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EXPERIMENTAL STUDIES ON THE EFFECT OF COHERENCY STRAINS ON COARSENING KINETICS: CURRENT STATUS AND FUTURE OUTLOOK

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G. Muralidharan ‡*, J. E. Epperson+ and Haydn Chen^{OSTI}

‡Materials Science Division and Intense Pulsed Neutron Source, Argonne National Laboratory, Argonne, IL-60439, USA

+ Materials Science Division, Argonne National Laboratory, Argonne, IL-60439, USA.

* Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL-61801, USA

ABSTRACT

The effect of coherency strains on the coarsening rate constant in Ostwald ripening is an area that is not well understood. We briefly review the extant experimental data on the effect of coherency strains on coarsening rates and explain the need to account for variations in coarsening rates due to composition and diffusivity effects before drawing any conclusions on the dependence of coarsening rates on the misfit parameter. Using the pre-existing theories for coarsening rates in multi-component systems, we suggest a simple method to account for the composition dependence of coarsening rates arising from factors unrelated to coherency strain effects. We then present some of the results from our on-going work in the Ni-Al-Si system and explain the relevance of this study to our understanding of coarsening in internally-stressed systems. We conclude the presentation with our views on the direction of future research in this aspect of coarsening.

OSTWALD RIPENING: A GENERAL INTRODUCTION

The term 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 average size and the disappearance of particles smaller than this critical size; this results in an increase in the average size of the particles resulting in a lowering of the total surface energy.

The first quantitative analysis of this phenomenon came from Lifshitz and Slyozov [LS61] and Wagner [Wag61], 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 an ideal fluid matrix. They showed that in such a situation, the average size of the particles obeys the law

$$R^3 - R_0^3 = K(t - t_0), \quad (1)$$

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

$$K = \frac{8\gamma DV^2 C_e}{9RT}, \quad (2)$$

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 coefficient of the solute in the matrix.

Further, they showed that in the asymptotic limit (long times), the particle size distribution approaches a form independent of the original particle size distribution.

A number of experimental studies have been conducted in various systems to test the validity of the theory. It is generally observed that the $t^{1/3}$ law is valid in all systems within experimental error. However the particle size distribution observed in real systems does not seem to follow the predictions of the LSW theory. One of the obvious shortcomings of the original theory was that it was applicable only to a system with a vanishingly small volume fraction of precipitate. This is considered to be one of the important factors that causes the discrepancy between the predicted and observed particle size distributions [JN89, Voo85, SS87, Voo92]. Particle-particle correlations have also been proposed as an explanation for the particle size distribution in real materials being broader than the one predicted by the LSW theory [Mar85, Voo92]. In this paper, we will not concern ourselves further, with this aspect of coarsening

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but will primarily examine the factors affecting the coarsening rate constant K .

One of the factors that has received significant attention is that of volume fraction. There have been a number of theories in recent years that predict an increase in coarsening rates with increase in volume fraction of the coarsening phase. This has not been proved to be universally true. This aspect of coarsening is discussed in [Voo85, Voo92].

In some recent work on internally stressed solids [Doi92], it has been observed that the LSW theory does not provide a satisfactory description for the microstructural evolution occurring in these solids. The nature and origin of these observations are discussed below.

ORIGIN AND EFFECT OF COHERENCY STRAINS

Although coarsening has been studied in a wide variety of alloys, Ni-base alloys are among the more popular alloys for such studies. Most Ni-base alloys are strengthened by the precipitation of coherent γ' precipitates of $L1_2$ structure. In the Ni-Al system for example, by a proper ageing treatment, one can obtain the precipitation of coherent Ni_3Al precipitates, with the misfit parameter δ defined as,

$$\delta = \frac{(a_p - a_m)}{a_m}, \quad (3)$$

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 0.5%.

Most studies in these systems have been focussed at studying the microstructure evolution during coarsening and relating it to the predictions of the LSW theory. For a detailed discussion of the following observations, readers are referred to [Doi92] and the references therein. Although the $t^{1/3}$ law has been found to be true in such systems, some unexpected features have been observed in these internally strained alloys. It has been found that particle morphology can vary from spherical to cuboidal depending upon the misfit observed in these alloys. Further, particles may start out as spheres but with the progress in coarsening, may change to cuboids and finally split into multiple particles at even later stages in coarsening. It has also been shown that these particles can align themselves along certain preferred directions in the matrix. More recently, it has been observed that the cubic rate law is not obeyed in systems that are highly constrained (high value of δ). Computer simulations have also shown that inverse coarsening, that is, growth of smaller particles at the expense of larger particles, is possible. Such non-traditional growth behaviour is now understood to be due to inter-particle elastic interactions [Doi92].

Although the effect of internal stress on micro-structural evolution is reasonably well characterized, its effect of the

coarsening rate constant has been studied to a lesser extent and is not very well understood. Designing an experiment to observe the effect of internal stresses is no complicated since the coarsening rate constant can be affected by many factors. To study the effect of δ on coarsening rates, the primary aim is to find a system in which the lattice parameters of both γ and γ' can be varied in a systematic manner. Since in a binary system, the composition of the two phases in equilibrium in a two-phase field (and hence the value of δ) at any particular temperature is independent of the alloy composition, there is a need to use ternary and other multi-component systems to achieve the desired variation in δ . However, significant difficulties arise in the interpretation of results in multi-component systems. We briefly discuss the expressions available for describing coarsening in multi-component systems.

DESCRIPTION OF COARSENING IN MULTI-COMPONENT SYSTEMS

Although the original LSW theory was developed for binary systems, this work has subsequently been extended to multi-component systems. Early work in this area has been that of Bhattacharyya and Russell [BR72], who studied the growth of compound precipitates of the type $A_{v_1}^{(1)}A_{v_2}^{(2)}$ in a matrix M . This is illustrative of growth of precipitates like Al_2O_3 and SiO_2 in a matrix like Ni. They were primarily concerned with the interpretation of the values of activation energies obtained in studies on coarsening in such systems. They derived expressions for the activation energies and coarsening rates in the special case where one of the two components dominated the process. Slezov and Sagalovich [SS76, SS77] considered the same problem, but in a more comprehensive manner. They express the fluxes of the components as

$$J_{ir} = \frac{D_i n_0 (\bar{C}_i - C_{ir})}{r}, \quad (4)$$

where J_{ir} are the fluxes of the individual components at the interface, D_i is the diffusion coefficient of component i , n_0 is the number of lattice sites per unit volume, C_{ir} is the concentration of species i at the interface, and \bar{C}_i is the concentration of i in the matrix. Further, the fluxes of the two species are related by the expression

$$\frac{J_{1r}}{v_1} = \frac{J_{2r}}{v_2}, \quad (5)$$

The interface composition was assumed to be given by the law of mass action written as

$$C_{1r}^{v_1} C_{2r}^{v_2} = K_r, \quad (6)$$

where K_r is the equilibrium rate constant for the dissociation reaction of the compound at the surface.

