tend to form in an ordered structure of the rectangular type. Since the γ'' phase has a large misfit with the matrix lattice, the γ' /matrix interfaces can provide favorable nucleation sites for γ'' particles by accommodating elastic strain. A morphology of adjacent γ' and γ'' particles will hence tend to form. In alloys systems reported to form both γ' and γ'' , the γ' precipitation reaction has invariably been observed to precede the γ'' precipitation which supports this argument (Fig. 9). Hence both kinetic and thermodynamic factors promote the coexistence of γ' and γ'' precipitates in age-hardened Fe-Ni alloys.

B. ALLOY DESIGN

It has been demonstrated in this investigation that the Fe-Ni base austenitic alloys can be effectively strengthened by either the γ' or the γ'' precipitate. The yield strength obtained after proper thermal treatment can exceed 170 ksi (1170 MPa). With such a high strength, the alloys still exhibit relatively good ductility and fracture toughness.

Figure 7 permits a graphical estimate of the type of precipitate which will appear as a function of alloy content. Various combinations of hardening elements can be manipulated to design alloys with the desired properties.

In the γ' -hardened Fe-Ni base austenitic alloys, titanium has been determined to be the most efficient and effective hardening element. Small amounts of aluminum are commonly added to achieve a slow rate of overaging, and to retard the nucleation of cellular η -Ni₃Ti. The age hardening effect can be further enhanced by an addition of tantalum, which increases the misfit and hence coherency strains between γ' and the matrix. The use of niobium alone is not beneficial, since it does not promote the precipitation of a desirable metastable phase. Instead it increases the tendency of the alloy to form the detrimental Laves phase along grain boundaries.

There is no commercial Fe-Ni base alloy strengthened by γ'' precipitates. The present work suggests that such an alloy would have to contain a certain amount of tantalum. The high cost of tantalum would probably discourage the wide use of Ta-bearing alloy. Inexpensive niobium may replace tantalum only to a limited degree. Aluminum should be avoided, since it is a strong γ' former.

At least 5 wt pct Cr addition is necessary, in either type of alloy, to insure the mechanical stability of the non-magnetic austenitic matrix in the fully hardened condition. A higher Cr content can be introduced, depending upon the requested oxidation resistance and the service temperature of the alloys. A retardation of the aging response always accompanies the addition of Cr.

If possible, alloys of this class should be given a thermo-mechanical treatment (TMT) before aging. Hot working has a beneficial effect on both strength and ductility. If an intermediate solution anneal is necessary to produce a soft initial alloy, an optimum annealing temperature should be used, and appears to be just above the solvus of the equilibrium phase.

The increase in strength on aging depends on the aging temperature. Double aging techniques usually improve the aging response and make it possible to achieve the high strength associated with low-temperature aging during reasonable aging time. The γ'' -strengthened alloys have lower optimal aging temperatures than the γ' -strengthened alloys does.

VI. CONCLUSIONS

1. The ordering structure of metastable Ni_3X precipitates in Fe-Ni base austenites can be controlled by the hardening element content. An increase in the Ti or Al content will promote the formation of the triangularly ordered γ' precipitate, while a Ta addition will favor the rectangularly ordered γ'' precipitate. Nb promotes the formation of the γ'' precipitate only if a certain amount of Ta is present.
2. The coexistence of γ' and γ'' has been observed in alloys having an atomic ratio, $(\text{Ti} + \text{Al})/(\text{Ta} + \text{Nb})$, between 1.5 and 1.9. The concurrent precipitation can be plausibly explained from either a thermodynamic or a kinetic point of view.
3. The growth of spherical γ' particles follows the Lifshitz-Wagner model of diffusion controlled coarsening. The peak yield strength of the γ' -hardened austenitic alloys can reach the 170 ksi (1170 MPa) level by adding 3 wt pct of Ta to increase the effect of the coherency strain hardening.
4. The coarsening of disc-shaped γ'' precipitates follows a $t^{1/2}$ growth law in the plane of the precipitates. The expected large coherency strain of γ'' indirectly confirmed by the higher activation energy associated with γ'' precipitation process than that for γ' . The equilibrium β phase, under some circumstances, can nucleate on carbide surfaces. The β phase grows through either a grain boundary cellular reaction or an intragranular Widmanstätten reaction.

