

# The Coarsening Kinetics of $\gamma'$ Particles in Nickel-Based Alloys

X. LI, N. SAUNDERS, and A.P. MIODOWNIK

The present article describes a method for calculating the coarsening rate of  $\gamma'$  in Ni-based superalloys, which has been applied to both binary Ni-Al alloys and a wide range of multicomponent alloys. A standard coarsening equation is utilized, but innovative methods for calculating the critical input parameters are presented. The article details methods of estimating interfacial energies and the effective diffusion coefficients that are key parameters for the coarsening model. Self-consistent calculations are made *via* a computer program in which the only input required is the composition of the alloys and the temperature of coarsening. The effects of coherent strain on the coarsening process have also been analyzed and discussed.

## I. INTRODUCTION

NICKEL-BASED superalloys are widely used in applications requiring strength at high temperature. Most of these alloys are precipitation hardened by a fine dispersion of  $\gamma'$  particles that have an ordered fcc structure (L1<sub>2</sub>). These fine particles coarsen into a lower density of larger particles with a smaller total interfacial area during high-temperature heat treatment or usage. Ardell and co-workers<sup>[1,2,3]</sup> have demonstrated that in binary  $\gamma$ - $\gamma'$  systems, the growth of the  $\gamma'$  precipitates obeys a diffusion-controlled coarsening model where the average particle radius increases linearly with  $t^{1/3}$ , as would be expected from simple coarsening theory.<sup>[4,5]</sup> A similar  $t^{1/3}$  law has also been observed for a wide range of complex commercial alloys containing a large volume fraction of the  $\gamma'$  phase.<sup>[6]</sup> However, as concerns the quantitative modeling of coarsening kinetics, most of the existing information relates to the binary Ni-Al system and is not always consistent even in this simple case. For example, different formulas have been used to calculate the coarsening rate and at least one critical input parameter has had to be “back-calculated” by fitting to experimental data. Usually, the interfacial energy between the matrix and precipitate ( $\sigma$ ) is derived in this way.

The main theoretical approach to modeling coarsening rates has been based on the work of Lifshitz and Slyozov<sup>[4]</sup> and Wagner,<sup>[5]</sup> who independently proposed the following relationship:

$$[\bar{r}_t^3 - \bar{r}_0^3]^{1/3} = kt^{1/3} \quad [1]$$

where  $k$  is often referred to as the coarsening rate coefficient,  $\bar{r}_0$  is the mean radius at time  $t = 0$ , and  $\bar{r}_t$  is the average particle size at time  $t$ . The term  $k$  can then be derived as

$$k = \left[ \frac{8D_{\text{eff}}\sigma N_{\alpha} V_m}{9RT} \right]^{1/3} \quad [2]$$

where  $D_{\text{eff}}$  is the effective diffusion coefficient,  $\sigma$  is the precipitate-matrix interfacial energy per unit area,  $N_{\alpha}$  is the

total equilibrium mole fraction of solute in the matrix,  $V_m$  is the molar volume of the precipitate,  $R$  is the gas constant, and  $T$  is the absolute temperature.

Equation [2] was originally derived assuming the conditions  $N_{\alpha} \approx 0$  and  $N_{\beta} \approx 1$ . It therefore does not take into account significant ranges of solubility of the solute in the matrix and precipitate. In the general case,  $k$  becomes<sup>[7]</sup>

$$k = \left[ \frac{8D_{\text{eff}} V_m \sigma}{9G_m^{\alpha\alpha} (N_{\beta} - N_{\alpha})^2} \right]^{1/3} \quad [3]$$

where  $N_{\beta}$  is the total mole fraction of solute(s) in the precipitate;  $G_m^{\alpha\alpha}$  is the second derivative of the Gibbs energy of the matrix  $\gamma$  phase with respect to composition and the other parameters have the same meaning as before. For the case of an ideal solution, Eq. [3] becomes<sup>[7]</sup>

$$k = \left[ \frac{8D_{\text{eff}}\sigma N_{\alpha} (1 - N_{\alpha}) V_m}{9(N_{\beta} - N_{\alpha})^2 RT} \right]^{1/3} \quad [4]$$

Before Eqs. [1] through [4] can be used to calculate coarsening rates, all of the various parameters need to be determined quantitatively. Thermodynamic calculations have been used to derive solute concentrations in  $\gamma$  and  $\gamma'$  and to estimate  $\sigma$ . The latter aspect will be discussed in more detail in Section II. The calculations are quite insensitive to the likely change in  $V_m$  and its value can be taken as constant and equal to that for Ni<sub>3</sub>Al. We have used the value of Calderon *et al.*<sup>[7]</sup> and Ardell.<sup>[8]</sup>

In binary alloys, estimation of diffusion coefficients and solute concentrations in the matrix and precipitate is reasonably straightforward as is the calculation of  $G_m^{\alpha\alpha}$ . However, in multicomponent alloys, the position becomes substantially more complex and, hence, it is no surprise that little modeling work has been done for commercial Ni-based superalloys. The aim of the present article is to describe means by which modeling can nevertheless be achieved for superalloys by the input of only the composition of the alloy and the temperature.

## II. ESTIMATION OF CRITICAL PARAMETERS

### A. Ideality and Departures from Ideality

Ni-Al alloys, as well as multicomponent Ni-based superalloys, are quite nonideal in their thermodynamic behavior.

X. LI, Materials Scientist, N. SAUNDERS, Director, and A.P. MIODOWNIK, Emeritus Professor, are with the Surrey Technology Centre, Thermotech Ltd., Surry GU2 7YG, United Kingdom. Contact e-mail: x.li@thermotech.co.uk

Manuscript submitted November 15, 2001.

