Coarsening kinetics of coherent $\gamma'$ precipitates in ternary Ni-based alloys: the Ni–Al–Si system

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Abstract

Coarsening of coherent precipitates $\gamma'$ in alloys such as Ni-based alloys has been studied extensively not only for its practical significance in the design of engineering alloys but also in an effort to understand the phenomenon of coarsening. However, a complete understanding of the role of the multiple factors that can affect the coarsening kinetics in such systems is still lacking. Although some advances have been made through computer simulations, studying experimentally the influence of the volume fraction of the second phase and that of coherency strains on the kinetics of coarsening has been particularly challenging.

This paper will highlight some of the issues that are relevant to the study of coarsening in multi-component alloy systems. Recent results obtained for the kinetics of coarsening of $\gamma'$ precipitates in different alloys within the Ni-Al-Si system will be presented. Compositions of these alloys have been chosen so as to vary both the magnitude and the sign of coherency strains between the precipitate and the matrix. Some anomalies related to the composition dependence of the kinetics of coarsening will be highlighted. This paper will conclude with a discussion on the role of the volume fraction of the second phase and coherency strains in contributing to these anomalies and identify directions for future work. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Ni-based superalloys; Intermetallic compounds; Coherency strains; Coarsening kinetics; Small-angle neutron scattering

1. Introduction

Many Ni-based superalloys are strengthened by the precipitation of one or more coherent intermetallic compounds. For example, alloy 718, which is a commonly used Ni-based alloy, is strengthened by the precipitation of $\gamma'$ and $\gamma''$, both being ordered intermetallic compounds. In such alloys, optimum strengthening is achieved by the presence of small, finely dispersed coherent particles. Experiments have shown that during high temperature exposure, the microstructures of these alloys evolve with time. Particles have been observed to change their size, size distribution, shape, and spatial distribution, resulting in potential loss of the desirable mechanical properties. This phenomenon, termed coarsening, has been studied in a wide range of alloys ranging from simple binary alloys to more complex multi-component alloys [1–6]. From an engineering standpoint, the kinetics of coarsening in these alloys determines the deterioration in alloy performance with time and hence the factors that control this have to be examined in detail.

The term coarsening or Ostwald ripening refers to the micro-structural changes occurring during the late stages in precipitation and growth transformations. The simplest of these changes involves the growth of particles larger than a certain critical size and the disappearance of particles smaller than this size; this results in an increase in the average size of the particles resulting in a lowering of the total surface energy. The first complete quantitative analysis of this phenomenon was from Lifshitz and Slyozov [7] and Wagner [8], commonly referred to as the LSW theory. The LSW theory is strictly applicable only to the growth of an infinitesimally small volume fraction of precipitates in a dilute fluid matrix. They showed that in such a system, the average size of the particles obeys the law

$$R^3 - R_0^3 = K(t - t_0),$$

where $R$ is the average radius at time $t$, $R_0$ is the average radius at time $t_0$ (beginning of ripening stage), and $K$ is the rate constant. For spherical precipitates in binary systems under conditions where volume diffusion predominates, the
rate constant is given by the expression
\[ K = \frac{8 \gamma D V_m^2 C_e}{9RT}, \tag{2} \]
where \( \gamma \) is the interfacial energy of the particle–matrix interface, \( C_e \) is the equilibrium solute concentration of the matrix, \( V_m \) is the molar volume of the precipitate, and \( D \) is the bulk or volume diffusion coefficient of the solute in the matrix. Further, they showed that in the long-time limit, the particle size distribution approaches a time-invariant form, independent of the initial particle size distribution.

Although the original LSW theory was developed for binary systems, this analysis has subsequently been extended to multi-component systems. Slezov and Sagalovich [9–11] studied the growth of compound precipitates of the type \( A_iB_j \) in a matrix \( M \). Using the methods adopted by Lifshitz and Slyozov, they showed that the coarsening rate for an alloy that is only slightly supersaturated with respect to all the components, can be expressed as
\[ K = \frac{8 \gamma V_m^2 n_0}{9kT\left(\frac{p_i^1}{Q_1} + \frac{p_i^2}{Q_2}\right)}, \tag{3} \]
where \( \gamma \) is the interfacial energy, \( Q_i \) \((i = 1, 2)\) denote the solute contents of the alloy, \( D_i \) are the diffusion coefficients of the components in the matrix, \( n_0 \) is the number of lattice sites per unit volume and
\[ p_i = \frac{v_i}{v_1 + v_2}. \tag{4} \]
An obvious feature of Eq. (3) is that the coarsening rates vary within the ternary system depending on the composition of the precipitate phase and the relative values of the two diffusion coefficients. This effect, for ease of future reference will be termed the chemical effect and will be discussed in detail in a later section.

A number of experimental studies have been conducted in various systems to test the validity of the kinetics of coarsening [1–6]. It has been observed that the \( t^{1/3} \) law is generally valid except in systems that are highly constrained. However, the particle size distributions observed in real systems are broader than that predicted by the LSW theory. Two factors are considered as contributing to this discrepancy between the experimental results and calculations. These include the volume fraction of precipitates and the presence of coherency strains.