5. Double aging treatment produces independent nucleation of precipitates at the second aging temperature, hence an excellent aging response can be attained within a reasonable aging time.
6. The addition of Cr stabilizes the austenite phase. Small Cr additions (≈ 5 wt%) do not significantly change the peak strength attainable after aging, but do slow the kinetics of precipitation.
7. If the alloys is solution annealed prior to precipitation, the solution annealing temperature significantly affects the mechanical properties of the alloy. Intergranular fracture occurs when Cr-free alloys are annealed above 1100°C . Addition of Cr suppresses this embrittlement. High annealing temperature decreases the ripening rate of metastable precipitates.

ACKNOWLEDGEMENTS

The author wishes to express his appreciation to Professor J. W. Morris, Jr. for his continuous guidance and encouragement during the course of this investigation. Special thanks are extended to Professor G. Thomas, Professor I. Finnie, and Professor A. G. Khachaturyan for their review and constructive criticism of this manuscript.

The assistance of the technical staff of the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, is gratefully acknowledged, particularly Mr. L. Johnson (metallography), Mr. R. Lindberg (scanning electron microscopy), Mr. B. Pope (ingot melting), Mr. H. Riebe (machining), Mr. J. Holthius (alloy preparation), Mr. D. Krieger (mechanical testing), and Mrs. G. Pelatowski (figure drawing). The author especially wishes to thank his colleague, Mrs. K. Mahin, for her help in preparing this manuscript.

The author is indebted gratefully to his family, especially his parents and his wife, Hwa-Gan, for their patience and support with great confidence.

This work was supported by the Electric Power Research Institute through Contract #RP-636-2, and supported by the Department of Energy through the Materials and Molecular Research Division of Lawrence Berkeley Laboratory.

APPENDIX

ELECTRON DIFFRACTION AND PHASE IDENTIFICATION OF γ' AND γ'' PRECIPITATES

The crystallographic unit cells of the γ' ($L1_2$ type) and γ'' (DO_{22} type) phases are shown schematically in Fig. 4. Both precipitate phases have the cubic/cubic crystal orientation relationship with the fcc matrix:

$$\{100\}_{\gamma} \parallel \{100\}_{\gamma'} ; \quad \langle 010 \rangle_{\gamma} \parallel \langle 010 \rangle_{\gamma'} ,$$

and
$$\{001\}_{\gamma} \parallel \{001\}_{\gamma''} ; \quad \langle 100 \rangle_{\gamma} \parallel [100]_{\gamma''} .$$

Their lattice constants are approximately the same as those of the parent matrix:

$$a_{\gamma} \approx a_{\gamma'} ,$$

and
$$a_{\gamma} \approx a_{\gamma''} \approx \frac{1}{2} c_{\gamma''} .$$

It is convenient to consider these phases as ordered fcc structures. Since the ordering process yields a reduction in the symmetry of a disordered solution, some superlattice spots are expected to appear in the diffraction patterns in addition to the fundamental fcc reflections. All indices used in the following discussion are based on the fcc lattice. The unit cell of the γ'' phase consists of two fcc unit cells stacked along the c-axis, thus the reflection in the reciprocal lattice may have the form $(h \ k \ \frac{n}{2})$, where h, k, n are integers:

Due to the very short wavelength of electrons under normal operating voltages, the low order Bragg angles are small. The intensity of a diffracted beam (hkl) is governed primarily by the structure factor,

$$F(hkl) = \sum_{n=1}^N f_n \left[e^{2\pi i (h \cdot x_n + k \cdot y_n + l \cdot z_n)} \right]$$

where the summation extends over all N atoms of the unit cell, and f_n is the atomic scattering factor of the n th atom located at (x_n, y_n, z_n) .