Using these expressions they arrive at the following expression:

$$\frac{dr}{dt} = \frac{D_{\sigma} \bar{V} n_s}{r} \left(\Delta - \frac{\alpha}{r} \right), \quad (7)$$

where

$$\Delta = p_1 \left(\frac{\bar{C}_1 - C_{1\infty}}{C_{1\infty}} \right) + p_2 \left(\frac{\bar{C}_2 - C_{2\infty}}{C_{2\infty}} \right), \quad (8)$$

$$\alpha = \frac{2\sigma \bar{V}}{kT}, \quad (9)$$

$$D_{\sigma}^{-1} = \frac{p_1^2}{D_1 C_{1\infty}} + \frac{p_2^2}{D_2 C_{2\infty}}, \quad (10)$$

and

$$p_i = \frac{v_i}{v_1 + v_2}, \quad (11)$$

$C_{2\infty}$ and $C_{1\infty}$ are the concentrations at the surface of the particles of infinite radius, σ is the interfacial energy and \bar{V} is the molar volume of the precipitate. Using the methods adopted by [LS61], they show that the coarsening rate for an alloy that is only slightly supersaturated with respect to all the components, can be expressed as,

$$K = \frac{8\sigma \bar{V}^2 n_s}{9kT \left\{ \frac{p_1^2}{D_1 Q_1} + \frac{p_2^2}{D_2 Q_2} \right\}}, \quad (12)$$

where Q_i denote the total quantities of solute in the alloy. For the case where the initial concentrations correspond to the stoichiometric composition, (i.e.)

$$\frac{Q_1}{p_1} = \frac{Q_2}{p_2}, \quad (13)$$

the coarsening rate is given by the expression,

$$K = \frac{8\sigma \bar{V}^2 n_s}{9kT \left\{ \frac{p_1}{D_1} + \frac{p_2}{D_2} \right\}} \frac{1}{p_1} \left\{ \frac{p_2}{p_1} \right\}^{\frac{1}{n}} K_{-}^{-\frac{1}{n}}. \quad (14)$$

The coarsening rate when the concentration of one of the components is much larger than that of the other is,

$$K = \frac{8\sigma \bar{V}^2 n_s}{\frac{p_1^2}{D_1 Q_1} + \frac{p_2^2}{D_2 Q_2 (1 - \frac{Q_1 p_2}{Q_2 p_1})}} \left(\frac{K'}{\left(1 + \frac{Q_1 p_2}{Q_2 p_1} \right)^{p_2}} \right)^{\frac{1}{n}}, \quad (15)$$

where

$$K' = \frac{K_{-}^{-\frac{1}{n}}}{Q_1^{p_1} Q_2^{p_2}}. \quad (16)$$

In a later section we will outline the application of these equations to real alloy systems.

Although there have been several other studies done on coarsening in multi-component systems [CA86, LAG91], we will refer only to some recent work by Umantsev and Olson [UO93]. They considered the coarsening of β particles of composition $(X_j^{\beta} (R), j=1, \dots, n)$ surrounded by a matrix of composition $(X_j^{\alpha}, j=1, \dots, n)$ where n is an arbitrary number of components of an alloy. Their expression for the coarsening rate is given as

$$K = \frac{8\sigma V_m^{\beta}}{9\Phi}, \quad (17)$$

where,

$$\Phi = \sum_{j=1}^n \sum_{i=1}^n (\bar{X}_i^{\beta} - \bar{X}_i^{\alpha}) \frac{G_{m,ij}^{\alpha}}{D_j} (\bar{X}_j^{\beta} - \bar{X}_j^{\alpha}), \quad (18)$$

$$G_{m,ij}^{\alpha} = \frac{\partial^2 G_m^{\alpha}(\bar{X}^{\alpha})}{\partial X_i \partial X_j}, \quad (19)$$

and \bar{X}_i^{β} and \bar{X}_i^{α} are the equilibrium compositions of the precipitate and matrix respectively. Note that the coarsening resistance is dependent upon the difference in the equilibrium concentrations of the solutes in the precipitate and the matrix, the thermodynamics of the solid-solution and the diffusivities. If one assumes that the solution behaves ideally, then the expression for the coarsening resistance reduces to

$$\Phi^{\alpha} = RT \sum_{i=2}^n \frac{\bar{X}_i^{\alpha}}{D_i} (k_i - 1)(k_i - k_1), \quad (20)$$

where

$$k_i = \frac{\bar{X}_i^{\beta}}{\bar{X}_i^{\alpha}}. \quad (21)$$

We see that in the limit that $\bar{X}_i^{\beta} = 0$ (the precipitate consists primarily of the solute atoms), $p_1 = \bar{X}_1^{\beta}$ and in the limit of small supersaturation, $\bar{X}_i^{\alpha} = X_i^{\alpha} = Q_i$. Using these expressions, (20) reduces to the denominator in (12).

Let us now examine how the coarsening rate varies with composition with an example. Let us consider the variation with composition of the expression

$$F = \frac{1}{\frac{p_1^2}{D_1 Q_1} + \frac{p_2^2}{D_2 Q_2}}, \quad (22)$$

which accounts for the composition-dependence of the coarsening rates (12) (assuming that the interfacial energy is only weakly dependent on the composition). We make an additional assumption that (13) is also valid and that $Q_1 + Q_2 = \text{constant} = 10$. Fig. 1 shows the variation of F as a function of the solute content under these constraints for different relative values of D . Note that even in the absence of volume fraction and stress effects, there is a variation in the coarsening rates with composition, arising from the difference in the diffusivities and the equilibrium compositions. Thus before any inference is drawn about the effect of factors like stress and volume fraction, one has to account for this composition dependence in coarsening rates in any multi-component system! The effect is much lower if the diffusivities of the components in the matrix are approximately equal. However in most real systems, this is rarely achieved, which will be apparent from the following discussion on coarsening in multi-component systems.