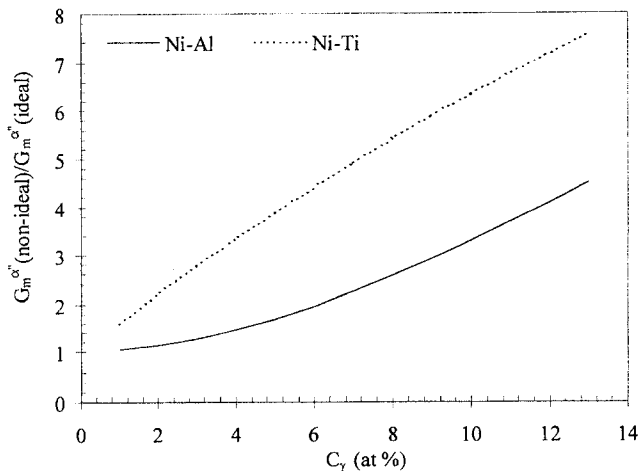


Fig. 1—The ratio of  $G_m^{\alpha}$  (nonideal)/ $G_m^{\alpha}$  (ideal) vs solute concentration for Ni-Al and Ni-Ti binary alloys.

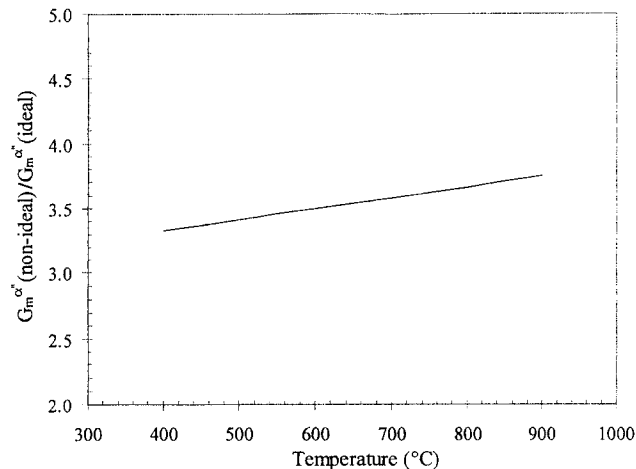


Fig. 2—The ratio of  $G_m^{\alpha}$  (nonideal)/ $G_m^{\alpha}$  (ideal) vs temperature for Ni-Al binary alloys.

Calderon *et al.*<sup>[7]</sup> examined the possible effect of nonideality using thermodynamic mixing functions drawn from the work of Kaufman and Nesor,<sup>[9]</sup> and deduced there would be only a relatively small deviation from the ideal case. The model of Kaufman and Nesor is now quite old and other models have been used<sup>[10]</sup> to give an improved representation of alloy systems such as Ni-Al. It is therefore instructive to re-examine this conclusion in light of more recent work.<sup>[11]</sup>

Figure 1 shows results for the ratio  $G_m^{\alpha}$  (nonideal)/ $G_m^{\alpha}$  (ideal) using a current thermodynamic model for both Ni-Al and Ni-Ti,<sup>[11]</sup> which are the major elements that need to be considered here. It can be seen that at equilibrium concentrations for  $\gamma/\gamma'$  Ni-Al binary alloys (where  $C_{\gamma} \approx 10$  to 14 at pct Al), there is substantial deviation from ideality, far more so than would be expected from the earlier work of Kaufman and Nesor.<sup>[9]</sup> Other recent calculations for Ni-Al using the data of Ansara *et al.*<sup>[12]</sup> and Dupin<sup>[13]</sup> provide answers that are very similar and even slightly larger than those calculated here.

While there appears to be a substantial deviation for the case of binary alloys, the solute levels for Al and Ti in the  $\gamma$  phase in equilibrium with  $\gamma'$  in multicomponent alloys are much lower; typically, Al + Ti lies between 3 and 5 at pct at 600 °C, with Al usually the predominant element. If the ratio  $G_m^{\alpha}$  (nonideal)/ $G_m^{\alpha}$  (ideal) in these alloys (denoted as  $\phi$ ) lies somewhere between the values for  $C_{Al}$  and  $C_{Ti}$  in the corresponding binary systems, a reasonable assumption for  $\phi$  would be  $\approx 2$  for the multicomponent alloys of interest here. Accordingly, Eq. [4] has been modified to include  $\phi$  and becomes

$$k = \left[ \frac{8D_{\text{eff}}\sigma N_{\alpha}(1 - N_{\alpha})V_m}{9\phi(N_{\beta} - N_{\alpha})^2 RT} \right]^{1/3} \quad [5]$$

We have then used this formula for multicomponent alloys, with  $\phi = 2$ , but have retained explicit values of  $G_m^{\alpha}$  for binary Ni-Al alloys.

A further aspect that needs to be considered is the temperature dependence of  $\phi$ . Figure 2 shows calculated values of  $\phi$  vs temperature for Ni-Al binary alloys in the  $\gamma + \gamma'$  two phase region, which remains almost constant. This is surprising at first sight, as the Al concentration of the  $\gamma$

solvus increases with increasing temperature and examination of Figure 1 implies that  $\phi$  increases with increasing Al. However, there is a strong negative excess entropy of mixing in Ni-Al; this causes  $\phi$  to decrease with increasing temperature and these two effects counterbalance almost exactly. It should further be noted that there is an empirically observed linear relationship between the excess enthalpy and entropy of mixing,<sup>[14]</sup> which means that large negative enthalpies of mixing are invariably accompanied by large negative excess entropies of mixing. A similar compensating effect is therefore likely to occur for other  $\gamma'$  forming elements such as Nb, Ta, and Ti, which also have strong thermodynamic interactions with Ni.