1.1. Effect of volume fraction on coarsening behavior

One of the shortcomings of the original theory was that it was applicable only to a system with an infinitesimally small volume fraction of the precipitate. This is considered to be one of the important factors that cause the discrepancy between the predicted and observed particle size distributions. In recent years, there have been a number of theories and computer simulations that predict an increase in coarsening rates with an increase in volume fraction of the coarsening phase [2,3]. Experiments show that this is generally true in liquid–solid systems. However, in solid–solid systems, experimental evidence to support these theories is lacking [2].

1.2. Effect of coherency strains on coarsening behavior

Another factor that significantly complicates experiments in solid–solid systems is the presence of coherency strains. Although coarsening has been studied in a wide variety of alloys, Ni-base alloys are one of the more popular alloys for such studies. Most Ni-base alloys are strengthened by the precipitation of coherent \( \gamma' \) precipitates of \( L1_2 \)-type structure. In the Ni–Al system for example, by a proper aging treatment, one can obtain the precipitation of coherent NiAl precipitates, with the misfit parameter \( \delta \) defined as
\[ \delta = \frac{(a_p - a_m)}{a_m}, \tag{5} \]
where \( a_p \) is the lattice parameter of the precipitate and \( a_m \) is the lattice parameter of the matrix, being of the order of 0.3%. Many interesting microstructural phenomena have been reported to occur during coarsening of \( \gamma' \) precipitates in Ni-base alloys [5,6,12–15]. It has been observed that particles can start as spheres in the early stages of coarsening and evolve into cubes and then split into octets. Precipitates have been found to align themselves along elastically soft crystallographic directions. In some cases, particles have even been observed to resist coarsening. All these effects have been explained based on interparticle elastic interaction arising from coherency strains. Most advances in the area of understanding the effect of coherency strains on coarsening rates has come from analytical treatments or computer simulations of coarsening in the presence of interparticle interactions. The results of some of the computational studies have been discussed in a recent review [6]. In the present paper, only a brief mention will be made of the important conclusions from these studies.

Johnson et al. [16–18] considered the effect of the coherency strains on the rate of growth of two particles in the presence of interparticle elastic interactions arising solely from a difference in the modulus of the precipitate and the matrix. For equal sized particles, there was a tendency for particles harder than the matrix to dissolve, while particles softer than the matrix tended to grow. For particles with unequal sizes, they found that if the particles were softer than the matrix, there was a tendency for “inverse coarsening”—the smaller particle grew at the expense of the larger particle. When the particles were harder than the matrix, the growth of the larger particle was accelerated. Further, they found evidence for particle migrations. In another study, they examined the effect of elastic anisotropy on the growth rate of a pair of particles in an elastically homogeneous system using a kinetic approach. They observed that the relative growth rates of two unequal sized particles were
dependent on their orientation with respect to the elastically hard and soft directions in the matrix. If the particles were aligned along a hard direction, the growth rate of the larger particle was enhanced while if these were aligned along a soft direction, inverse coarsening occurred. Again, they found that the tendency for particle migration very high.

These observations were explained based on minimization of the total system energy. In this system with no elastic inhomogeneity, the interaction energy arises from the presence of coherency strains and elastic anisotropy and hence is dependent on the misfit, elastic anisotropy parameter, interparticle spacing, particle orientation with respect to the crystallographic directions and the relative sizes of the particles. They argue that elastic effects are prominent at small interparticle distances and large particle sizes. It should also be noted the elastic anisotropy effect has a much stronger influence ($L^{-3}$ dependence) on the degree of interparticle elastic interactions than the elastic inhomogeneity effect in isotropic systems ($L^{-6}$ dependence) confirming the results of earlier studies on the elastic energy of two particle systems.

Abinandanan and Johnson [19] performed numerical simulation of coarsening of tetragonally misfitting precipitates in an isotropic matrix. Their results showed strong tendency for non-classical effects including tendency for particle migration and development of spatial correlation of particles and inverse coarsening. Again, for small particle sizes, they found that capillarity dominates the microstructural evolution, while at larger particle sizes elastic interactions have a significant effect. Interestingly, they observe that strong spatial correlation could develop even before a change in the average size of the particles could be detected. Particle translation, reverse coarsening and long-range spatial correlation of particles have been shown to occur in systems with long-range elastic interactions by Wang et al. [20].

Kawasaki and Enomoto [21] examined the dynamics of the coarsening process in the presence of elastic interactions. They assumed that for small differences in the elastic constants between the particle and the matrix, the elastic interaction energy of the multi-particle system ($E_{\text{int}}$) can be expressed as

$$E_{\text{int}} = \frac{1}{2} \beta' \sum_{i,j} \sum_{j',j''} r_j^3 \left( \frac{r_j^3}{L_{ij}^2 - r_j^2} + \frac{r_j^3}{L_{ij'}^2 - r_j^2} \right),$$

(6)

where $\beta' \propto (\Delta \mu)^{\frac{2}{3}}, \Delta \mu$ is the difference between the shear moduli of the particle and the matrix, and $r_j$ and $r_j'$ are the radii of $i$th and $j$th particle, respectively, and $L_{ij}$ is the inter-center distance between these two particles. Note that $E_{\text{int}}$ drops to zero for either $\Delta \mu = 0$ or for $\delta = 0$ and changes as $\delta^2$ (and hence independent of the sign). Using this expression, they showed that for immobile particles, if the particles were softer than the matrix, they could be stabilized against coarsening. They also found that the $t^{1/3}$ law holds in the early stages even in the presence of elastic interaction, but in the later stages, coarsening is accelerated to $t^{1/2}$ kinetics if the particles were harder than the matrix.