Another complication that arises in ternary systems is that of the ternary diffusion coefficients. Unlike the binary system which is characterized by a single interdiffusion coefficient, cross-terms have to be considered in ternary systems. The effect of these cross-terms is not well understood at this stage: however it must be recognised

that it may have an effect on coarsening in multi-component systems.

EXPERIMENTAL WORK ON COARSENING IN MULTI-COMPONENT SYSTEMS

There have been many efforts in the past to study coarsening in ternary and higher order systems. We will briefly review the work that is directly related to the interpretation of the effect of coherency strains on coarsening rates. For a more comprehensive review please see [JN89].

Gibbons and Hopkins [GH71] studied coarsening of γ particles in several Ni-Cr-Al, Ni-Cr-Al-Nb, Ni-Cr-Al-Ti alloys at 750°C. In the Ni-Cr-Al alloys, the measured misfit parameters were less than 0.02%. They found that the coarsening rates in these alloys were independent of the volume fraction of the second phase precipitates. They also found that with the addition of either Ti or Nb, the volume fraction of the precipitates and the coarsening rates decreased, while the misfits increased in magnitude. They found that this effect became more pronounced with an increase in the Ti:Al and Nb:Al ratios. They attributed the decrease in coarsening rates to the increasing values of these ratios rather than to the volume fraction, since volume fraction was found to have a negligible effect on coarsening in Ni-Cr-Al alloys. No effort was made to correlate the magnitude of change in coarsening rates to that of the volume fraction or the misfit parameter. It is

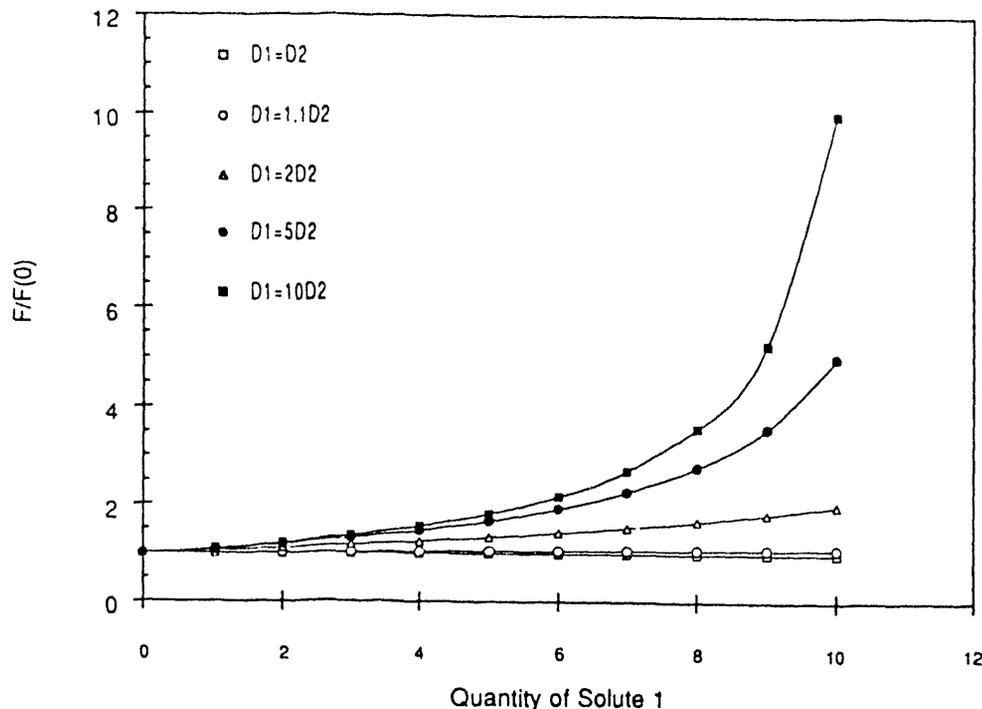


Fig. 1 Calculated Variation of Coarsening Rates as a Function of Diffusion Coefficients and Composition in a Ternary System (see text for details) [MEH94a]

interesting to note that the diffusivity in the Ni-Al system [MB88] at 750°C is lower ($4.63 \times 10^{-14} \text{ cm}^2/\text{sec}$) than the diffusivity in the Ni-Ti system ($7.66 \times 10^{-14} \text{ cm}^2/\text{sec}$) while the addition of Ti results in a *decrease* in the coarsening rates in this Ni-based alloy system, which is contrary to what one would expect based upon the simple analysis presented before.

In another study, Chellman and Ardell [CA74] confirmed that coarsening in Ni-Cr-Al system was independent of the volume fraction. In contrast to the case of the Ni-Al and the Ni-Ti systems, the diffusivities at 750°C in the Ni-Cr and Ni-Al systems [MB88] are *very similar* (Ni-Cr: $5.3 \times 10^{-14} \text{ cm}^2/\text{sec}$, Ni-Al: $4.63 \times 10^{-14} \text{ cm}^2/\text{sec}$). Based on the analysis for coarsening in ternary systems presented before, one would indeed expect very little variation with composition in coarsening rates in this system!

Biss and Sponseller [BS73] studied the effect of Mo on coarsening in several Ni-Cr-Al-Mo-Ti systems at 760°C and 925°C. They found that the addition of Mo resulted in a decrease in the coarsening rates, which they attributed to the lowering of the mobility of solute atoms due to the presence of Mo. They also discuss qualitatively, the likelihood of coherency strains influencing the diffusion rates. Chung and Chaturvedi [CC75] investigated the effect of volume fraction on the coarsening behaviour of γ in several Co-Ni-Cr-Ti alloys at 800°C and 900°C. They concluded that coarsening rates in these alloys were independent of the volume fraction.

Calderon and Fine [CF84] investigated the coarsening of coherent β' particles (NiAl-type) in ferritic Fe-Ni-Al and Fe-Ni-Al-Mo matrix. They measured coarsening rates in two alloys: Alloy 1: Fe-3Ni-9.7Al ($\delta=0.2\%$) and Alloy 2: Fe-2.5Ni-5.7Al-2Mo ($\delta=0.8\%$), at 700°C using transmission electron microscopy. They found that the coarsening rate constant in alloy 2 was larger ($K=146.6 \text{ nm}^3/\text{hr}$) compared to that measured in alloy 1 ($K=140.9 \text{ nm}^3/\text{hr}$). They analyzed their data using the LSW theory for binary systems by considering NiAl as a constituent. They considered the values for the diffusion coefficient at 700°C for different species in the Fe-based alloy. These values are listed below:

$$D_{\text{Ni}}=1.2-1.8 \times 10^{-13} \text{ cm}^2/\text{sec},$$

$$D_{\text{Al}}=3.6 \times 10^{-13} \text{ cm}^2/\text{sec},$$

$$D_{\text{Mo}}=3.0 \times 10^{-12} \text{ cm}^2/\text{sec}.$$

Since Ni is the slowest diffusing species, they assumed that this step was rate-controlling. It is not possible to explain the results in quantitative terms based on the known diffusion coefficients, since this is a quaternary system and no data is available on the equilibrium compositions of the phases. Further, there is no information on the composition dependence of the diffusion coefficients or of any solute-solute interactions.