## B. Interfacial Energy

One of the main parameters in Eq. [5] is the interfacial energy term  $\sigma$ , which is generally obtained by back-calculation from the experimental coarsening data. Quite varied values can be obtained, depending on the experimental conditions, the model for coarsening that is used, and the assumptions made to define parameters such as the diffusion coefficient and molar volume. The following range of values have been reported for Ni-Al alloys based on coarsening studies: 6 to 8,<sup>[18]</sup> 14.4,<sup>[12]</sup> 17 to 20,<sup>[15]</sup> 19,<sup>[16]</sup> 17.5,<sup>[17]</sup> and 42 to 80<sup>[7]</sup> (all values in  $\text{mJ/m}^{-2}$ );  $\sigma$  is also a critical component in nucleation where recently a value of  $16 \text{ mJm}^{-2}$  has been obtained from studies in this area.<sup>[18]</sup> It should be noted that the lowest value is provided by a recent stringent analysis from Ardell.<sup>[8]</sup> However, as part of his model for deriving  $\sigma$ , these authors followed a treatment by Calderon *et al.*,<sup>[7]</sup> which used the thermodynamics from Kaufman and Nesor.<sup>[9]</sup> Using the value of  $G_m^{\alpha}$  (nonideal) derived previously leads to a correction to the calculated value of  $\sigma$  that is directly proportional to the value of  $\phi$ . When the new values of  $\phi$  are taken into account, their calculated value of  $\sigma$  would be increased by a factor between  $\times 3.5$  and  $\times 4$ , giving  $\sigma = 21$  to  $24 \text{ mJ/m}^{-2}$  in line with other results. There are few reports of experimental values for multicomponent alloys,

but a value of  $90 \text{ mJ/m}^{-2}$  has been reported for a NIMONIC\* PE16 alloy,<sup>[19]</sup> which is substantially larger than most values

\*NIMONIC is a trademark of INCO Alloys International, Inc., Huntington, WV.

reported for Ni-Al binary alloys.

For the case of the  $\gamma/\gamma'$  transformation, the interface is usually coherent and, in that case, it has been considered that  $\sigma$  should consist of only a chemical component.<sup>[20,21]</sup> In the present article, we therefore use a method that considers that the interfacial energy is proportional to the enthalpy difference between the  $\gamma$  and  $\gamma'$  in equilibrium at the coarsening temperature. In its basic form, the relationship between various interfacial energies, vapor-solid, liquid-solid, *etc.*, and the enthalpy difference between the phases taking part can be expressed as

$$\sigma = \alpha \Delta H_m \quad [6]$$

where  $\alpha$  is a constant, usually empirically determined, as in the case of liquid/solid interfacial energies.<sup>[22]</sup> In other cases, a more theoretical approach has been used, such as that of Becker,<sup>[23]</sup> which relates bond energies across the interface to estimate  $\alpha$ . This approach has also been used by Nishizawa *et al.*<sup>[24]</sup> and Turnbull,<sup>[25]</sup> whereby

$$\sigma = \frac{z^* N^*}{z N_o} \Delta H_m \quad [7]$$

where  $z^*$  is the number of atoms per unit area of the interface,  $N^*$  the number of cross bonds per atom at the interface,  $z$  the coordination number of nearest neighbors in the lattice (in this case 12),  $N_o$  Avogadro's number, and  $\Delta H_m$  the enthalpy of solution of 1 mole of  $\gamma'$  in the matrix  $\gamma$  in equilibrium at the coarsening temperature. This must be considered only a first approximation with the following limitations. First, the method uses only first nearest neighbor energies; and second, it considers the particles bounded by  $\{111\}$  interfaces. Analysis by Ardell and Nicholson<sup>[26]</sup> has stressed the potential importance of second nearest neighbor interactions, and it has also been shown that for  $\gamma'$ , third nearest neighbor energies are also required for the calculation of APB energies in  $\gamma'$ .<sup>[27]</sup> Despite these important reservations, the direct application of Eq. [7] results in values for  $\sigma$  of between 20 to 24  $\text{mJm}^{-2}$  for Ni-Al binary alloys and 91  $\text{mJm}^{-2}$  for NIMONIC PE16, which are very close to previously reported values<sup>[19]</sup>. A possible reason for this result may be found from First Principle calculations. These indicate that for  $\text{Ni}_3\text{Al}$  and  $\text{Ni}_3\text{Ti}$ , the third nearest neighbor energy is about one-eighth of the value of the magnitude of the first nearest neighbor energy. When combined with the relative number of such neighbors, this much reduces the difference that might be expected from taking extra neighbors into account. This is an area of potentially great complexity, but because of the very reasonable agreement with previously reported values for  $\sigma$ , and the success of the calculations presented in Section III, we have retained the method of estimating  $\alpha$  via Eq. [7] in this article.

### C. Diffusion Coefficient

Considering that the interdiffusion coefficients in the  $\gamma$  matrix should be related to the fluxes of the components,

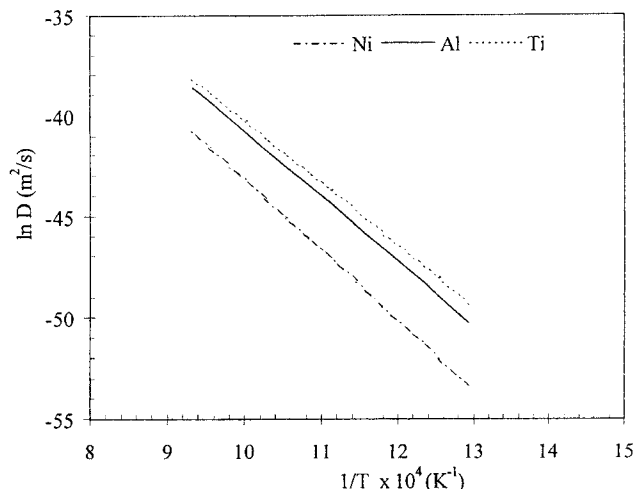


Fig. 3—Diffusion coefficients of Ni, Al, and Ti in nickel-based alloys.

the following expressions have been proposed<sup>[28]</sup> to calculate the effective diffusion coefficient:

$$D_{\text{eff}} = D_o^\gamma \exp(-Q_{\text{eff}}/RT) \quad [8]$$

where

$$D_o^\gamma = \sum_i x_i D_i^0 \quad [9]$$

and

$$Q_{\text{eff}} = \sum_i x_i Q_i \quad [10]$$

In Eqs. [9] and [10],  $x_i$  is the mole fraction of element  $i$  in the precipitate and  $D_i^0$  and  $Q_i$  are the frequency factor and activation energy for the diffusion of element  $i$  in the  $\gamma$  matrix taken from literature.<sup>[29,30]</sup> Figure 3 shows the values for the most critical diffusion coefficients used in the present work.