The γ' crystal has three Ni and one X atoms per unit cell, located as follows:

$$\begin{array}{cccc} \text{Ni} & \frac{1}{2} & \frac{1}{2} & 0 \\ & \frac{1}{2} & 0 & \frac{1}{2} \\ & 0 & \frac{1}{2} & \frac{1}{2} \\ \text{X} & 0 & 0 & 0 \end{array}$$

Its structure factor is

$$F = f_X + f_{\text{Ni}} \left(e^{i\pi(h+k)} + e^{i\pi(h+1)} + e^{i\pi(k+1)} \right)$$

1. If h , k , and l are unmixed,

$$|F|^2 = |3f_{\text{Ni}} + f_X|^2, \text{ yielding fundamental reflections.}$$

2. If h , k , and l are mixed

$$|F|^2 = |3f_{\text{Ni}} - f_X|^2, \text{ yielding superlattice reflections.}$$

The γ'' crystal has six Ni and two X atoms per unit cell, located as follows:

$$\begin{array}{ccccccc} \text{Ni} & \frac{1}{2} & \frac{1}{2} & 0 & 0 & \frac{1}{2} & \frac{1}{2} \\ & \frac{1}{2} & 0 & \frac{1}{2} & \frac{1}{2} & 0 & 0 \\ & 0 & 0 & 1 & \frac{1}{2} & 0 & \frac{3}{2} \\ & 0 & \frac{1}{2} & \frac{3}{2} & 0 & \frac{1}{2} & \frac{3}{2} \\ \text{X} & 0 & 0 & 0 & \frac{1}{2} & \frac{1}{2} & 1 \end{array}$$

$$F = f_X \left(1 + e^{i\pi(h+k+2l)} \right) + f_{\text{Ni}} \left[e^{i2\pi l} + e^{i\pi(h+k)} + e^{i\pi l} \times (1 + e^{i2\pi l}) \times (e^{i\pi h} + e^{i\pi k}) \right]$$

1. If $h+k+2l$ is odd

$$|F|^2 = 0, \text{ yielding forbidden reflections.}$$

2. If $h+k+2l$ is even, and
- a. if $2l$ is odd, (then $h+k$ is odd)

$$|F|^2 = 4|f_{Ni} - f_X|^2, \text{ yielding superlattice reflections;}$$

- b. if $2l$ is even, (then $h+k$ is even), and also

(i) when h and l are mixed (or k and l are mixed)

$$|F|^2 = 4|f_{Ni} - f_X|^2, \text{ yielding superlattice reflections;}$$

(ii) when h and l are unmixed, (or k and l are unmixed)

$$|F|^2 = 4|3f_{Ni} + f_X|^2, \text{ yielding fundamental reflections.}$$

The calculated results are summarized in Table VI for all possible reflections. The values of h , k and l can interchange with one another for γ' , but only h and k can interchange for γ'' . All γ' precipitates are members of the same crystallographic variant in the parent matrix, but three different orientation variants are possible for the γ'' structure with respect to the disordered fcc lattice. These γ'' particles yield a pattern in reciprocal space that is a composite of reflections from all three orientations of the precipitates. Figure 43 shows schematically the six most commonly populated reciprocal lattice planes for γ' and γ'' . It should be noted that when γ'' is present in a matrix there is no unique superlattice reflection for the γ' precipitates. In this case a dark field imaging technique can be used to determine the presence of γ' .

The γ'' precipitates yield streaked superlattice reflections during the early stages of their growth, a phenomenon characteristic of

precipitates having a plate-like morphology. Since the plane of the γ'' particles is normal to the crystallographic direction of the c-axis, the $(001)_{\gamma''}$ superlattice reflections will always be streaked and only observed when the foil is in an edge-on orientation for the γ'' particles. No streaking of the γ' superlattice reflections will be observed due to the spherical shape of the particles. This characteristic difference is illustrated in Fig. 44, which shows selected area electron diffraction patterns for the $[100]$ matrix zone axis. From the dark field micrograph taken from the (001) superlattice reflection one can easily distinguish between the γ' and γ'' precipitates: the spherical particles are γ' , and the disc-shaped particles are γ'' , as seen in Fig. 45.

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Table I. Chemical Composition of Alloys