In a subsequent work, Calderon et. al [CFW88] studied the effect of volume fraction and coherency strains on coarsening of coherent precipitates in several Fe-Ni-Al-Mo systems. They measured coarsening rates in two

different series of alloys: one with a low volume fraction of the second phase (6%) and the other with a high volume fraction of the coherent precipitates (36%). Their results are summarized in Table 1. Note that in both series of alloys, the coarsening rates seem to follow the trend of the misfit parameters: (i.e) they both first decrease with the addition of Mo and then increase. However, it is not possible to calculate if all the changes observed are only due to the misfit parameter since there is no easy way of accounting for the chemical effect that was discussed earlier. Note that the diffusion coefficient of Mo in Fe is higher than that of the other components and hence an increase in the overall coarsening rates with increase in Mo content is to be expected.

Although from the data shown in Table 1 it is obvious that there is a significant increase in the coarsening rates in alloys with a higher volume fraction of precipitates, a glance at the composition of the alloys shows that the significant changes in the Al and Ni content have been made to achieve the desired increase in volume fraction. The natural question to ask is, what role, if any, does this composition change have on the magnitude of the coarsening rates and can this be quantified? As clearly demonstrated in ternary systems, a combination of diffusion coefficients and equilibrium phase compositions has a significant role in determining coarsening rates. Such a behaviour can be expected in higher-order multi-component systems too! However with the very limited knowledge available on phase equilibria and diffusion coefficients in multi-component systems, a quantitative estimate of the chemical effects in such systems is very difficult. Accounting for such effects is *crucial* in any study designed at understanding the effect of other factors like volume fraction and coherency strains, since the magnitude of the effects of these factors are not known at this stage and one may be drawn to the wrong conclusions if the chemical effects are ignored.

Conley et. al [CFW89] and Calderon and Kostorz [CK90] studied coarsening in Ni-Al-Mo alloys. Conley et. al used transmission microscopy to measure coarsening rates in a series of Ni-Al-Mo alloys. The compositions of the alloys and the coarsening rates along with other relevant information are shown in Table 1. Note that the coarsening rate decreases from $380 \text{ nm}^3/\text{hr}$ in alloy 1 with a misfit of 0.4% to $3 \text{ nm}^3/\text{hr}$ in alloy 3 with a misfit of -0.1%. However the reduction in misfit also corresponds to an increase in the Mo:Al ratio. In their analysis of their data, the authors consider the role of diffusion coefficients in determining the variation in coarsening rates. Note that the inter-diffusion coefficient [MB88] at 750°C in the Ni-Mo system is $7.11 \times 10^{-15} \text{ cm}^2/\text{sec}$ and is much lower than that of the Ni-Al system ($4.63 \times 10^{-14} \text{ cm}^2/\text{sec}$). They argue that the diffusion coefficient would be an unlikely cause of the observed variations in coarsening rates since the major change in the coarsening rate occurred when the Mo:Al ratio was changed from 0.5 to 1.0 while a further increase from 1.0 to 1.5 caused a smaller change in the coarsening rates. They point out that the coarsening rates

follow the trends in misfit parameter better than the trends in the Mo:Al ratio; the misfit decreases fairly rapidly initially and then at a much slower rate.

A study of Fig. 1 shows that the rate of change of coarsening rates with composition can vary, depending on composition of the alloy. Note that for the case where $D_1=10D_2$, the coarsening rate decreases quite rapidly with the initial addition of the slower diffusing species but with further additions, the decrease is at a much lower rate. It is possible that such a phenomenon may be occurring in the Ni-Al-Mo system, primarily due to the large difference in the two diffusion coefficients. Thus, it is necessary to consider composition-related effects in any analysis of coarsening rates before any inference is made regarding the effect of coherent stresses.

Calderon and Kostorz [CK90] used small angle neutron scattering techniques to study coarsening in several Ni-Al-Mo systems at 560°C. Their results are also shown in the Table 1.

In a more recent study, Mackay and Nathal (MN90) studied coarsening in Ni-6wt.% Al- 6 wt. % Ta- x wt. % Mo alloys using transmission electron microscopy. The volume fraction of the second phase in these alloys was about 60%. Fig. 2 shows the variation of coarsening rates in these alloys as a function of the Mo content and the misfit parameter. Note that the coarsening rate decreases with an increase in the Mo content and progressively larger negative values of the misfit parameter. They argue 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.

Based on the work presented so far, it is quite evident that there has been no effort made to *quantitatively* characterize the role of coherency strains on coarsening in multi-component alloys. Most studies have clearly avoided accounting for the effect of composition and

diffusivities on coarsening rates. Although researchers have recognized the necessity to account for such effects [CFW89] a solution to this problem was not available. We propose [MEH94a] that a prudent use of the expressions for coarsening rates (equations (12), (14), (15), (18)) provides us with an approximate method for accomplishing this task. We illustrate the use of these expressions in studying coarsening in ternary systems.

ANALYSIS OF COARSENING DATA IN TERNARY SYSTEMS

Coarsening in Ni-Al-Ti alloys was studied by Njah and Dimitrov [ND89] and Hein [Hei89]. Njah and Dimitrov used three different alloys for their study (Table 2) and made their measurements at 610, 752 and 860°C. Note that alloys B and C have a similar volume fraction of γ while A has a lower volume fraction. The measured values of the rate constants for the three alloys at 752°C are shown in Table 2. Based on their data, they concluded that the coarsening rate constant increases with an increase in the volume fraction of the second phase. They compare the experimentally measured variation in the coarsening rate constant with volume fraction, to that predicted by the various theories explaining the volume fraction dependence of the coarsening rates. Based on the fact that the coarsening rate in alloy C ($\delta=0.4\%$) is lower than that observed in alloy B ($\delta=0.6\%$), one may be tempted to argue that decreasing the misfit parameter lowers the coarsening rate. In the ensuing discussion, we show how the combination of diffusivities and phase-composition could account for a large proportion of this difference in coarsening rates.