The above discussion shows that in the model systems that were considered for the studies, elastic effects were clearly manifested in the microstructural evolution. It is generally understood that both capillarity effects and coherency strains have a role to play in the evolution of microstructure. However, to the knowledge of the authors, there is no study that predicts quantitatively, the effect of misfit parameter, elastic anisotropy and elastic inhomogeneity on the kinetics of coarsening. Efforts to observe experimentally, the effect of coherency strains on coarsening rates have been plagued with difficulties, as outlined below.

An important consideration in the experimental study of coherency strains on coarsening rates is the ability to vary the lattice parameters of the precipitates and the matrix at a constant temperature. This necessitates the use of multi-component systems, since in a binary system, the equilibrium compositions and hence the lattice parameters of the two phases are fixed for a particular temperature. However, the change in the composition of the matrix and precipitates also changes the coarsening rates due to the “chemical effect” as outlined earlier. Hence, to understand the effect of coherency strains, the contribution from the chemical effect has to be subtracted from the overall change in coarsening rates with the composition of the alloy. This has proved quite difficult in the past due to complications associated with the ternary and higher component systems [22].

Calderon and Fine [23] and Calderon et al. [24] investigated the coarsening of coherent $\beta'$ particles (NiAl-type) in ferritic Fe–Ni–Al and Fe–Ni–Al–Mo matrix. The measured coarsening rates increased with an increase in the magnitude of the misfit parameter from $\delta = 0.2\%$ to $\delta = 0.8\%$ [23]. This change in lattice parameter ensued from the addition of 2.0% Mo. The diffusion coefficient of Mo in Fe is the largest amongst those of Ni, Al and Mo. Hence it is not clear if this increase is due to the compositional change from alloy 1 to alloy 2 or whether it is due to the increase in the value of the misfit parameter. Further work on the same system [24], showed that with the initial addition of Mo, the misfit decreases and the coarsening rate decreases but with further addition of Mo, the misfit increases and the coarsening rate increases. However, it is difficult to separate out the effect of the addition of Mo from that of the change in the misfit parameter.

Conley et al. [25] used transmission electron microscopy to measure coarsening rates in a series of Ni–Al–Mo alloys. In their study, the measured coarsening rate decreased when the misfit decreased from 0.4 to $-0.1\%$. However, the reduction in misfit also corresponds to an increase in the Mo to Al ratio. Note that the interdiffusion coefficient for dilute solute contents at 750°C in the Ni–Mo system is much lower than that of the Ni–Al system [26]. Other studies in the Ni–Al–Mo system [27,28] show that as the Al to Mo ratio decreases, the misfit decreases accompanied
by a decrease in the coarsening rates. Clearly, the direction of change in the coarsening rates is such that it decreases with the addition of a slower diffusing species. Again it is difficult to prove that the coarsening rates decrease because of a decrease in the misfit parameters since the decrease in coarsening rates could be due to the replacement of Al with Mo, which has a smaller diffusion coefficient.

In another recent study, Mackay and Nathal [29] studied coarsening in Ni-6 wt.% Al-6 wt.% Ta-x wt.% Mo alloys as a function of the Mo content using transmission electron microscopy with the volume fraction of the second phase in these alloys being about 60%. They found that the coarsening rate decreased with an increase in the Mo content and progressively larger negative values of the misfit parameter. They argued that since the composition dependence of the effective diffusion coefficient in concentrated Ni–Mo alloys is weak, this lowering in coarsening rates with addition of Mo must be due to the variation in the misfit parameter. Again, the role of the addition of Mo is not clearly addressed.

Another complication in analyzing coarsening in ternary systems is that unlike a binary system, that is characterized by a single interdiffusion coefficient, cross-terms may have to be considered in ternary systems. The inter-diffusion flux of a component \( i \) in a multi-component system can be expressed as [30]

\[
J_i = -\sum_{j=1}^{n-1} D_{ij}^\text{eff} \frac{\partial C_j}{\partial x}, \quad i = 1, 2, 3, ..., n-1, \tag{7}
\]

where \( D_{ij} \) are the \((n-1)^2\) interdiffusion coefficients and \((\partial C_j/\partial x)\) is the concentration gradient of component \( j \). Thus, a matrix consisting of four interdiffusion coefficients is necessary for the complete description of diffusion in a ternary system. However, other approximations can be used in the absence of the complete matrix of interdiffusion coefficients. It can be assumed that the primary interdiffusion coefficients are equal to the interdiffusion coefficient in the corresponding binary system. Alternatively, the discrete average effective interdiffusion coefficient, which incorporates the effect of cross-terms by defining effective interdiffusion coefficients, can be used. In this approach the flux of a component \( i \) is expressed as

\[
J_i = -D_i^\text{eff} \frac{\partial C_i}{\partial x}, \quad i = 1, 2, ..., n, \tag{8}
\]

where the average effective interdiffusion coefficient \( D_i^\text{eff} \) is related to the matrix of interdiffusion coefficients [31–33]. Although both approaches have been used for the interpretation of results [34], the present study will concentrate only on the first approach.