In order to calculate the coarsening rate coefficients of  $\gamma'$  particles, thermodynamic calculations have been carried out to obtain  $\Delta H_m$  and the equilibrium compositions of  $\gamma'$  and  $\gamma$  by using a combination of the thermodynamic software calculation package EQLIB<sup>[31,32]</sup> and a thermodynamic database for Ni-based superalloys.<sup>[33,34]</sup> For the case of multicomponent alloys,  $N_\alpha$  and  $N_\beta$  are taken as the sum of the fractions of the  $\gamma'$  forming elements such as Al, Ti, Nb, *etc.*, in  $\gamma$  and  $\gamma'$ , respectively.

## III. RESULTS AND DISCUSSION

### A. Multicomponent Alloys

Using the method as detailed previously, coarsening rates have been calculated and compared with experiment for a wide variety of multicomponent alloys<sup>[6,35-38]</sup> and Ni-Al binary alloys.<sup>[2,15-18]</sup> The results of the comparison are shown in Figure 4. The results for the multicomponent alloys are excellent, but there is a small, systematic deviation for the binary Ni-Al alloys, where coarsening rates are calculated to be generally too slow. This is considered to be due to the higher lattice mismatch in Ni-Al binary alloys, where  $\delta \approx 0.4$  to 0.6 pct<sup>[39,40,41]</sup> ( $\delta = 100 \times |(a_{\gamma'} - a_\gamma)/a_\gamma|$ ). By comparison, values reported in multicomponent alloys are

**Table I. The Compositions (Weight Percent), the Calculated  $\gamma'$  Solvi ( $^{\circ}\text{C}$ ), and the Mole Percentage of  $\gamma'$  at  $750^{\circ}\text{C}$  for the Alloys Studied**

Alloys	Solvus	Mole Pct	Al	Co	Cr	Mo	Ti	C	B	Other
115	1152	55.3	4.9	13.2	14.3	—	3.7	0.15	0.16	2.5Fe
IN738	1140	51.0	3.4	8.5	16.0	1.7	3.4	0.17	0.01	0.9Nb 1.7Ta 2.6W
U700	1146	49.9	4.1	17.5	14.5	5.1	3.7	0.08	0.015	—
105	1064	42.4	4.7	20.0	15.0	5.0	1.2	0.13	0.005	—
PK33	1012	22.0	2.0	14.0	18.5	7.0	2.0	0.05	0.01	—
90	976	19.6	1.5	16.5	19.5	—	2.5	0.07	0.003	—
80A	925	16.0	1.4	0.5	19.7	—	2.4	0.07	—	1.0Fe
PE11	959	11.7	0.8	—	18.0	5.2	2.3	0.05	0.03	35Fe
PE16	874	8.6	1.1	0.2	16.7	3.3	1.3	0.07	0.002	34Fe
263	787	2.1	0.4	20.1	19.6	5.7	2.1	0.06	0.001	0.5Fe

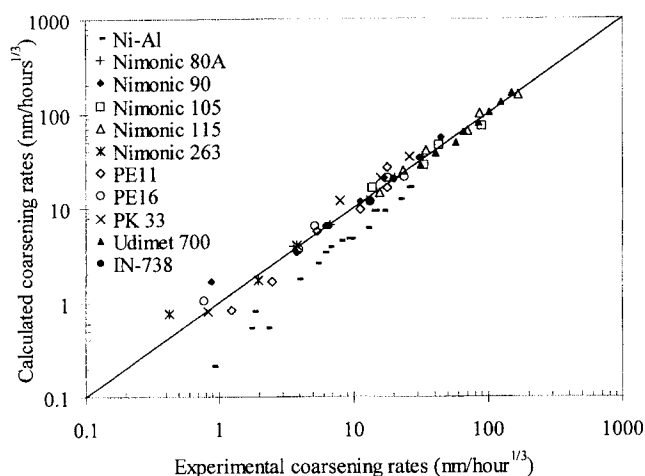


Fig. 4—Comparison between calculated and experimentally observed  $\gamma'$  coarsening rate coefficients for Ni-based superalloys and Ni-Al binary alloys.

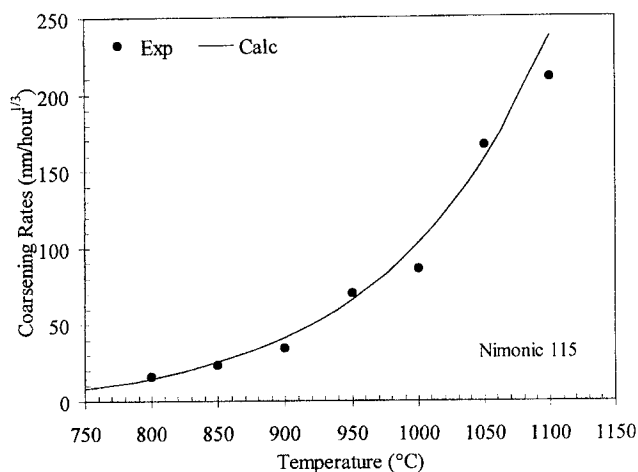


Fig. 5—Comparison between calculated and experimentally observed  $\gamma'$  coarsening rate coefficients for NIMONIC 115 Ni-based superalloy as a function of temperature. The experimental data are from Betteridge and Heslop.<sup>161</sup>

often much lower, with reported values of  $\delta$  all less than 0.34 pct in the alloys considered here.<sup>[42–45]</sup> A more detailed discussion of the results for binary alloys and the effect of coherency strains will be made later in this article.

The success of the approach for multicomponent alloys is quite startling and it is instructive to analyze the results by looking at certain alloys, where reported results for  $k$  are available over a range of temperatures. The composition of these alloys is given in Table I. Figure 5 shows the comparison between calculated and experimental values of  $k$  for NIMONIC 115, while values for the critical parameters  $\sigma$ ,  $D_{\text{eff}}$ , and the composition parameter  $(1-N_{\alpha})/(N_{\beta}-N_{\alpha})^2$  are given in Table II.