Table 1. Coarsening Rates as a Function of Alloy Composition in Various Systems

Composition of the Alloy	δ	Vol. Fraction	Coarsening Rate nm^3/hr	Temp $^\circ\text{C}$
Fe-10Al-3Ni [CFW88]	0.21	6 ± 0.1	141 ± 3.5	700
Fe-10Al-3Ni-2.5Mo	-0.06	6 ± 0.1	126 ± 3.4	700
Fe-10Al-3Ni-4Mo	0.8	6 ± 0.1	160 ± 4.0	700
Fe-15Al-10Ni	0.1	36 ± 0.4	397 ± 8.0	700
Fe-15Al-10Ni-1Mo	0.03	36 ± 0.4	377 ± 7.5	700
Fe-15Al-10Ni-2Mo	0.8	36 ± 0.4	401 ± 8.0	700
Ni-10.2Al-5.1Mo [CFW89]	0.4	12.0	380	750
Ni-8.2Al-7.9Mo	0.0	9.0	68	750
Ni-6.5Al-9.8Mo	-0.1	11.0	31	750
Ni-12Al [CK90]	1.2	9.5 ± 1.0	4.7	560
Ni-10.3Al-5.5Mo	0.6	19.0 ± 2.0	0.7	560
Ni-6.5Al-9.6Mo	0.0	13.7 ± 1.0	0.2	560
Ni-6.1Al-9.5Mo	0.0	13.7 ± 1.0	2.2	610

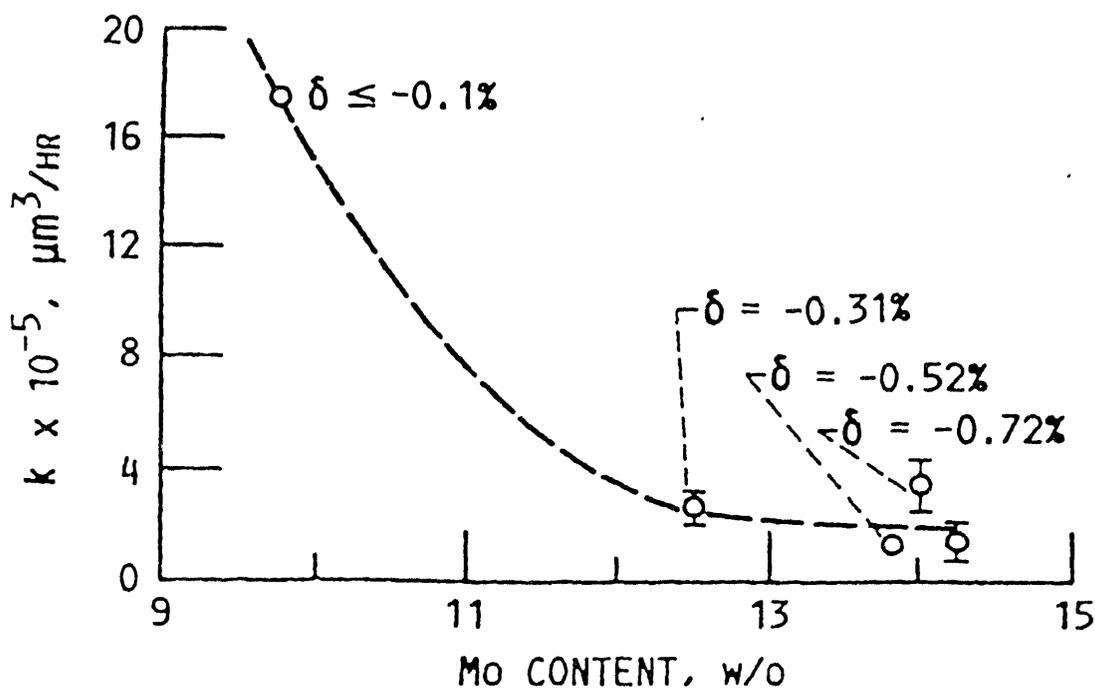


Fig. 2 Variation of Coarsening Rates as a Function of Mo content in Ni-Al-Ta-Mo Alloys [MN90]

Although equations (12), (14) and (15) were derived for the growth of compound precipitates in a matrix, they can be applied to the Ni-Al-Ti system and other similar systems, provided some simple criteria are satisfied. In the Ni-Al-Ti system, the composition of the γ can be written as $\text{Ni}_3\text{Al}_x\text{Ti}_{(1-x)}$. Thus, if the overall composition of a series of alloys is selected such that the Ni composition in the matrix (determined by the γ solvus) remains approximately the same, then it can be assumed that the growth of the $\text{Ni}_3\text{Al}_x\text{Ti}_{(1-x)}$ can be approximated by the growth of $\text{Al}_y\text{Ti}_{(1-y)}$, where,

$$\frac{x}{1-x} = \frac{y}{1-y} \quad (23)$$

For the diffusion coefficients, we use the values of the coefficients in the binary systems, since D_{ij} in the ternary system are not known at the present time. At 752°C, the diffusion coefficient in the Ni-Al system is calculated [MB88], to be $D_{\text{Al}} = 4.89 \times 10^{-14} \text{ cm}^2/\text{sec}$ while that in the Ni-Ti system this value is $D_{\text{Ti}} = 8.12 \times 10^{-14} \text{ cm}^2/\text{sec}$. We calculate the variation of the coarsening rates as a function of composition using both equations (12) and (20). For the use of (12), we make an additional assumption that (13) is valid. For the use of (20), we obtained the composition of the phases from the tie-line provided by [ND89] (Figure 1 in their paper). Shown in Table 3 is the summary of the

results. The calculated coarsening rates are expressed in terms of the ratio K/K_C where K_C is the coarsening rate in alloy C. Also shown in the table are the compositions of the γ and γ' phases in equilibrium at this temperature. The measured values are shown for comparison. Note that both methods of calculation predict an decrease in the coarsening rates with an increase in the Al content. Although there is insufficient data to conclude which one is a better fit to the observed data, we have demonstrated that such an analysis is possible in simple multi-component systems like the Ni-Ti-Al where phase-diagram and diffusion data are available. Such an analysis has also been applied to the Ni-Al-Co system studied by Davies et. al [DNS80]. Details of this analysis can be found in [MEH94a].

