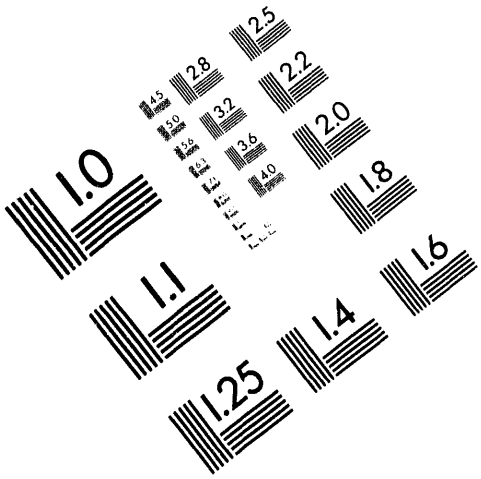

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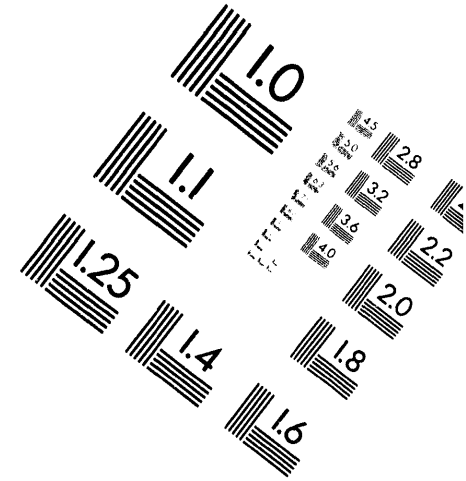

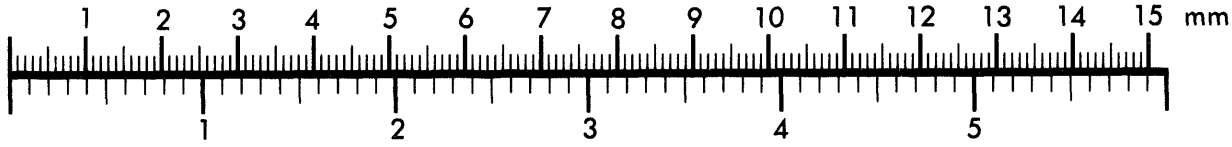

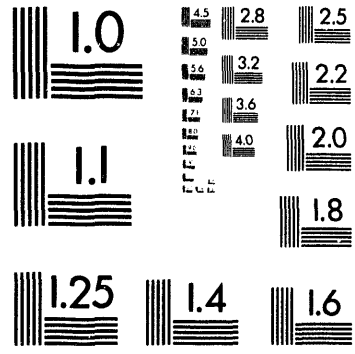

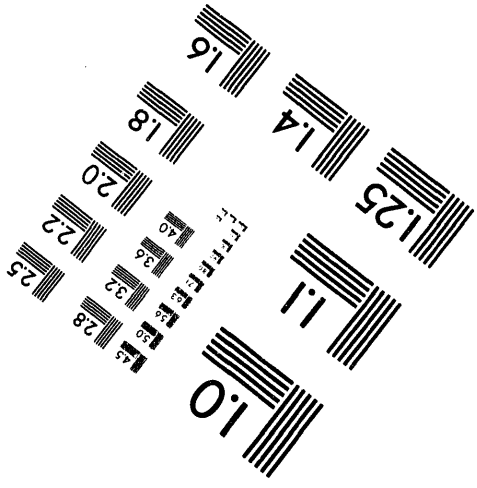

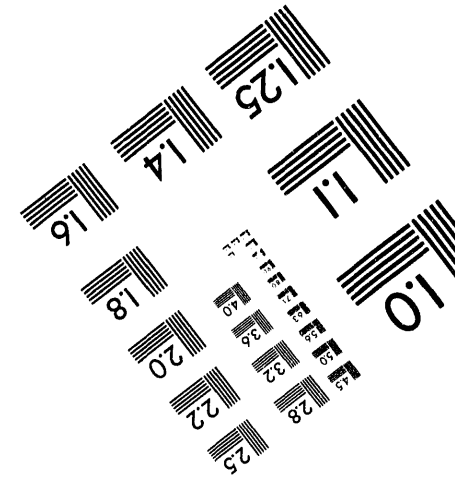

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Coherency Strains and Coarsening in Ni-Al-Si Alloys: An Experimental Study

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Abstract

Coarsening rates have been measured in a series of alloys in the ternary Ni-Al-Si system using *in-situ* Small Angle Neutron Scattering, the alloys having a constant Ni content and their Si content varying from 4.0 at. % to 11.0 at. %. Using expressions available in the literature for describing coarsening in multi-component systems, it is shown that it is possible to account for the variation in coarsening rates due to chemical effects. It is observed that the quality of the fit is improved if the composition dependence of the diffusion coefficient is considered in the analysis. Finally, the possible contribution of coherency strains to the measured coarsening rates is discussed.