Similar calculations for UDIMET\* 700 and NIMONIC

\*UDIMET is a trademark of Special Metals.

PE16 are shown in Figures 6 and 7, respectively. For UDIMET 700, the calculated coarsening rate coefficients agree well with the work of Van Der Molen *et al.*<sup>[35]</sup> For NIMONIC PE16, the calculated solvus temperature of  $\gamma'$  is about  $870^{\circ}\text{C}$ , which means both that coarsening rates are slow and particle sizes are small in comparison to NIMONIC 115 and UDIMET 700 (Figures 5 and 6). The calculated coarsening rate coefficients match well with the experimental data from Betteridge and Heslop,<sup>[61]</sup> Bhanu Sankara Rao *et al.*<sup>[36]</sup> and Reppich *et al.*<sup>[37]</sup>

It is noted that the preceding alloys, and their heat treatment, provide cases that are widely different. The composition and solvus temperatures of the alloys are quite different (Table I), the amounts of  $\gamma'$  vary between 2 and 55 mole pct, and aging temperatures lie between  $650^{\circ}\text{C}$  and  $1100^{\circ}\text{C}$ . These alloys therefore represent a stiff challenge to the approach used here and the degree of success is highly encouraging.

It can be seen from Table II that all the critical parameters vary significantly with temperature. However, as might be expected, the biggest effect is due to  $D_{\text{eff}}$ , which varies by more than four orders of magnitude. The agreement with the experimental results for  $k$  as a function of temperature is rather good, despite the empirical method for calculating  $D_{\text{eff}}$ , suggesting that the activation energy is being reproduced satisfactorily. The composition effect changes by almost 3 times. Confidence can be placed in the value of  $N_{\alpha}$  and  $N_{\beta}$  as the thermodynamic calculation is made using a database for Ni-based superalloys that has been extensively validated against experimental results for  $\gamma/\gamma'$  equilibria.<sup>[33,34]</sup>

It is interesting to see that calculated values of  $\sigma$  for multicomponent alloys lie between 58 and  $91\text{ mJ/m}^2$  and are substantially larger than for binary alloys, where  $\sigma$  is calculated to lie between 20 and  $24\text{ mJ/m}^2$ . This large difference in  $\sigma$  between multicomponent and binary alloys reflects

**Table II. Calculated Mole Percentage of  $\gamma'$ , the Composition Term  $(1 - N_\alpha)/(N_\beta - N_\alpha)^2$ , the Effective Diffusion Coefficients  $D_{\text{eff}}$ , the Interfacial Energies  $\sigma$ , and Coarsening Rate Coefficients  $k$ , for Alloy NIMONIC 115 at Different Temperatures**

$T$ (°C)	Mole Pct	$(1 - N_\alpha)/(N_\beta - N_\alpha)^2$	$D_{\text{eff}}$ ( $\text{m}^2 \text{s}^{-1}$ )	$\sigma$ ( $\text{mJ}/\text{m}^2$ )	$k$ ( $\text{nm h}^{-1/3}$ )
750	55.31	27.28	$8.94 \times 10^{-19}$	66.90	8.22
800	53.33	29.25	$4.21 \times 10^{-18}$	65.03	14.74
850	51.04	31.71	$1.72 \times 10^{-17}$	63.29	25.17
900	48.18	34.89	$6.24 \times 10^{-17}$	61.55	41.34
950	44.56	39.14	$2.04 \times 10^{-16}$	59.82	65.79
1000	33.92	46.01	$6.02 \times 10^{-16}$	57.74	103.27
1050	25.33	54.91	$1.65 \times 10^{-15}$	55.81	157.57
1100	15.08	67.99	$4.18 \times 10^{-15}$	54.55	237.74

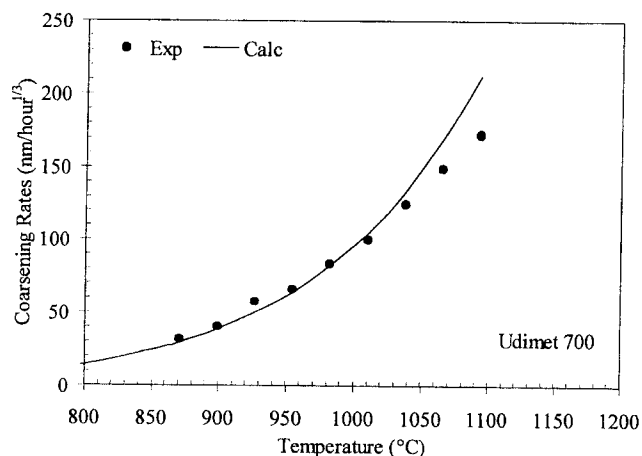


Fig. 6—Comparison between calculated and experimentally observed  $\gamma'$  coarsening rate coefficients for UDIMET 700 Ni-based superalloy as a function of temperature. The experimental data are from Van Der Molen *et al.*<sup>[35]</sup>

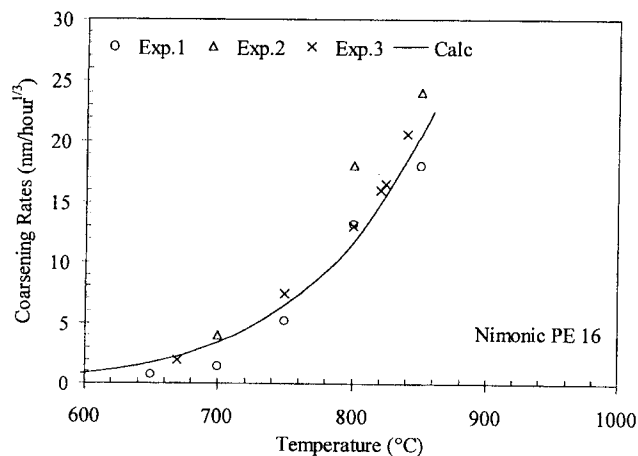


Fig. 7—Comparison between calculated and experimentally observed  $\gamma'$  coarsening rate coefficients for NIMONIC PE16 Ni-based superalloy as a function of temperature. The experimental data are from Betteridge and Heslop<sup>[6]</sup> (experiment 1), Bhanu Sankara Rao<sup>[36]</sup> (experiment 2), and Reppich<sup>[37]</sup> (experiment 3).