### 1.3. Study of coarsening in the Ni–Al–Si system

The binary phase diagrams of the Ni–Si and the Ni–Al systems have been extensively used for the study of coarsening. Both phase diagrams indicate the presence of an intermetallic \( L1_2 \) phase of nominal composition \( \text{Ni}_3X \) where \( X \) is Al or Si. Ochiai et al. [35] used a diffusion couple consisting of \( \text{Ni}_3\text{Al} \) and \( \text{Ni}_3\text{Si} \) and showed that the two compounds form a continuous solid solution at temperatures below 1100°C. Mitsuhashi et al. [36] confirmed that at 1000°C, the \( \gamma' \) solid solution is continuous between the two binary systems, and that the \( \gamma - \gamma' \) solvus line is roughly linear between about 14.5 at.% Si on the Ni–Si binary edge to about 13.5 at.% Al at the Ni–Al binary edge.

An additional factor to be considered in the Ni–Al–Si system is that of the lattice parameters of \( \gamma \) and \( \gamma' \). Mishima et al. [37] have shown that the addition of Si to both \( \gamma \) and \( \gamma' \) lowers the lattice parameters, while the addition of Al results in an increase in the lattice parameter of the two phases. Further, it should be noted that the lattice parameter of \( \text{Ni}_3\text{Si} \) is smaller than that of the Ni–Si solid solution it is in equilibrium with at 600°C. For the same temperature the lattice parameter of \( \text{Ni}_3\text{Al} \) is larger than that of the Ni–Al solid solution with the equilibrium composition. Clearly, for some composition within the two-phase region in the ternary system, the \( \gamma \) and the \( \gamma' \) in equilibrium will have equal lattice parameters. The significance of this will be discussed in a later section.

In the current study, coarsening was followed in a series of alloys that have a constant Ni content of 88 at.% while the Si content varied from 4.0 at.% to 11.0 at.% (except the binary Ni–Si alloy where the Si content was 12.5 at.%). Although it is not possible to provide an accurate value for the volume fraction of the second phase in the absence of precise phase boundary and tie-line information, it is estimated that the volume fraction of \( \gamma' \) in these series of alloys is about 15.0%. It is expected that the variation of the volume fraction in these alloys would be small since the \( \gamma \) solvus line and the \( \gamma' \) phase boundary line are roughly parallel to the constant Ni line in the isothermal section.

Recently, Muralidharan et al. [38] have measured the room temperature lattice parameters of \( \gamma \) and \( \gamma' \) in a series of alloys with a constant Ni content of 88 at.% along with the thermal expansion coefficients of \( \gamma \) and \( \gamma' \) in one of these alloys. Based upon the composition dependence of the lattice parameters presented by Mishima et al. [37], they have calculated the compositions of the \( \gamma' \) in these alloys and hence presented a schematic of the Ni-rich portion of the isotherm at 600°C. Note that at this temperature, the solid solubility of both Si and Al in Ni as indicated by the binary phase diagrams is about 10 at.% Although \( \gamma' \) exists over a range of Ni concentrations, for the sake of simplicity it is assumed that it is stoichiometric (line compound). This data will be used for the calculation of the composition dependence of the coarsening rates in this study.

### 1.4. Small-angle neutron scattering and coarsening

Small-angle neutron scattering was used to follow the kinetics of coarsening in the current study and Guinier
radius was the characteristic length scale used to characterize the microstructural evolution. The difficulties associated with the use of Guinier approximation for extracting a characteristic particle size in the presence of a particle-size distribution and inter-particle interference effects are well-recognized [39,40]. One of the important characteristics of the use of Guinier radius in this study is that no attempt is made to address the issue of actual average particle radius in the microstructure and its relationship to the Guinier radius obtained from the small-angle neutron scattering measurements. However, it is assumed that this relationship is invariant with the microstructural evolution occurring in a particular sample. This assumption will be true if dynamical scaling is shown to exist during the coarsening of these alloys since dynamical scaling implies that the microstructure evolves in a self-similar manner. Dynamical scaling holds if the small-angle neutron scattering intensity follows the relationship [39,40]

\[
\frac{S(Q,t)}{\tilde{I} V} = L^3(t)s(QL(t)),
\]

where \(\tilde{I}\) is the integrated small-angle scattering intensity given as

\[
\tilde{I} = \frac{1}{V} \int S(Q)dQ.
\]

\(Q\) is the scattering vector, \(L(t)\) is the characteristic length scale, \(s(QL(t))\) is the time-independent scaling function and \(V\) is the volume of the sample. It will be shown later that dynamical scaling is indeed valid for the alloys used in the present series of measurements when the characteristic length scale \(L(t)\) is replaced by the Guinier radius extracted from the small-angle neutron scattering data. Hence, the kinetics of coarsening can be obtained by following the time dependence of this characteristic length scale of the system. It will also be shown that the time invariant function \(s(QL(t))\) remains essentially the same from sample to sample and thus \(L(t)\) obtained from the small-angle scattering spectrum of one sample can be compared with that obtained from another sample.

Most studies on coarsening are performed using transmission electron microscopy and thus emphasize much larger particle sizes than those observed in the present study. Further, such studies are not performed in-situ. Thus, very little is known about the dynamics of coarsening in the very early stages and this could be one of the important reasons for the present lack of comprehensive understanding of the effect of coherency strains on coarsening rates. This becomes particularly important in reference to the calculations of Abinandanan and Johnson [19], which show that spatial correlations develop early in the evolution and may affect the coarsening behavior of the particles. The present study provides information regarding coarsening rates in a regime that is not easily studied by any other technique. Additionally such information is obtained in-situ.