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Introduction

The term Ostwald ripening or coarsening refers to the growth of larger particles at the expense of smaller particles that occurs during the late stages in precipitation and growth transformations. The LSW theory [1, 2] strictly applicable only to the growth of an infinitesimally small volume fraction of precipitates in an ideal fluid matrix shows that the average size of the particles obeys the law

$$R^3 - R_o^3 = K(t - t_o), \qquad (1)$$

where R is the average radius at time t, R_o is the average radius at time t_o (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

$$K = \frac{8\gamma D V_m^2 C_e}{9RT}, \qquad (2)$$

where γ is the 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.

To extend this study to a ternary system, Slezov and Sagalovich [3] considered the growth of compound precipitates of the type $A^{(1)}_{\nu_1}A^{(2)}_{\nu_2}$ in a matrix M containing $A^{(1)}$ and $A^{(2)}$. This is illustrative of the growth of precipitates like Al_2O_3 or SiO_2 in a matrix like Ni. Using the methods adopted by Lifshitz and Slyozov [1], they arrived at the following expression for the coarsening rate constant K for the special case when the alloy is only slightly supersaturated with both components $A^{(1)}$ and $A^{(2)}$:

$$K = \frac{8\sigma \overline{V}^2 n_o}{9kT\left\{\frac{p_1^2}{D_1Q_1} + \frac{p_2^2}{D_2Q_2}\right\}} \qquad (3)$$

Here,

$$p_i = \frac{\nu_i}{\nu_1 + \nu_2}, \qquad (4)$$

σ is the interfacial energy of the particle-matrix interface, $\overline{V}$ is the molar volume of the precipitate, n_o is the number of lattice sites per unit volume, Q_1 and Q_2 are the total quantities of the solutes $A^{(1)}$ and $A^{(2)}$ respectively and D_1 and D_2 are the corresponding diffusion coefficients of the solutes in the matrix M. Umantsev and Olson [4] considered the role of the thermodynamics of the solid solution in the coarsening of β particles of composition ($X_j^\beta(R)$, j=1,.....n) surrounded by a matrix of composition (X_j^α, j=1,....n) where n is an arbitrary number of components of an alloy. It can be shown that [5] for an ideal solid solution in the limit that the precipitate consists primarily of the solute atoms and small supersaturation, both studies yield identical results.

Many experimental studies done on coarsening show that the $t^{1/3}$ law is valid in all systems within experimental error [6-9]. However, the magnitude of the coarsening rate constant is in some cases significantly different from that predicted by the LSW theory. The presence of a finite volume fraction of precipitates in real systems is believed to be one of the important factors that may cause this discrepancy [6-9]. However, most real systems also show the presence of strains arising from the coherency between the coarsening precipitates and the matrix: the effect of this on coarsening rates is not very clear at this time.

Effect of Coherency Strains on Coarsening

Coherency strains are characterized by the value of the misfit parameter

$$\delta = \frac{(a_p - a_m)}{a_m}, \qquad (5)$$

where a_p is the lattice parameter of the precipitate and a_m is the lattice parameter of the matrix. It is well known that coarsening under the presence of coherency strains can cause changes in particle morphology during coarsening and cause alignment of particles along preferred directions in space [10]. However, the effect of these strains on the rate of coarsening is not very well understood. Both analytical work [11] and computer simulations [10] show that the temporal law is generally obeyed but the magnitude of the rate constant K can vary depending on the magnitude of the misfit parameter. In one recent study, however, Doi et al. [10] observed that in highly constrained systems (high value of δ), the temporal law was no longer obeyed at long coarsening times. Thus it is clear that more experiments are needed to clearly outline the effect of internal strains on coarsening.