substantial changes in the thermodynamic properties associated with  $\gamma/\gamma'$  equilibria in alloys containing increased number of solutes. This perhaps should not be too surprising as  $\gamma/\gamma'$  partition coefficients are known to be quite different in multicomponent alloys when compared to those in binary

**Table III. Calculated Interfacial Energies for Some Nickel-Based Superalloys at 800 °C**

Alloy	$\sigma$ ( $\text{mJ}/\text{m}^2$ )	Ti/Al
NIMONIC 105	57.69	0.20
NIMONIC 115	65.03	0.46
UDIMET 700	71.10	0.51
IN 738	75.85	0.63
NIMONIC PK 33	74.78	0.78
NIMONIC 80A	61.13	1.12
NIMONIC 90	72.17	1.26
NIMONIC PE 16	90.92	1.46

and ternary alloys.<sup>[11]</sup> The value of  $\sigma$  depends on a large number of factors; temperature, the composition of the  $\gamma$  matrix, and the volume fraction of  $\gamma'$ . However, in the alloys studied here, the most noticeable effect seems to be associated with the Ti/Al ratio of  $\gamma'$ . Generally speaking, the higher the Ti/Al ratio, the higher the value of  $\sigma$  that is calculated. This is shown in Table III.

#### B. Binary Ni-Al Alloys and the Effect Coherency Strains on Coarsening Rate

It is noticeable that the calculated results for binary alloys, as well as being consistently too slow, exhibit a further systematic deviation in that the difference between calculation and experiment becomes worse with decreasing values of  $k$  (Figure 4). As the value of  $k$  is dependent on temperature (the lower the temperature the smaller the value of  $k$ ), it is instructive to reanalyze the error as a function of temperature. Figure 8(a) shows a plot of the difference ( $\Delta$ ) between calculated and experimental values of  $k$ , where  $\Delta = |k_{\text{Calc}} - k_{\text{Exp}}|/k_{\text{Calc}}$ , against the temperature of heat treatment. It is clear that the comparison improves with increasing temperature and  $\Delta$  would effectively become negligible somewhere between 900 °C and 1000 °C.

The basic reason for this effect is considered to be the result of the lattice misfit. In Ni-Al alloys, the lattice misfit decreases with increasing temperature because of the changing Al content of  $\gamma$  in the  $\gamma + \gamma'$  two-phase field and lies between 0.4 to 0.6 pct in the temperature range 620 °C to 750 °C.<sup>[40,41]</sup> At 1000 °C, where  $\Delta$  is significantly smaller,  $\delta$  begins to approach the lower limit of the range and approaches the values observed in multicomponent alloys. It is possible to plot the difference,  $\Delta$ , as a function of lattice misfit  $\delta$  (Figure 8(b)) instead of temperature as in Figure 8(a). We interpret the results shown in Figure 8(b) as meaning that any effect of lattice misfit on coarsening is small

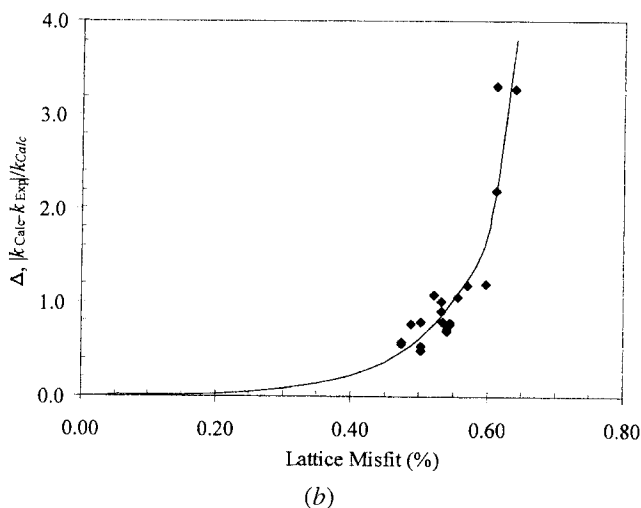
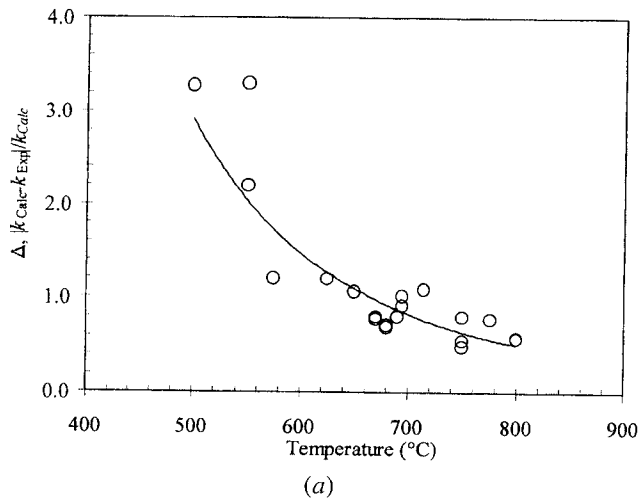


Fig. 8—The variation between calculated and experimentally observed coarsening rate coefficients of  $\gamma'$  particles in Ni-Al binary alloys as a function of (a) temperature and (b) lattice misfit.

when  $\delta$  is less than  $\sim 0.4$  pct. Although the chemical part of the interfacial energy has been considered to dominate in this article, it has been experimentally reported by Fine *et al.*<sup>[46]</sup> that coarsening rates can be significantly increased with high values of  $\delta$ ,  $\sim 0.65$  pct. These authors suggest that this could be explained qualitatively by reference to algorithms derived by Laraia *et al.*,<sup>[47]</sup> but we have found no quantitative results in the literature regarding application of this formulation, and it is not clear if this is an appropriate route to follow. It will clearly be important to consider the role of coherency strains on coarsening when treating precipitates that do have a high lattice mismatch, and this is accentuated by work currently being undertaken on coarsening of  $\gamma''$ .<sup>[48]</sup> However, this is beyond the scope of the current article, as is the effect of elastic fields between growing particles on the microstructural development of  $\gamma + \gamma'$  alloys, discussed by Thornton *et al.*<sup>[49]</sup>

The overall effect of coherency strains on coarsening can be summarized as follows.