2. Experimental method

The Ni–Al–Si alloys used in this study were prepared from pure Ni, Al and Si in an arc-melting furnace equipped with a copper hearth, in batches of approximately 10 g. Weight losses were measured to be less than 0.2% in most cases. The nominal compositions of all the alloys used are shown in Table 1. The buttons were homogenized at 1100°C for 2–3 days in evacuated quartz tubes following which they were rolled into sheets 1.75 mm thick. For small-angle neutron scattering measurements, samples in the form of disks of diameter 16 mm were punched out from these sheets. These disks were solution treated at 1020°C for 1–10 h in flowing helium. The heat-treatment times were varied to ensure that the average grain size in the samples

Table 1
Composition of alloys used in this study

| Alloy designation | Nominal composition (at.%) | Measured composition (at.%) |
|------------------|---------------------------|-----------------------------|
| 4                | Ni-4.0 Si-8.0 Al          | Ni-3.94 Si-8.2 Al           |
| 9                | Ni-7.0 Si-5.0 Al          | Ni-6.6 Si-5.0 Al            |
| 12               | Ni-7.5 Si-4.5 Al          | Ni-7.71 Si-5.25 Al          |
| 11               | Ni-7.8 Si-4.2 Al          | Ni-8.37 Si-3.52 Al          |
| 1                | Ni-8.1 Si-3.9 Al          | Ni-8.1 Si-3.4 Al            |
| 13               | Ni-8.4 Si-3.6 Al          | —                           |
| 8                | Ni-8.75 Si-3.25 Al        | Ni-8.85 Si-2.16 Al          |
| 16               | Ni-9 Si-3 Al              | —                           |
| 14               | Ni-9.3 Si-2.7 Al          | Ni-9.5 Si-2.3 Al            |
| 2                | Ni-9.5 Si-2.5 Al          | —                           |
| 7                | Ni-9.75 Si-2.25 Al        | Ni-9.6 Si-2.2 Al            |
| 6                | Ni-10.25 Si-1.75 Al       | Ni-10.0 Si-1.54 Al          |
| 15               | Ni-10.6 Si-1.4 Al         | Ni-10.5 Si-1.6 Al           |
| 3                | Ni-11.0 Si-1.0 Al         | —                           |
| 12.5 Si          | —                         |                             |

Fig. 1. Transmission electron micrograph of precipitates in composition 11 after a 12 h heat treatment at 600°C.
was 1 mm. or larger. At the conclusion of the heat-treatment, the samples were rapidly quenched into iced-brine to retain the supersaturated solid solution. Samples were subsequently polished using standard metallographic techniques and etched with Kalling’s 2 reagent.

Coarsening in these samples was studied in-situ at 600°C using the small-angle diffractometer at the Intense Pulsed Neutron Source of Argonne National Laboratory. The temperature of the sample was continuously monitored by a K-type thermocouple in contact with it. To minimize oxidation of the samples, helium was purged through the system. Coarsening was followed for times ranging from 15 to 30 h depending on the observed rate of growth of the precipitates. Transmission Electron Microscopy was performed on selected samples aged ex-situ for similar lengths of time at 600°C to provide an alternate method for characterization of the particle growth rate in the samples.

3. Results

Figs. 1 and 2 show transmission electron micrographs of the precipitates in two alloys of composition 11 and composition 6 after a 12 h heat treatment at 600°C [41,42]. Note that the shape of the precipitates is essentially spherical with the average radius in composition 6 being much larger than that in composition 11. Fig. 3(a) and (b) shows the variation of the small-angle neutron scattering profile as a function of time at 600°C for composition 6 and composition 11, respectively. The raw SANS intensity profiles have been converted into absolute units. Note that for comparable times, the scattering intensity from composition 6 is much larger than that from composition 11. In all the alloys used in this study, it was observed that the scattering from the as-quenched condition was very weak denoting that the saturated solid solution had been retained.

Fig. 2. Transmission electron micrograph of precipitates in composition 6 after a 12 h heat treatment at 600°C.

Fig. 3. Variation in the small-angle neutron scattering profile as a function of time at 600°C in: (a) composition 6; and (b) composition 11.

Fig. 4(a) and (b) tests the applicability of the scaling behavior of the small-angle neutron scattering profiles by plotting $S(Q,t)/R_g^3$ as a function of $QR_g$. Only one representative spectrum is shown for each composition along with the $R_g$ used for scaling the data. Note that for composition 6, scaling is observed from about 2.8 h with the spectrum obtained after 0.28 h at 600°C clearly showing deviations from the scaling behavior. Fig. 4(b) shows that for composition 11, dynamical scaling is observed for data obtained from about 1.93 h.