The main objective of the current work is to study the effect of varying the misfit parameter δ on the coarsening rate constant K. The system being used for the study is the ternary Ni-Al-Si system. It is known that this system exhibits the precipitation of $L1_2$ type $Ni_3(Al,Si)$ (γ') from a supersaturated solid solution of Al and Si in Ni (γ) [13]. The composition of the two phases in equilibrium and hence the misfit parameter δ can be systematically varied by varying the overall alloy composition. To extract the contribution from coherency strains, one has to account for the variation in coarsening rates due to the chemical effects as decribed by (4). In this paper, we present some of our results on the Ni-Al-Si system and demonstrate the use of (4) to model the composition dependence of coarsening rates in this ternary system.

Experimental Method

Nine different alloys, their composition ranging from 4 at. % Si to about 12.5 at. % Si have been used for the study. The complete list of alloys and the calculated misfit parameters are shown in Table I. Note that the Ni content has been maintained constant at 88.0 at. %. Based on the available knowledge of the isotherms at higher temperatures, we believe that this would minimize the effect of variation in coarsening rates due to the variation in volume fraction. The lattice parameters of γ and γ' have been calculated based on the assumption that the Si/Al ratio is constant in both γ and γ' and is equal to that in the overall alloy composition. The lattice parameter as a function of composition was obtained from Michima et. al [13]. Fig. 1 shows the variation of the lattice parameters as a function of the Si content of the alloy.

Table 1 Composition and Misfit parameters of Ni-Al-Si Alloys used in the study

Alloy #	Composition	δ
4	Ni- 4.0 at.%Si- 8.0 at.% Al	+0.35%
9	Ni-7.0 at % Si-5.0 at. % Al	+0.08%
1	Ni- 8.1 at.% Si- 3.9 at.% Al	-0.02%
8	Ni- 8.75 at. %Si-3.25 at %Al	-0.08%
2	Ni- 9.5 at.% Si- 2.5 at.% Al	-0.15%
7	Ni-9.75 at.%Si- 2.25 at. % Al	-0.17%
6	Ni-10.25at.%Si-1.25at.%Al	- 0.26%
3	Ni-11.0 at.% Si- 1.0 at.% Al	-0.28%
10	Ni-12.5 at. % Si	-0.42%

The alloys were cast in the form of small buttons by arc melting from pure elements. These buttons were homogenized at 1100-1200°C for a couple of days. Small disks for the Small

Angle Neutron Scattering measurements were either cut from these buttons or punched out after rolling the buttons into sheets. These disks were then solutioned at 1020°C for 1- 8 hours, the higher times used when grain growth was desired. After solutioning, the disks were quenched into iced brine. In-situ Small Angle Neutron Scattering was carried out at different temperatures ranging from 481 to 630°C at the IPNS facility at Argonne National Laboratory.

To obtain the composition dependence of the diffusion coefficients and to measure the effect of the ternary interaction on the diffusion coefficients, diffusion measurements have been done at 1100°C. The diffusion couples used consisted of the following series of alloys: Ni-Ni-12.5 at% Si- Ni-12.5 at. % Al-Ni. Thus in one experiment it was possible to measure the diffusion coefficients in the ternary Ni-Al-Si system and compare it to those measured in the binary systems.

Results and Discussion

Guinier radii were obtained as a function of time at temperature from the SANS data. Using the $t^{1/3}$ law, coarsening rates were obtained as a function of the alloy composition. Fig. 2 shows the variation of the observed coarsening rates as a function of the Si content of the alloys at 550°C and 600°C. Errors arising from the measurements at 600°C have been calculated and are also shown in the figure. In some cases, the error bars were observed to be within the size of the data point.

A careful study of Fig. 2 shows that the coarsening rates do not vary monotically with the Si content. Note that at a composition of about 9.0 at % Si, there seems to be a local minimum and this trend in seen in the data collected at both temperatures. In order to study the relationship between this minimum in coarsening rates and coherency strains, one has to account for the variation in coarsening rates arising from the chemical effect. Although the expression (4) was originally derived for the coarsening of compound precipitates in a matrix, it can be applied to the coarsening problem in the current series of alloys since all the alloys used in the study have a constant Ni content. The essence of the composition dependence can be related to the expression

$$F = \frac{1}{\frac{p_1^2}{D_1Q_1} + \frac{p_2^2}{D_2Q_2}}, \qquad (6)$$

and we now proceed to calculate its variation as a function of composition. We need additional information on the equilibrium composition of the matrix and the precipitate to calculate p_1 and p_2. Since these are not available at this time, we assume that