- (1) When  $\delta < 0.4$  pct, the effect of coherency strain on coarsening kinetics appears to be small. As most multi-component Ni-based superalloys have values of  $\delta < 0.4$

pct, excellent results are obtained using the approach described in the current article.

- (2) As  $\delta$  becomes  $> 0.4$  pct, a further effect on coarsening comes into play. This may be due to the effect of coherency strains on  $\sigma$  itself, as has been suggested in previous work.<sup>[47]</sup> However, no further proof of this particular effect has been found.

### C. General Comments

It is worth discussing the sensitivity of the coarsening calculations to the various input parameters;  $R$  and  $T$  are, of course, fixed. Confidence can be placed in the calculated values of  $N_\alpha$  and  $N_\beta$  as the thermodynamic calculation has been extensively validated for  $\gamma/\gamma'$  equilibria. The assumption that  $V_m$  is constant will produce a negligible inaccuracy in the final calculation. This leaves the three critical parameters  $\sigma$ ,  $D_{\text{eff}}$ , and  $\phi$ , and, in reality, the accuracy of the calculation is dependent on the value of  $\sigma D_{\text{eff}}/\phi$ . A similar observation was made by Calderon *et al.*<sup>[7]</sup> using only the product  $\sigma D_{\text{eff}}$ , as in their case the effect of nonideality on  $G_m^{\alpha'}$  was considered small and  $\phi$  was essentially neglected.

It is also clear that the calculation of  $k$  is relatively insensitive to variation  $\sigma D_{\text{eff}}/\phi$ , because the function used in the final equation is the cube root of this value. Thus, a factor of  $\times 2$  gives only a variation of 25 pct in the final result for  $k$ . Taking into account that  $k$  changes by orders of magnitude over the temperature range considered here, a reasonable answer (to within 60 pct) would be found for the calculations even if the product of  $\sigma D_{\text{eff}}/\phi$  was in error by a factor of  $\times 4$ . As such, it would appear that it is not possible to make any definitive statements concerning the exact values of individual parameters, other than to say the function  $\sigma D_{\text{eff}}/\phi$  is being well matched.

However, there are limits to the introduction of complementary changes in the various parameters. For example,  $D_{\text{eff}}$  could be changed, by providing a complementary modification in  $\sigma$  to try and match  $k$ . The diffusion of only the  $\gamma'$  forming elements could be considered instead of the present method, which includes some effect of Ni self-diffusion. However, this would lead to a systematic deviation from the current calculations with respect to the temperature dependence of  $k$ . At present, this is matched rather well. The only clear systematic deviation is for the case of binary Ni-Al alloys, which has been discussed in Section B.

## IV. CONCLUSIONS

The coarsening rate of  $\gamma'$  in Ni-Al binary alloys and Ni-based superalloys has been calculated by a method based on the well-established model of Lifshitz, Slyozov and Wagner. The success of the current approach is considered to be due to the self-consistent estimation of the critical input parameters for the relevant equations. In this case, these are the  $\gamma/\gamma'$  interfacial energy ( $\sigma$ ), the compositions of  $\gamma$  and  $\gamma'$ , and the effective diffusion coefficient. The approach gives excellent results for multicomponent Ni-based superalloys, but there is a small, systematic difference between calculation and experiment for Ni-Al binary alloys. This difference has been analyzed and is considered to be due to the higher lattice mismatch ( $\delta$ ) in Ni-Al binary alloys

in comparison to values of  $\delta$  found in multicomponent alloys. Analysis suggests that good results will be obtained when  $\delta < 0.4$  pct, which applies to most multicomponent alloys considered here. When  $\delta > 0.4$  pct, a further effect needs to be considered, which may be due to a direct effect of coherency strains on  $\sigma$ .