Ingot	Chemical Compositions, wt pct									
	<u>Fe</u>	<u>Ni</u>	<u>Cr</u>	<u>Ti</u>	<u>Al</u>	<u>Ta</u>	<u>Nb</u>	<u>Mo</u>	<u>V</u>	<u>B</u>
BI-1	bal.	36	--	--	--	9	--	--	--	--
BI-2	bal.	36	--	1	--	6	--	--	--	--
BI-3	bal.	36	--	2	--	6	--	--	--	--
BI-4	bal.	36	--	2.5	--	5	--	--	--	--
BI-5	bal.	36	--	2.5	--	3	--	--	--	--
BI-6	bal.	36	--	2	.3	6	--	--	--	--
BI-7	bal.	36	--	2	.6	6	--	--	--	--
BI-8	bal.	36	--	1	--	--	3	--	--	--
BI-9	bal.	36	--	2	--	--	3	--	--	--
I	bal.	38	--	3	.3	2.5	2	--	--	.01
II	bal.	36	--	3	--	3	2.5	1	.3	.01
III	bal.	36	--	3	.5	3	--	1	.3	.01
		(36.8)		(2.64)	(.44)	(2.97)		(1.15)	(.28)	(.007)
IV	bal.	36	--	2	--	6	--	1	.3	.01
		(36.5)		(2.29)		(5.97)		(.91)	(.31)	(.006)
V	bal.	34.5	5	3	.5	3	--	1	.3	.01
		(34.8)	(4.5)	(2.55)	(.42)	(2.97)		(.91)	(.28)	(.008)
VI	bal.	35	5	2	--	6	--	1	.3	.01
		(34.9)	(4.98)	(1.69)		(5.98)		(.93)	(.28)	(.007)

() indicates the analyzed value.

Table II. Hardening Element Content and Precipitation Behavior of Alloys

Ingot	Hardening Element Contents								Type of	
	Weight pct				Atomic pct					Precipitate
	Ti	Al	Ta	Nb	Ti	Al	Ta	Nb	(Ti+Al)/(Ta+Nb)	
BI-1	--	--	9	--	--	--	3.0	--	0.0	γ''
BI-2	1	--	6	--	1.2	--	2.0	--	0.60	None
BI-3	2	--	6	--	2.5	--	2.0	--	1.25	γ''
BI-4	2.5	--	5	--	3.1	--	1.6	--	1.9	γ' ($+\gamma''$)
BI-5	2.5	--	3	--	3.0	--	.96	--	3.1	γ'
BI-3	2	--	6	--	2.5	--	2.0	--	1.25	γ''
BI-6	2	.3	6	--	2.5	.66	2.0	--	1.58	$\gamma'+\gamma''$
BI-7	2	.6	6	--	2.5	1.3	2.0	--	1.9	γ'
BI-8	1	--	--	3	1.2	--	--	1.85	0.65	None
BI-9	2	--	--	3	2.4	--	--	1.85	1.3	γ'
I	3	.3	2.5	2	3.6	.64	.80	1.25	2.1	γ'
II	3	--	3	2.5	3.7	--	1.0	1.6	1.4	γ''

Table III. Selected Heat Treatments and Mechanical Properties of Alloy III

Heat Treatment	725°C/16hrs	725°C/16hrs+ 650°C/16hrs	750°C/6hrs+ 650°C/8hrs
Yield Strength, ksi (MPa)	154 (1063)	172 (1187)	180 (1242)
Tensile Strength, ksi (MPa)	208 (1435)	220 (1518)	222 (1532)
Elongation, %	28	26	22
Reduction in Area, %	64	56	46
Fracture Toughness, Ksi $\sqrt{\text{in}}$ (MPa $\sqrt{\text{m}}$)	123 (135)	103 (113)	-- --

Table IV. Selected Heat Treatments and Mechanical Properties of Alloy IV

Heat Treatment	700 °C/16hrs	700°C/16hrs+ 600°C/16hrs	700°C/16hrs 600°C/64hrs
Yield Strength, ksi (MPa)	168 (1159)	178 (1228)	182 (1256)
Tensile Strength, ksi (MPa)	193 (1332)	198 (1366)	200 (1380)
Elongation, %	25	23	21
Reduction in Area, %	53	54	52
Fracture Toughness, ksi $\sqrt{\text{in}}$ (MPa $\sqrt{\text{m}}$)	89 (98)	-- --	90 (99)

Table V Selected Heat Treatments and Mechanical Properties of Alloys V and VI

Alloy	V				VI	
Heat Treatment	750°C/8hrs	750°C/8hrs+ 650°C/8hrs	750°C/8hrs+ 650°C/16hrs	700°C/16hrs	700°C/16hrs+ 600°C/16hrs	700°C/16hrs+ 600°C/64hrs
Yield Strength, ksi	147	164	166	145	151	157
(MPa)	(1014)	(1132)	(1145)	(1001)	(1042)	(1083)
Tensile Strength, ksi	203	212	214	186	189	194
(MPa)	(1401)	(1463)	(1477)	(1283)	(1304)	(1339)
Elongation, %	22	20	21	30	30	29
Reduction in Area, %	48	44	43	60	57	55
Fracture Toughness	110	--	109	198	--	184
ksi√in (MPa√m)	(121)	--	(120)	(218)	--	(202)