Based on the brief review presented here, it is apparent that further experimental work is needed to understand the effect of coherency stresses on coarsening behaviour. One important aspect of any such study would be the alloy system used. For proper analysis, this system should be simple, preferably a ternary system, where the tailoring of the mismatch between the coherent phases is possible. Knowledge of the compositions of the phases inequilibrium and the availability of diffusivity data are essential for a detailed interpretation of the chemical effect. A study that is designed to satisfy these criteria is the on-going work in the Ni-Al-Si system [Mur94].

Table 2 Composition of the Various Alloys and Coarsening Rates in the Ni-Al-Ti System [ND89]

Alloy Designation	Alloy Composition (at. %)	γ Vol. fraction	δ	Coarsening rate $K(10^{-21} \text{ cm}^3/\text{sec})$	K/K_C
A	Ni-4.5Al-6.5Ti	11.6%	0.6%	1.06 ± 0.06	2.4
B	Ni-6.0Al-7.1Ti	27.1%	0.6%	1.86 ± 0.11	4.2
C	Ni-10.6Al-2.5Ti	21.0%	0.4%	0.44 ± 0.02	1.0

Table 3 Composition of γ and γ' and calculation of the variation of coarsening rates (for the alloys in Table 2)*

Alloy Composition (at. %)	Composition of γ (at. %)	Composition of γ' (at. %)	(13)	K/K_C (19)	Exper
89Ni-4.5Al-6.5Ti	90.0Ni-4.5Al-5.5Ti	77Ni-12.5Al-6.5Ti	2.1	1.6	2.4
86.9Ni-6.0Al-7.1Ti	same as above	same as above	2.1	1.6	4.2
86.9Ni-10.6Al-2.5Ti	91.4Ni-6.6Al-2Ti	77Ni-20Al-3Ti	1.0	1.0	1.0

*Volume fraction correction not applied

STUDY OF COARSENING IN THE Ni-Si-Al SYSTEM

Consider the ternary Ni-Al-Si system. Both the Ni-Si binary and the Ni-Al binary show the presence of an intermetallic $L1_2$ phase of nominal composition Ni_3X where X is Al or Si. Ochiai et. al [OOS83] found that Ni_3Al and Ni_3Si form a continuous solid solution at all temperatures below 1100°C . Fig. 3 shows a schematic of a typical isothermal section drawn on the basis of [OOS83]. In the two phase ($\gamma + \gamma'$) region, the composition of the two phases in equilibrium are determined by the thermodynamics of the phases and can be indicated on the phase diagram using tie-lines; however, these are not known at the present time. Thermodynamic modeling of the two phase γ - γ' equilibrium is the subject of an ongoing study [Mur94]. For an approximate analysis, we assume that the tie-lines are oriented such that the Al:Si ratio in both γ and γ' are equal to that of the value in the overall composition of the alloy. Since the lattice-parameters are determined by the composition of the two phases in equilibrium, all compositions located on a single tie-line will have identical misfit parameter. Thus, one can obtain alloys with different misfit parameters by varying the composition so that they all do not lie on the same tie-line or obtain the same δ but different volume fraction of the second phase by choosing alloys that lie on the same tie-line. In a study that is designed to observe the variation of coarsening rates as a function of misfit such as the current work, one can choose alloys with a constant Ni content and varying amounts of Si and Al, thus obtaining a range of misfit parameter values. An additional advantage with this ternary system is that the phase

boundaries of the two-phase region are almost parallel to the constant Ni lines: thus the variation in the volume fraction of the second phase in alloys with constant Ni content would be very small.

The selection of alloys for this study was based upon the principles just outlined. It was desirable to keep the volume fraction low and to vary the misfit parameter over the maximum range possible. Ni_3Al has a lattice parameter larger than that of the solid solution it is in equilibrium with, while Ni_3Si has a lattice parameter smaller than that of the saturated solid solution of Si in Ni at the same temperature. Hence a wide range of misfit parameters (both sign and magnitude) can be obtained by choosing alloys from the Si-rich region to the Al-rich region, at the same time keeping the volume fraction of the second phase approximately constant.

Table 4 shows the composition of the alloys used in this study. Note that the Ni content has been maintained constant at 88 at. %. The lattice parameters of the two phases as a function of composition have not been measured yet, but is a part of the on-going work. We show in Table 4, the calculated misfit parameter values. To do this calculation, use was made of the composition-lattice parameter relationship obtained from [MOS85]. The compositions of the phases were obtained using the procedure mentioned earlier. Coarsening in polycrystalline samples of these alloys were studied at 531, 550, 582, 600 and 630°C using *in-situ* small angle neutron scattering. Details of the experimental work will be published elsewhere [MEH94b].

Table 4 Composition and Misfit parameters of Ni-Al-Si Alloys (Listed in the order of Decreasing δ Values)

Alloy #	Composition	δ
4.	Ni- 4.0 at.%Si- 8.0 at.% Al	+0.35%
5.	Ni- 6.0 at.%Si-6.0 at.%Al	+0.17%
1.	Ni- 8.1 at.% Si- 3.9 at.% Al	-0.02%
2.	Ni- 9.5 at.% Si- 2.5 at.% Al	-0.15%
6.	Ni-10.25at.%Si-1.25at.%Al	- 0.26%
3.	Ni-11.0 at.% Si- 1.0 at.% Al	-0.28%

Fig. 4 shows the variation of the lattice parameters of the two phases as a function of at. % Si. Note that the misfit is positive with low Si contents and becomes progressively more negative with the addition of Si. Fig. 5 shows the variation of coarsening rates as a function of Si content for studies done at two different temperatures: 550°C and 600°C. The curves shown are spline fits to the data points. At both temperatures, it is fairly clear that the overall trends is for an increase in the coarsening rate with increasing Si content. This can be understood on the basis of our earlier discussion on coarsening rates in ternary systems. The diffusion coefficient in the binary Ni-Si system [MB88] at 600°C is ($D_{Si} = 6.75 \times 10^{-16} \text{ cm}^2/\text{sec}$) and is higher than the diffusion coefficient in the Ni-Al system ($D_{Al} = 2.25 \times 10^{-16} \text{ cm}^2/\text{sec}$). Thus it is not surprising that the coarsening rates tend to increase with addition of Si. However, it is interesting to note that this trend is broken around 9.0 at. % Si. Note that this corresponds to roughly the region where one would expect a minimum in the absolute value of the misfit parameter. Hence it is possible that the observed variation

in coarsening rates is a sum of two effects: one of these arising from the chemical effect and the other due to coherency strain effect. To place this hypothesis on a firmer basis, one should model the variation of coarsening rates arising due to chemical effects. This is accomplished by the method used earlier for the Ni-Al-Ti system using equation (22).