Fig. 5 illustrates the composition dependence of the time-independent scaling functions obtained for the different alloys. Note that the shapes of the curves are very similar, with the maxima occurring at comparable $QR_g$ values. It is particularly useful to note that in spite of the possible differences in the spatial arrangement of particles in the various samples, the time-independent scaling functions are relatively independent of the composition of the sample. This is one of the consequences of using polycrystalline material and a relatively large neutron beam that enables spatial averaging and minimizes the effect of spatial correlations of particles on the shape of the small-angle neutron scattering spectrum. The overall similarity of the time-independent scaling functions without considering the factor $IV$ clearly indicates that this factor is not significant in the calculations and supports our assumption that the volume fractions of $\gamma'$ in these samples do not vary significantly.
The similarity of the shape of the time-independent scaling function implies that the length scale ($R_g$) obtained from one sample can be compared with that obtained from another sample. This can be easily seen from Eq. (9) by considering the intensity at the maximum in the interference peak occurring at $Q_m$, for two samples $A$ and $B$ (excluding $iV$)

$$S(Q^A_m, t) = R^3_{g,A}(t)[Q^A_m R_{g,A}(t)]$$

$$S(Q^B_m, t) = R^3_{g,B}(t)[Q^B_m R_{g,B}(t)].$$

Fig. 4. Scaling behavior of the small-angle neutron scattering profiles obtained at 600°C in: (a) composition 6; and (b) composition 11.

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$$S(Q^B_m, t) = R^3_{g,B}(t)[Q^B_m R_{g,B}(t)].$$

Fig. 5. Variation in the time-independent scaling function with composition for the small-angle neutron scattering data obtained at 600°C.

Fig. 6. $R_g^3$ as a function of time for composition 7.
Since in the scaling regime

\[ s[Q_m^A R_{q,A}(r)] = s[Q_m^B R_{q,B}(t)], \]

(12)

the ratio of the intensities at \( Q_m \) in the two samples is simply proportional to the ratio of the cube of the characteristic length scales at time \( t \) in the two samples. A comparison of the series of spectra in Fig. 3(a) and (b) shows that at any given time, the scattering from alloy 6 is more intense than that from alloy 11. From the previous arguments it can be concluded that such differences in intensity can arise only due to the differences in the size of the particles since the scattering length density differences from sample to sample are also expected to be very small.

Guinier radii have been extracted from the slope of the \( \ln(S(q)) \) vs. \( q^2 \) plot and the variation of \( R_g^3 \) as a function of time at 600°C was obtained for all alloys used in the study. Fig. 6 shows the variation in \( R_g^3 \) as a function of time for composition 7. As shown in the figure, it was generally observed that during the early stages, \( R_g^3 \) did not vary linearly with time. Such behavior has also been reported in the in-situ X-ray diffraction and SANS study of coarsening in Ni-12.5 at.% Si alloy by Polat et al. [39]. However in their work, they observed that during the same time period \( R_g^3 \) varied linearly with time and hence concluded that the alloys were still in the growth regime. In the present study, it was noted that the slope is closer to 0.33 rather than 0.5. Hence, it is possible that the alloys are actually in the transient coarsening regime where the time dependence of the average radius is variable and is dependent on the initial particle size distribution [43].

Since a linear region can be clearly identified in the \( R_g^3 \) vs. time plots and the small-angle neutron scattering spectra show dynamical scaling, it is clear that coarsening regime has been reached during these experiments. Coarsening rates have been obtained in these alloys from the linear regions in the plot of \( R_g^3 \) vs. time. The errors in the Guinier radii have been propagated to the coarsening rate constant by using a weighted linear least squares fit. Fig. 7 shows the variation of these coarsening rates as a function of the Si content in these alloys obtained from the small angle neutron scattering measurements. Also shown in the figure are the results of the TEM measurements. It should be recollected that the alloy composition is completely determined when the Si content is known since the Ni content is maintained at 88.0 at.% Since the functional form of the variation of coarsening rates with composition is unknown, a continuous line has been drawn through the data-points using spline-fitting. In the following sections, we will analyze this observed variation of coarsening rates by calculating the variation of coarsening rates with the Si content and argue that there are significant deviations from the calculated coarsening rates and provide possible explanations for this anomalous behavior.

4. Analysis of results

To rationalize the observed trend in the coarsening rates,
we first proceed to calculate the chemical effect in this system. Since the essential physics of multi-component growth is reflected in Eq. (3) we use this expression to calculate the composition dependence of $K$. Composition dependence of the coarsening rates in this ternary system can now be simplified to a function $F$ given by [22,34]

$$F = \frac{1}{\frac{p_{\text{Si}}^2}{D_{\text{Si}}Q_{\text{Si}}} + \frac{p_{\text{Al}}^2}{D_{\text{Al}}Q_{\text{Al}}}}.$$  

(13)

The equilibrium compositions of the precipitate and matrix at were obtained from Ref. [38]. From the composition of $\gamma^\prime$ (Ni$_3$(Si, Al)) it follows that $p_{\text{Si}} + p_{\text{Al}} = 1$;

$$Q_{\text{Si}} \text{ and } Q_{\text{Al}} \text{ that denote the total amount of solutes can be assumed to be equal to the mole fraction of solutes, } X_{\text{Si}} \text{ and } X_{\text{Al}}, \text{ respectively. Here, } D_{\text{Si}} \text{ denotes the diffusion coefficient for Si while } D_{\text{Al}} \text{ denotes that for Al.}$

Interdiffusion coefficients measured in the individual binary systems [44] have been used for $D_{\text{Si}}$ and $D_{\text{Al}}$. Since the diffusion coefficients were available for 1100°C, they were extrapolated to 600°C using activation energies obtained from the literature. A value of 276 kJ/mol was used for $Q$ in the Ni–Al system and for the Ni–Si system, the value used was 240 kJ/mol. Fig. 8 shows the comparison of the calculated trend in coarsening rates with the measured variation. Note that the calculated coarsening rates ($F$) have been scaled such that the measured $K$ for composition 12 and the calculated value for this composition are identical. Note that although the overall shape of the “background” is reasonably well modeled, significant differences exist between the calculated and measured values.