$$\frac{Q_1}{p_1} = \frac{Q_2}{p_2}. \qquad (7)$$

We consider two different sets of diffusion coefficients for D_{Si} and D_{Al}:
1. Composition independent interdiffusion coefficients for the binary systems [14]
2. Composition dependent D_{Si} obtained from the current study in the binary Ni-Ni-12.5 at. %Si couple. Extrapolation to 600°C was done by using the activation energy obtained from the literature [14]. Composition dependence of D_{Al} at 1100°C was found to be small and hence was not accounted for. The results of the comparison are shown in Fig. 3. The calculated variation is placed on the same scale as the measured values by appropriate scaling. Note that the fit is quite reasonable over the entire composition range, when the composition dependence of the diffusion coefficient is considered! Future analysis will use the diffusion data obtained from the ternary system.

It is evident from Fig. 3 that in the experimentally measured composition dependence of the coarsening rates, there is a component in addition to the chemical effect. Lattice parameters of γ

and γ are being measured as a function of composition and the results of that study would enable us to conclude whether this additional component is due to the coherency strain effect.

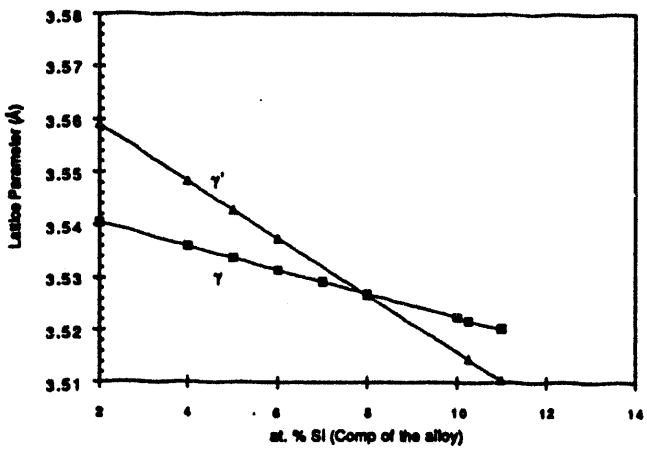

Fig. 1 Variation of the lattice parameters of γ and γ' as a function of alloy composition

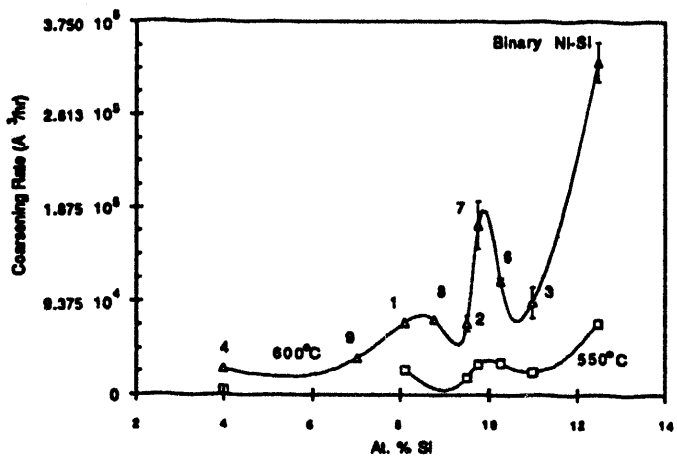

Fig. 2 Variation of Coarsening Rates as a Function of Si content

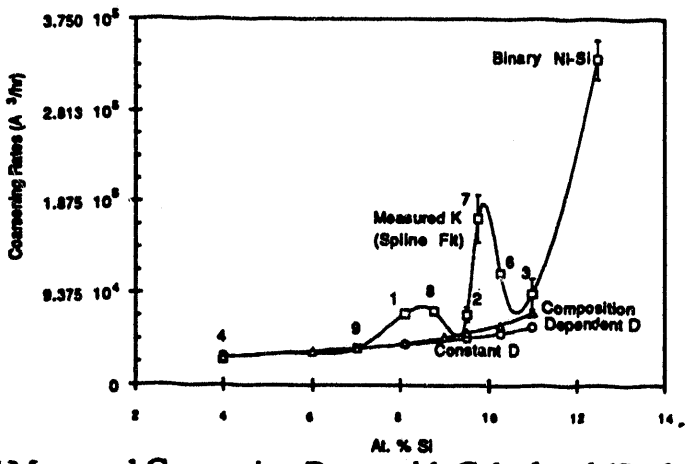

Fig. 3 Comparison of Measured Coarsening Rates with Calculated (Scaled) Values

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