Using equation (22) and the diffusivity values given above, the variation of coarsening rates was calculated for the series of alloys 1-6. As was assumed in the Ni-Al-Ti system, the ratio of Si:Al in both γ and γ' at equilibrium, was assumed to be equal to the Si:Al ratio in the overall composition of the alloy. To present the calculated variation and the observed variation of coarsening rates on the same scale, the calculated curve has been scaled such that the calculated and the measured coarsening rates for the alloy with Comp 2 are identical. Fig. 6 shows the results of such a comparison done for the data obtained at 600°C. Both curves are spline-fits to the data. Note that over the composition range of 6-11 at. % Si, the calculated variation seems to form a good "background" showing the presence of two additional "humps". We believe that these could be related to coherency strain effects. The on-going work in measuring the actual misfit-parameter values will help us in explaining this aspect of the work.

Note that the fit is poorer at the end with higher Al content (Comp 4). We believe that this is due to a strong concentration dependence of the diffusion coefficients in this system. Measurements using diffusion couples are currently being carried out [Mur94] to obtain values of the average effective diffusion coefficients [Day93] for both Si and Al in this system. These would be a better estimate for D_{Si} and D_{Al} to be used in (12) than the binary interdiffusion coefficients that have been used at this time.

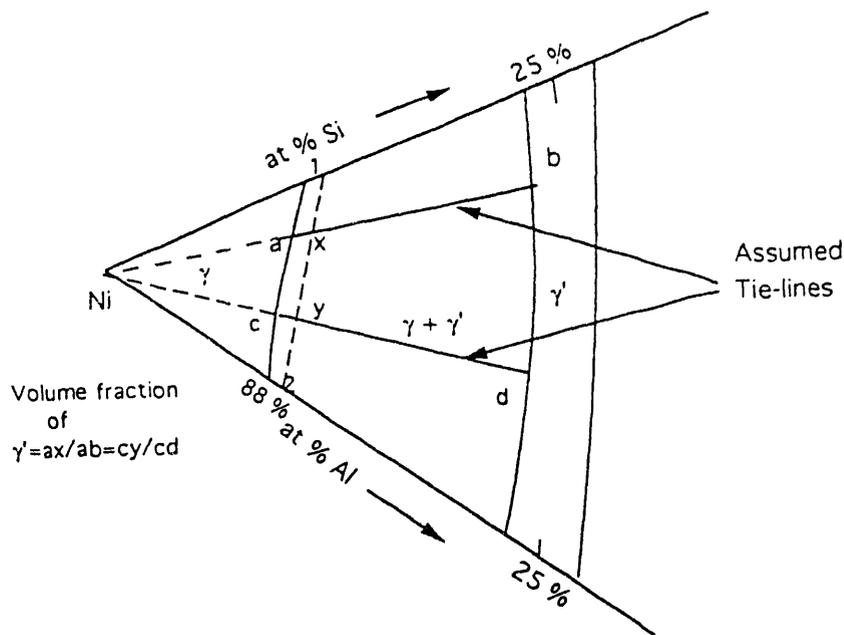


Fig. 3 Ni-rich Corner of a Typical Isothermal Section in the Ni-Al-Si Ternary System [adapted from OOS83]

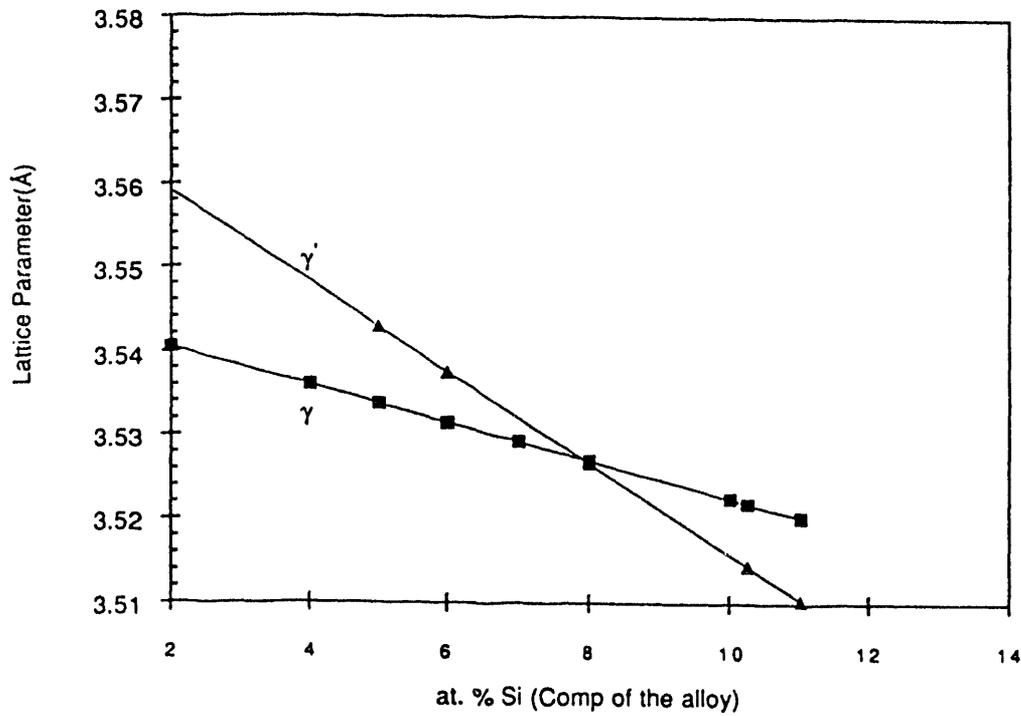


Fig. 4 Variation of the Lattice Parameters of γ and γ' as a Function of Si Content [Mur94]