In all cases $p_{\text{Si}}$ and $p_{\text{Al}}$ were calculated on the assumption that the sum of Al and Si contents in $\gamma^\prime$ was 25.0 at.%. However, it has been shown that in the binary Ni–Si system, the composition of $\gamma^\prime$ is closer to 23.5 at.% Si [37,45]. Hence the corrected $p_{\text{Si}}$ and $p_{\text{Al}}$ have been used in the alloy that is richest in the Si content, composition 3. Fig. 8 shows a comparison of the measured variation and the results of the calculations. Significant improvement in the modeling of the background is evident from the figure. However, the presence of two peaks over and above the background in the range of 7.5 at.% Si–11.0 at.% Si is clear from the figure. To understand the origin of these two peaks, further analysis is necessary.

5. Discussion

One of the characteristics of this work is the emphasis on relative values of coarsening rates instead of absolute values. This approach is for two reasons:

(1) Many of the physical parameters that are necessary for calculating the absolute magnitudes of $K$ are not known or inaccurate.

(2) In the presence of a particle size distribution, the Guinier radius obtained from small-angle neutron scattering data tends to be weighted towards larger particle sizes and hence is different from the average radius [39,40]. However, all coarsening theories consider the time evolution of the average particle size. The absolute magnitude of $K$ obtained by following the temporal evolution of the Guinier radius will be different from the value of $K$ obtained by using the average radius. Instead of relating the Guinier radius to the average radius (which involves previous knowledge of the particle size distribution) we have factored out the difference by considering only relative values of $K$. It should be emphasized here that Guinier radius has been used for the analysis only because of its simplicity. Any other appropriate length scale could have been chosen for the analysis with similar results since the data shows clear evidence of dynamical scaling.

An important feature of the current study is that it represents the first attempt to use Eq. (3) to analyze coarsening data in ternary Ni-base alloys. Traditionally, coarsening data obtained in such systems have been interpreted using Eq. (2) by employing an effective diffusion coefficient or by considering the product of the diffusion coefficient and the interfacial concentration of the rate-controlling species [22]. Such approximations were necessitated by the lack of diffusivity data and values for other physical parameters that are required for Eq. (3). It is clear from Fig. 8 that in spite of such limitations, use of Eq. (3) along with appropriate diffusion coefficients and reasonable values for the phase-compositions can result in successful modeling of the general shape of the composition dependence of the coarsening rate constants.

Fig. 9 shows the background from the chemical effect and
the measured coarsening rates in the region of interest. Note that the local minimum in the coarsening rates occurs around a composition of 9.15 at.% Si. One possible candidate for the enhancement of coarsening rates on either side of this composition is the volume fraction effect. It should be recalled that due to the nature of the phase diagram, all alloys in this study were expected to have approximately equal volume fractions of the second phase. If this assumption is not valid and the volume fraction were to increase for certain alloys, enhancement in coarsening rates would be observed. Recently Akaiwa and Voorhees [46] have shown using numerical simulation that when the volume fraction increases from 0.1 to 0.3, the value of \(K_{LSW}\) (where \(K_{LSW}\) is the coarsening rate at zero volume fraction of the second phase) increases from roughly 1.8–2.75, an increase of about 50%. Comparison with the approximately factor of 2 increase observed experimentally shows that this effect alone cannot contribute to the experimental observation. Further, such large volume fraction changes (an increase from 0.1 to 0.3) are unlikely to occur over small composition variations (about 0.75 at.% Si between composition 2 and composition 6) in the phase diagram under consideration. Although other models predict different magnitudes for the volume fraction effect [2–4], the model considered here predicts a ratio that is amongst the highest for such models and hence constitutes an upper bound for the enhancement due to the presence of a non-zero volume fraction of second phase precipitates.

Next, we analyze the possible role of coherency strains. Fig. 10 shows the variation in misfit parameter \(\delta\) as a function of composition. The misfit parameters at 600°C were calculated from the misfit parameters measured at room temperature and the measured thermal expansion coefficients of \(\gamma\) and \(\gamma'\) in composition 7 [38]. It is interesting to see that within experimental error, both \(\gamma\) and \(\gamma'\) are expected to have identical lattice parameters around 9.2 at.% Si. It is difficult to be very precise with this value since the actual functional form of the variation of \(\delta\) with composition is difficult to predict and only a spline fit has been utilized to obtain this value. Also shown in Fig. 10 is a plot of the variation of

\[
\Delta K = \frac{K_{\text{Meas}} - K_{\text{Calculated}}}{K_{\text{Calculated}}},
\]

as a function of the composition of the alloy. Superposed on this plot is a variation of \(\delta\) as a function of the Si content of the alloys. At around 9.2 at.% Si, the misfit parameter is close to zero and the coarsening rates are low. On either side of the zero misfit, the magnitude of \(\delta\) increases and so do the normalized coarsening rates. On the higher-Si side, the \(\delta\) increases monotonically and the coarsening rate increases, reach a maximum and then fall off. However, on the other side, the misfit parameter increases almost monotonically until about 8.5 at.% Si after which the increasing trend is broken (either remains constant or decreases slightly) and then continues to increase again when the Si content of the alloy is around 8.1 at.%.