Table VI. Diffraction Analysis for the γ' and γ'' Phases

$h^2+k^2+l^2$	γ' phase		Forbidden	γ'' phase	
	<u>Superlattice</u>	<u>Fundamental</u>		<u>Superlattice</u>	<u>Fundamental</u>
$\frac{1}{4}$			$00\frac{1}{2}$	---	---
1	100	---	100	001	---
$1\frac{1}{4}$			---	$10\frac{1}{2}$	---
2	110	---	101	110	---
$2\frac{1}{4}$			$00\frac{3}{2}, 11\frac{1}{2}$	---	---
3	---	111	---	---	111
$3\frac{1}{4}$			---	$10\frac{3}{2}$	---
4	---	200	---	---	200, 002
$4\frac{1}{4}$			$20\frac{1}{2}, 11\frac{3}{2}$	---	---
5	210	---	210, 102	201	---
$5\frac{1}{4}$			---	$21\frac{1}{2}$	---
6	211	---	211	112	---
$6\frac{1}{4}$			$20\frac{3}{2}, 00\frac{5}{2}$	---	---
7					
$7\frac{1}{4}$			---	$21\frac{3}{2}, 10\frac{5}{2}$	---
8	---	220	---	---	220, 202
$8\frac{1}{4}$			$22\frac{1}{2}, 11\frac{5}{2}$	---	---
9	300, 221	---	300, 212	003, 221	---
$9\frac{1}{4}$			---	$30\frac{1}{2}$	---
10	310	---	301, 103	310	---

All indices are based on the fcc lattice.

FIGURE CAPTIONS

- Fig. 1 Correlation of aged hardness with γ - γ' misfit in nickel-aluminum-ternary element alloys.¹⁷
- Fig. 2 Schematic diagrams of the unit cells and the close-packed planes of fcc $Li_2 \gamma'$ and bct $DO_{22} \gamma''$.
- Fig. 3 Goldschmidt atomic radii of elements.
- Fig. 4 Effects of the fraction of Nb or Ta replacing Ti on the close-packed lattice constant of the Ni_3X phases.
- Fig. 5 Coexistence of γ' and γ'' precipitates in BI-6; bright field and dark field from (001) reflection.
- Fig. 6 Laves phase along grain boundaries in BI-8, bright field.
- Fig. 7 Precipitation of metastable phases in Fe-Ni base austenites.
- Fig. 8 Estimated electron/atom ratio of metastable Ni_3X phase in Fe-Ni base austenites.
- Fig. 9 Coupled γ' and γ'' precipitation in Alloy I after aging at 720°C for (a) 8 hrs, (b) 24 hrs, (c) 72 hrs, and (d) 148 hrs; dark fields from (001) reflection.
- Fig. 10 Bright field of as annealed Alloy III.
- Fig. 11 Isothermal hardness curves of Alloy III.
- Fig. 12 Growth of spherical γ' particles in Alloy III at 725°C: (a) 2 hrs, (b) 9 hrs, (c) 24 hrs, and (d) 96 hrs; dark fields from (001) reflection.
- Fig. 13 Variation of the mean γ' particle size with aging time at 725°C.
- Fig. 14 Tensile properties of Alloy III as a function of the aging time at 725°C.
- Fig. 15 Cellular η precipitation in Alloy III, (a) bright field, (b) dark field from $(1\bar{2}10)_\eta$ reflection.
- Fig. 16 Double aging hardness curves of Alloy III.
- Fig. 17 Distributions of γ' particle size after single and double aging.
- Fig. 18 Bright field of as annealed Alloy IV.
- Fig. 19 Isothermal hardness curves of Alloy IV.