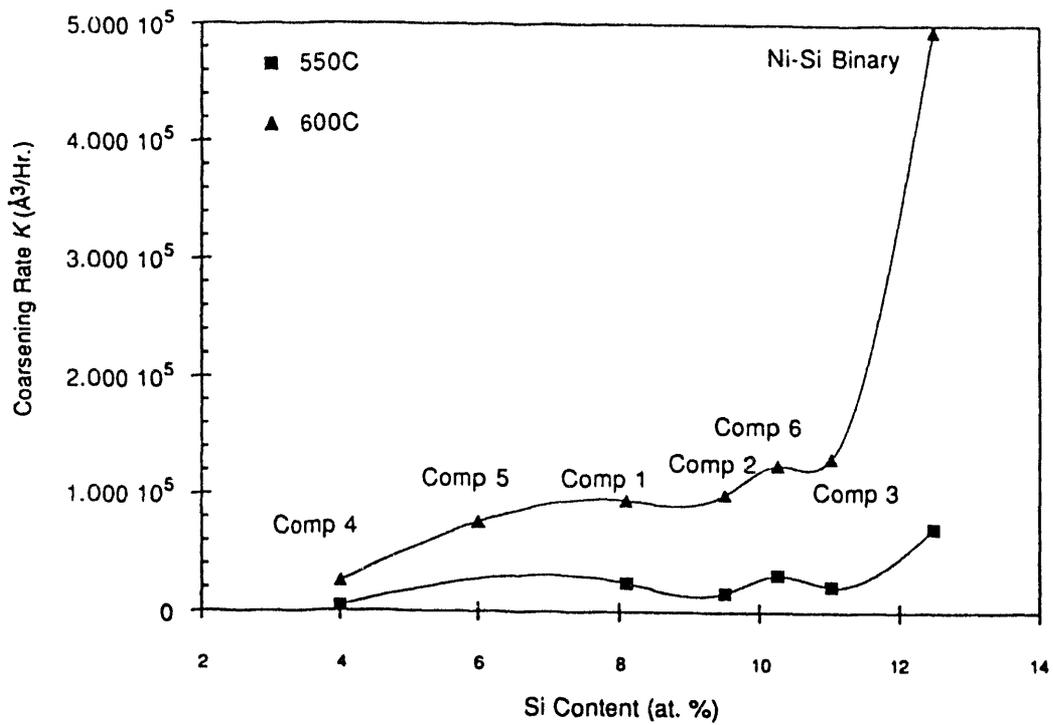


Fig. 5 Variation of Coarsening Rates in the Ni-Al-Si System as a Function of the Si Content [Mur94]

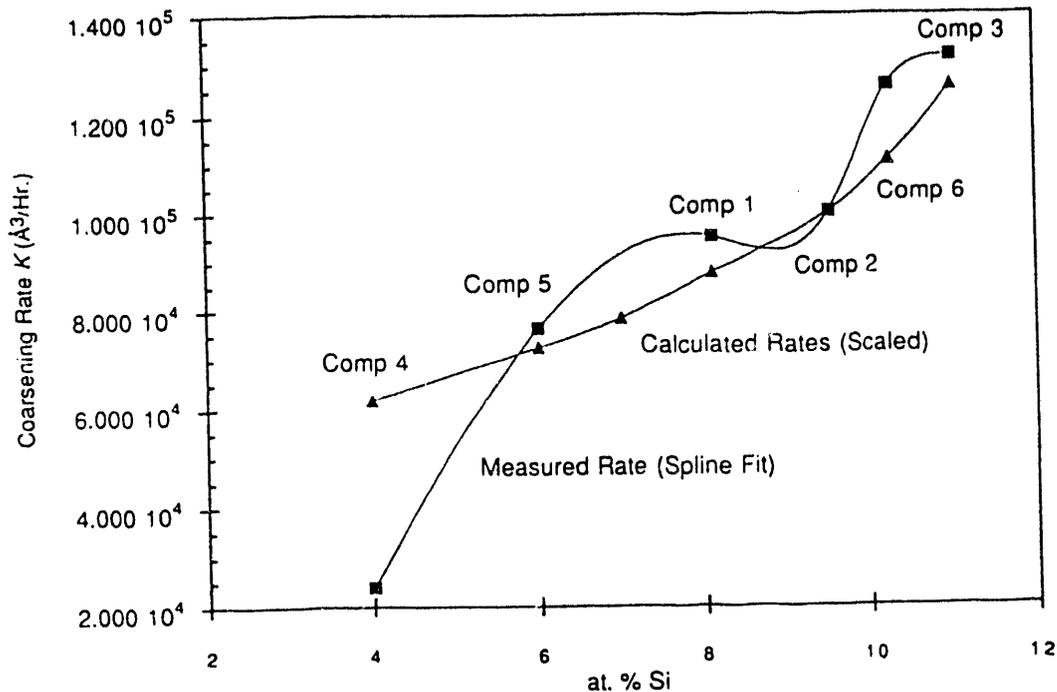


Fig. 6 Comparison of the Actual and Calculated Coarsening Rate Variation as a Function of Si Content [Mur94]

IMPACT OF ON-GOING RESEARCH AND FOCUS OF FUTURE WORK

As described in the previous section, we believe that on-going work in the Ni-Al-Si system will be useful in answering many questions that have not been addressed in the past. One of the important issues it addresses is that of the variation in coarsening rates due to chemical effects (composition of the alloy and diffusion coefficients). Although a reasonably good fit for this variation has been obtained using binary inter-diffusion coefficients, we hope that the use of both the measured average effective inter-diffusion coefficients and calculated phase compositions, will improve the agreement between the calculated and measured variation in coarsening rates, particularly in the high-Al region. On-going work at the General Purpose Powder Diffractometer (GPPD) at the Intense Pulsed Neutron Source (IPNS) to measure the variation of misfit parameter with composition will enable us to infer whether the anomalies in the variation in coarsening rates that occur around 9.0 at. % Si in our work, are related to coherency strains. Once the role of coherency effects is confirmed, attempt will be made to explain the experimental observations on the basis of the available theory for Ostwald ripening in internally-stressed systems with a low volume fraction of the second phase [LJV89].

Although the on-going work is designed to answer some of the pertinent questions, more work is necessary for a thorough understanding of the effect of coherency stresses in real systems. Some questions that we think future work should address are:

1. What, if any, is the nature of interaction between volume fraction and coherency strains?
2. What is the functional form of the relationship between coherency strains and coarsening rates? Is this independent of the system studied? What is the physical origin of this dependence?

CONCLUSIONS

In this presentation, we have briefly reviewed the status of our understanding of the effect of coherency strains on coarsening in internally-stressed systems. We outlined a method to account for the variation in coarsening rates that is observed in ternary systems due to composition and diffusion effects. A brief overview of the on-going work in the Ni-Al-Si was presented and its importance in the overall understanding of this area was discussed. To conclude the presentation, the necessity for future work, both in the Ni-Al-Si system and in other systems was emphasised.

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