The effect of this strange variation in \(\delta\) is reflected in the coarsening rates. The normalized coarsening rates increase when the \(\delta\) increases from zero until it reaches a maximum after which its value decreases (as on the Si-rich side). However, it increases again when the magnitude of the misfit parameter decreases and continues to decrease when the magnitude of \(\delta\) resumes its increasing trend. Thus, it is likely that the strange variation in coarsening rates around this composition is related to the effect of coherency strains.

In the following section, we try to offer a qualitative explanation of the interesting trend in coarsening rates observed in this study based on our current understanding of coarsening in coherent solids. In general, capillary effects dominate in the early stages of coarsening when the particles are small, while in the later stages elastic effects dominate as the particle sizes are large. However, elastic effects cannot be ignored even in the early stages, as the inter-particle separation is small. Although it is recognized that elastic effects can affect coarsening in simple situations,
extending this to multi-particle systems is not easy. As discussed earlier, coherency strains could alter the coarsening kinetics of particles with an elastic constant different from that of the matrix. However, the effect is very much dependent on the elastic constants (affected both by the difference in the elastic constants of the precipitate and the matrix and the anisotropy of these values), particle sizes, particle separation and relative particle orientations. These factors must be considered along with the capillary effect and the way a system evolves is based on a competition between the elastic effects and capillary effects.

With reference to the elastic interaction energy, both elastic inhomogeneity and elastic anisotropy were identified as possible contributors to the elastic interaction energy and have to be considered for the present series of alloys. Since in both binary systems, the particles are harder than the matrix, it can be assumed that this is true in the ternary system. If the spatial distribution of the particles were assumed to be independent of the alloy composition, and particle migration is assumed to be non-existent then the contribution to the interaction energy could increase as \( \delta^2 \). Since the particles are harder than the matrix, as discussed earlier accelerated kinetics of growth would be expected with an increase in the magnitude of the misfit parameter. However, computer simulations have clearly shown a strong tendency for particle migration and shape change. These would tend to negate the effect of the increase in interaction energy due to increase in \( \delta \), resulting in the coarsening kinetics being controlled by the capillary effect. To find out which effect dominates, it would be necessary to find out the factors affecting the migration rates and rates of shape change. One would expect that these would depend on the interdiffusion coefficients and the misfit parameter.

In the view of the authors, the present work is one of the first experimental studies that have clearly demonstrated the effect of coherency strains on coarsening rates. It is interesting to note that such effects are dominant only at very small values of \( \delta(|\delta| < 0.1\%) \), a range that is not usually studied by researchers. This may be one of the reasons why information on the effect of coherency strains has been difficult to obtain. Our results are in very good agreement with numerical simulations that show the possibility of enhancements in coarsening rates for precipitates that are harder than the matrix. Further experimental work is needed in this area to obtain more evidence for similar effect in other alloy systems.

6. Conclusions

Although the phenomenon of coarsening has been studied for many years, challenges still remain. In particular, understanding the effect of coherency strains on the microstructural evolution still needs additional experimental and theoretical work. Computer simulations of coarsening have provided some qualitative understanding of the many interesting phenomena that occur in highly constrained systems. However, a comprehensive understanding of the effect of coherency strains on coarsening kinetics is not available at present.

Small-angle neutron scattering was used to follow the coarsening of \( \gamma' \) precipitates at 600°C, in a series of alloys in the Ni–Al–Si system. In all the ternary alloys, Ni content was maintained constant at 88 at.% while the relative amounts of Al and Si were varied. Coarsening rates were obtained for the different alloys and have been plotted as a function of the Si content of the alloys. Methods developed in our earlier papers have been used to calculate the variation in coarsening rates as a function of the Si content of the alloys. Using the composition of \( \gamma' \) obtained from lattice parameter measurements for these calculations resulted in a better modeling of the variation of coarsening rates due to alloy composition effects.

Comparison of the measured coarsening rates with the calculated and scaled coarsening rates shows that in the composition range 7.5 at.% Si–11.0 at.% Si, the two are significantly different. The measured coarsening rates show the presence of two peaks over and above the variation that would be expected based on the change in alloy composition. It was observed that the local minimum in coarsening rates in this composition range occurs at a composition for which the misfit parameter \( \delta \) at the temperature of coarsening is measured to be close to zero. The coarsening rates increase with an increase in the magnitude of the misfit parameter until the misfit parameter reaches a critical value beyond which further increases in the magnitude of the misfit parameter results in a decrease in the coarsening rates.

Based upon these observations, we propose that the initial increase in coarsening rates for small values of the misfit parameter is due to an increase in the elastic interaction energy. Decreases in coarsening rates with further increase in the magnitude of the misfit parameter is attributed to the relaxation of this interaction energy by either particle translations and particle shape changes. It is interesting to note that significant effects are observed for very small misfit parameters (<0.1%), a range which is not very often studied. Experimental work is needed in other alloy systems to assess the universality of the proposed model.

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