- Fig. 20 Tensile properties of Alloy IV as a function of the aging time at 700°C.
- Fig. 21 Disc-shaped γ'' precipitates in Alloy IV after aging at 725°C for 2 hrs; (a) bright field, (b) dark field from (001) reflection.
- Fig. 22 Growth of γ'' particles in Alloy IV at 725°C: (a) 2 hrs., dark field from (001) reflection; (b) 9 hrs, bright field; (c) 24 hrs, bright field; (d) 96 hrs, bright field.
- Fig. 23 Variation of the mean γ'' particle size with aging time.
- Fig. 24 Nucleation of the equilibrium β phase along grain boundaries in Alloy IV after aging at 725°C for (a) 9 hrs, (b) 24 hrs, bright field.
- Fig. 25 Cellular β precipitation in Alloy IV, (a) bright field, (b) dark field from (200) reflection.
- Fig. 26 Nucleation of β phase on carbide surface, bright field.
- Fig. 27 Cellular growth of β phase nucleated on carbide surface, bright field.
- Fig. 28 Double aging hardness curves of Alloy IV.
- Fig. 29 True stress-strain curves for γ' - and γ'' -hardened austenitic alloys.
- Fig. 30 Isothermal hardness curves of Alloy V.
- Fig. 31 Isothermal hardness curves of Alloy VI.
- Fig. 32 Aging time for peak hardness as a function of aging temperature.
- Fig. 33 Double aging hardness curves of Alloy V.
- Fig. 34 Double aging hardness curves of Alloy VI.
- Fig. 35 Equilibrium phase solvus determinations for Alloy III; (a) as forged, (b) 900°C/1 hr, (c) 925°C/1 hr, (d) 950°C/1 hr, optical micrographs.
- Fig. 36 Tensile properties and grain size of double-aged Alloy III as a function of solution annealing temperature.
- Fig. 37 Fractographs of double-aged Alloy III, annealed at (a) 1150°C, (b) 1000°C.
- Fig. 38 Tensile properties of double-aged Alloy III as a function of solution annealing time at 1000°C.

- Fig. 39 Tensile properties of aged Alloy V as a function of solution annealing temperature.
- Fig. 40 Fractographs of aged Alloy V, annealed at (a) 1150°C, (b) 1000°C.
- Fig. 41 Comparison between 750°C hardness curves of Alloy V under the as forged and solution annealed at 1000° and 1150°C.
- Fig. 42 Schematic diagram of the free energy curves for metastable precipitates.
- Fig. 43 Schematic depictions of six reciprocal space planes for a typical fcc lattice γ containing γ' and γ'' , respectively.
- Fig. 44 Selected area diffraction patterns along the [100] axis of the fcc matrix, which contains (a) γ' , (b) γ'' .
- Fig. 45 Dark fields from the (001) reflection showing (a) spherical γ' , (b) disc-shaped γ'' particles.

XBL 787-5364

Fig. 1 Correlation of aged hardness with γ - γ' misfit of nickel-aluminium-ternary element alloys.¹⁷ XBL 787-5364.

γ' : $L1_2$ Type (f.c.c.)

γ'' : DO_{22} Type (b.c.t.)

XBL 789-5832

Fig. 2 Schematic diagrams of the unit cells and the close-packed planes of fcc $L1_2$ γ' and bct DO_{22} γ'' .

XBL 793-5953

Fig. 3 Goldschmidt atomic radii of elements.

Fig. 4 Effects of the fraction of Nb or Ta replacing Ti on the close-packed lattice constant of the Ni_3X phases.

Fig. 5 Coexistence of γ' and γ'' precipitates in BI-6; bright field and dark field from (001) reflection. (XBB 7810-13048)

Fig. 6 Laves phase along grain boundaries in BI-8, bright field.

(XBB 786-7292)

XBL7810-5921

Fig. 7 Precipitation of metastable phases in Fe-Ni base austenites.

XBL 7810-11830

Fig. 8 Estimated electron/atom ratio of metastable Ni_3X phase in Fe-Ni base austenites.

Fig. 9 Coupled γ' and γ'' precipitation in Alloy I after aging at 720°C for (a) 8 hrs, (b) 24 hrs, (c) 72 hrs, and (d) 148 hrs; dark fields from (001) reflection. (XBB 788-10252)

Fig. 10 Bright field of as annealed Alloy III. (XBB 791-49)

XBL793-595

Fig. 11 Isothermal hardness curves of Alloy III.