## REFERENCES

1. A.J. Ardell and R.B. Nicholson: *Acta Metall.*, 1966, vol. 14, pp. 1295-1306.
2. A.J. Ardell: *Acta Metall.*, 1968, vol. 16, pp. 511-16.
3. D.M. Kim and A.J. Ardell: *Scripta Mater.*, 2000, vol. 43, pp. 381-84.
4. I.M. Lifshitz and V.V. Slyozov: *J. Phys. Chem. Solids*, 1961, vol. 19, pp. 35-50.
5. C. Wagner: *Z. Elektrochem.*, 1961, vol. 65, pp. 581-91.
6. W. Betteridge and J. Heslop: *The Nimonic Alloys*, 2nd ed., Edward Arnold Ltd., London, 1974, pp. 78-94.
7. H.A. Calderon, P.W. Voorhees, J.L. Murray, and G. Gkостorz: *Acta Metall.*, 1994, vol. 42, pp. 991-1000.
8. A.J. Ardell: *Interface Sci.*, 1995, vol. 3, pp. 119-25.
9. L. Kaufman and H. Nesor: *Metall. Trans.*, 1974, vol. 5A, pp. 1623-29.
10. N. Saunders and A.P. Miodownik: *CALPHAD—Calculation of Phase Diagrams*, Pergamon Materials Series, R.W. Cahn, ed., Elsevier Science, Oxford, UK, 1998, vol. 1.
11. N. Saunders: *Superalloys 1996*, R.D. Kissinger, D.J. deye, D.L. Anton, A.D. Cetel, M.V. Nathal, T.M. Pollock, and D.A. Woodford, eds., TMS, Warrendale, PA, 1996, pp. 101-10.
12. I. Ansara, B. Sundman, and P. Willemin: *Acta Metall.*, 1988, vol. 36, pp. 977-82.
13. N. Dupin: Ph.D. Thesis, Laboratoire de Thermodynamique and Physico-Chimie Metallurgiques de Grenoble, 1995.
14. O. Kubaschewski, C.B. Alcock, and P.J. Spencer: *Materials Thermochimistry*, 6th ed., Pergamon Press, Oxford, UK, 1993.
15. T. Hirata and D.H. Kirkwood: *Acta Metall.*, 1977, vol. 25, pp. 1425-34.
16. H. Wendt and P. Hassen: *Acta Metall.*, 1983, vol. 31, pp. 1649-59.
17. S.Q. Xiao and P. Haasen: *Acta Metall.*, 1991, vol. 39, pp. 651-59.
18. R. Wagner, R. Kampmann, and P.W. Voorhees: *Phase Transformations in Materials*, G. Kostorz, ed., Wiley-VCH, Weinheim, Germany, 2001, pp. 309-406.
19. R.J. White: *Mater. Sci. Eng.*, 1978, vol. 33, pp. 149-57.
20. J.W. Martin, R.D. Doherty, and B. Cantor: *Stability of Microstructure in Metallic Systems*, Cambridge University Press, Cambridge, UK, 1997.
21. D.A. Porter and K.E. Easterling: *Phase Transformations in Metals and Alloys*, Chapman & Hall, London, 1992.
22. D. Turnbull: *J. Appl. Phys.*, 1950, vol. 21, pp. 1022-28.
23. R. Becker: *Ann. Phys.*, 1938, vol. 32, pp. 128-40.
24. T. Nishizawa, I. Ohnuma, and K. Ishida: *J. Phase Equilibria*, 2001, vol. 22, pp. 269-75.
25. D. Turnbull: *Impurities and Imperfections*, ASM, Cleveland, OH, 1955, pp. 121-43.
26. A.J. Ardell and R.B. Nicholson: *J. Phys. Chem. Solids*, 1966, vol. 27, pp. 1793-1804.
27. A.P. Miodownik and N. Saunders: *Applications of Thermodynamics in the Synthesis and Processing of Materials*, P. Nash and B. Sundman, eds., TMS, Warrendale, PA, 1995, pp. 91-94.
28. X. Li, N. Saunders, and A.P. Miodownik: *Mater. Sci. Technol.*, in press.
29. J. Askill: *Tracer Diffusion Data for Alloys and Simple Oxides*, Plenum Press, New York, NY, 1970.
30. W.J. Boettinger, U.R. Kattner, S.R. Coriell, Y.A. Chang, and B.A. Mueller: *Modelling of Casting, Welding and Advanced Solidification Processes, VII*, M. Cross and J. Campbell, ed., TMS, Warrendale, PA, 1995, pp. 649-56.
31. N. Saunders, X. Li, A.P. Miodownik, and J.-P. Schillé: *Proc. Symp. Materials Design Approaches and Experiences*, J.-C. Shao, T.M. Pollock, and M.J. Farhmann, eds., TMS, Warrendale, PA, 2001, pp. 185-197.
32. N. Saunders, S. Kucherenko, X. Li, A.P. Miodownik, and J.-P. Schillé: *J. Phase Equilibria*, 2001, vol. 22, pp. 463-69.
33. N. Saunders: *Computer Aided Innovation of New Materials II*, M. Doyama, J. Kihara, M. Tanaka, and R. Yamamoto, eds., Elsevier Science, Amsterdam, 1993, pp. 731-734.
34. N. Saunders: *Phil. Trans. R. Soc. London, A*, 1995, vol. 351, pp. 543-61.
35. E.H. Van Der Molen, J.M. Oblak, and O.H. Kriege: *Metall. Trans.*, 1971, vol. 2, pp. 1627-33.
36. K. Bhanu Sankara Rao, V. Seetharaman, S.L. Mannan, and P. Rodriguez: *Mater. Sci. Eng.*, 1998, vol. 58, pp. 93-106.
37. B. Reppich, W. Kühlein, G. Meyer, D. Puppel, M. Schulz, and G. Schumann: *Mater. Sci. Eng.*, 1986, vol. 83, pp. 45-63.
38. R.A. Stevens and P.E.J. Flewitt: *Mater. Sci. Eng.*, 1979, vol. 37, pp. 237-47.
39. M. Doi and T. Miyazaki: *Superalloys 1992*, S.D. Antolovich, R.W. Stusrud, R.A. Mackay, D.L. Anton, T. Khan, R.D. Kissinger, and D.L. Klarstrom eds., TMS, Warrendale, PA, 1992, pp. 537-46.
40. P.K. Rastogi and A.J. Ardell: *Acta Metall.*, 1969, vol. 17, pp. 595-602.
41. A.B. Kamara, A.J. Ardell, and C.N.J. Wagner: *Metall. Mater. Trans. A*, 1996, vol. 27A, pp. 2888-96.
42. W.T. Loomis, J.W. Freeman, and D.L. Sponseller: *Metall. Trans.*, 1972, vol. 3, pp. 989-1000.
43. H. Harada, K. Ohno, T. Yamagat, T. Yokokawa, and M. Yamazaki: *Superalloys 1988*, S. Rechman *et al.*, eds., TMS, Warrendale, PA, 1988, pp. 733-42.
44. D. Raynor and J.M. Silcock: *Met. Sci.*, 1970, vol. 4, pp. 121-30.
45. R.A. Ricks, A.J. Porter, and R.C. Ecomb: *Acta Metall.*, 1983, vol. 31, pp. 43-53.
46. M.E. Fine, J.R. Weertman, and J.G. Conley: *Phase Transformations '87*, G.W. Lorimer, ed., The Institute of Metals, London, 1988, pp. 501-03.
47. V.J. Laraia, W.C. Johnson, and P.W. Voorhees: *Scripta Metall.*, 1989, vol. 23, pp. 1749-54.
48. X. Li, N. Saunders, and A.P. Miodownik: research in progress.
49. K. Thornton, N. Akaiwa, and P.W. Voorhees: *Phys. Rev. Lett.*, 2001, vol. 86, pp. 1259-62.