Fig. 12 Growth of spherical γ' particles in Alloy III at 725°C:
(a) 2 hrs, (b) 9 hrs, (c) 24 hrs, and (d) 96 hrs; dark
fields from (001) reflection. (XBB 791-63)

XBL793-5943

Fig. 13 Variation of the mean γ' particle size with aging time at 725°C.

XBL 793-5952

Fig. 14 Tensile properties of Alloy III as a function of the aging time at 725°C.

Fig. 15 Cellular η precipitation in Alloy III, (a) bright field, (b) dark field from $(1\bar{2}10)_\eta$ reflection. (XBB 793-3353)

XBL793-5947

Fig. 16 Double aging hardness curves of Alloy III.

Fig. 17 Distributions of γ' particle size after single and double aging.

Fig. 18 Bright field of as annealed Alloy IV. (XBB 791-48)

XBL 793-5950

Fig. 19 Isothermal hardness curves of Alloy IV.

XBL 793-5940

Fig. 20 Tensile properties of Alloy IV as a function of the aging time at 700°C.

Fig. 21 Disc-shaped γ'' precipitates in Alloy IV after aging at 725°C for 2 hrs; (a) bright field, (b) dark field from (001) reflection. (XBB 791-54)

Fig. 22 Growth of γ'' particles in Alloy IV at 725°C: (a) 2 hrs, dark field from (001) reflection; (b) 9 hrs, bright field; (c) 24 hrs, bright field; (d) 96 hrs, bright field. (XBB 791-62)

XBL 793-5941

Fig. 23 Variation of the mean γ'' particle size with aging time.

Fig. 24 Nucleation of the equilibrium β phase along grain boundaries in Alloy IV after aging at 725°C for (a) 9 hrs, (b) 24 hrs; bright field. (XBB 791-60)

Fig. 25 Cellular β precipitation in Alloy IV, (a) bright field,
(b) dark field from (200) reflection. (XBB 791-55)

Fig. 26 Nucleation of β phase on carbide surface, bright field.

(XBB 791-50)

Fig. 27 Cellular growth of β phase nucleated on carbide surface,
bright field. (XBB 791-64)

XBL 793-5945

Fig. 28 Double aging hardness curves of Alloy IV.

austenitic alloys.

Fig. 29 True stress-strain curves for γ' - and γ'' -hardened

XBL 79-3-5937

Fig. 30 Isothermal hardness curves of Alloy V.

XBL 93-5949

XBL 793-5948

Fig. 31 Isothermal hardness curves of Alloy VI.

XBL 793-5935

Fig. 32 Aging time for peak hardness as a function of aging temperature.

XBL 793-5946

Fig. 33 Double aging hardness curves of Alloy V.

Fig. 34 Double aging hardness curves of Alloy VI.

XBB 793-3354

Fig. 35 Equilibrium phase solvus determinations for Alloy III;
(a) as forged, (b) 900°C/1hr, (c) 925°C/1hr, (d) 950°C/1hr,
optical micrographs.

XBL793-5933

Fig. 36 Tensile properties and grain size of double-aged Alloy III as a function of solution annealing temperature.

Fig. 37 Fractographs of double-aged Alloy III, annealed at
(a) 1150°C, (b) 1000°C. (XBB 793-3352)

XBL793-5932

Fig. 38 Tensile properties of double-aged Alloy III as a function of solution annealing time at 1000°C.

XBL 793-5934

Fig. 39 Tensile properties of aged Alloy V as a function of solution annealing temperature.

Fig. 40 Fractographs of aged Alloy V, annealed at (a) 1150°C,
(b) 1000°C. (XBB 793-3350)

XBL 793-5939

Fig. 41 Comparison between 750°C hardness curves of Alloy V under the as forged and solution annealed at 1000°C and 1150°C .

XBL 793-5936

Fig. 42 Schematic diagram of the free energy curves for metastable precipitates.

Fig. 43 Schematic depictions of six reciprocal space planes for a typical fcc lattice γ containing γ' and γ'' , respectively.

Fig. 44 Selected area diffraction patterns along the [100] axis of the fcc matrix, which contains (a) γ' , (b) γ'' .

(XBB 789-10891)

Fig. 45 Dark fields from the (001) reflection showing (a) spherical γ' ,
(b) disc-shaped γ'' particles. (XBB 793-3351)