The Role of Alloying Elements on γ′ Phase Growth Kinetics in Ni-Base Alloys

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ABSTRACT

This work concerns the kinetics of γ′ precipitation in experimental Ni-base alloys. The work was motivated by the need for the partial substitution of Cr for Al to prevent TCP phase formation while maintaining the corrosion resistance of the alloys.

The composition of the alloys was characterized by low Cr content (15 wt.% instead of 20 wt.% in commercial wrought Ni-base superalloys), various Al contents, 1.5 wt.% of Ti and 5 wt.% of Mo.

The alloys were solution-treated followed by aging for up to 1100h at 700°C and 144h at 900°C. The coarsening of γ′ particles was studied using SEM, EDS and TEM techniques. The results show that the coarsening follows the Lifshitz-Slyozov-Wagner (LSW) law.

The kinetic constant, determined experimentally, depends on the lattice parameter mismatch between γ and γ′ phases, which in turn reflects the effect of elastic strains on the coarsening.

INTRODUCTION

The compositions of the γ and the γ′ phases in a multicomponent system determine the lattice parameters of both phases. These parameters correlate with the concentration of each element in the γ matrix and Ni_3Al by the following formulas /1-3/:

$$a_\gamma = 3.524 + 0.130C_{Cr} + 0.024C_{Co} + 0.421(C_{Mo} + C_W) + 0.183C_{Al} + 0.360C_{Ti} \quad (1)$$

$$a_\gamma = 3.567 + 0.156C_{Ti} + 0.372(C'_{Nb} + C'_{Ta}) + 0.248(C'_{Mo} + C'_W) \quad (2)$$

where a_γ and $a_{\gamma'}$ are the lattice parameters of the γ and the γ′ phase, respectively. C_i and C'_i – the atomic fraction of the i-element in the γ and the γ′, respectively.

The effect of the relative lattice parameter mismatch ε [$\varepsilon=(a_{\gamma'}-a_\gamma)/a_\gamma$] on morphological changes in the γ′ phase phase in Ni-base superalloys was studied by a number of authors /4-7/. Loomis *et al.* /7/ reported that increasing the Al content in Ni-Cr-Al-Mo alloys results in an increase in the solubility of molybdenum in γ′ which, in turn, increases the lattice parameter mismatch between γ and γ′ while accelerating the morphological changes in the γ′ precipitates. Khachaturyan *et al.* /8/ have developed a theoretical analysis of the morphological changes occurring during coarsening. In that analysis it is assumed that the elastic constants of the precipitate and those of the matrix are approximately the same. The model predicts the following morphological shape transitions for the Ni-Al system: (1) sphere to cube, $2a_0 \geq 7.7r_0$, (2) cube to doublet, $2a_0 \geq 27r_0$, (3) doublet to octet, $2a_0 \geq 82r_0$, (4) octet to platelet, $2a_0 \geq 377r_0$, where r_0 is the ratio between the interfacial energy, σ, and the elastic energy per unit volume, the latter originating from the lattice parameter mismatch, ε, and $2a_0$ is the edge length of the cube. Assuming σ is equal to 12 mj/m^2, the value of r_0 is

$$r_0 \frac{0.172 \times 10^{-3}}{\varepsilon^2} \text{ Å} \quad (3)$$

Coarsening kinetics of the γ′ phase in Ni-base superalloys are in good agreement with the Lifshitz-Slyozov-Wagner (LSW) theory /9,10/, which predicts a linear dependence of the precipitate volume change on the aging time, i.e.,

$$\bar{r}^3 - \bar{r}_0^3 = kt \quad (4)$$

where the rate constant k is given by

$$k = \frac{8\sigma V_m^2 D C_e}{9RT} \quad (5)$$

and $\bar{r}$ – the mean radius of the particles at time, t, $\bar{r}_0$ – the mean radius of the particles at time t = 0, i.e., at the beginning of coarsening, R – the gas constant and T – the absolute temperature.

Although no quantitative correlation has been found between the lattice mismatch and the coarsening rate, Ardell /11/ has made the general observation that, at a particular aging temperature, the greater the lattice mismatch, the greater the particle size.

In this paper the effect of increasing the Al content in the Ni-Cr-Al-Ti-Mo system on the lattice parameter mismatch and γ' growth kinetics is discussed.

EXPERIMENTAL

Experimental alloys, the compositions of which are given in Table 1, were manufactured by the central laboratory of Metallgesellschaft AG, Frankfurt, Germany, in the form of rolled bars of 10 mm diameter.

Specimens 10 mm long were solution-treated at 1200°C for 4 hr followed by water quenching and aging at two temperatures for various times.

A scanning electron microscope SEM (JSM-840) combined with EDS (LINK) was used for γ' morphology examination and quantitative compositional phase analysis. The lattice parameter mismatch between γ and γ' phases is determined by formulas (1) and (2).

The coarsening kinetics were studied utilizing the TEM (JEOL 2000FX) with an acceleration voltage of 200 kV. The techniques used in the TEM examinations were bright-field and dark-field imaging and selected area electron diffraction. Particle size was measured directly on the dark-field images obtained from superlattice reflections of the ordered γ' precipitates. A minimum of 300 measurements were made to obtain the average particle size and particle size distribution.

RESULTS AND DISCUSSION

The effect of the Al content on the lattice parameter mismatch and on the precipitate morphology was studied on alloy 66 after aging at 850°C for 168 h and

Table 1
Compositions of Experimental Alloys, wt.%

Alloy	Ni	Cr	Mo	Al	Ti
66	77.0	15.0	5.0	1.5	1.5
67	75.5	15.0	5.0	3.0	1.5
68	74.0	15.0	5.0	4.5	1.5

Table 2
Compositions of the γ and the γ' Phases of the Experimental Alloys, wt.%

Alloy	Phase	Ni	Cr	Ti	Al	Mo
66	γ	75.4	16.6	1.62	1.27	5.06
	γ'	83.8	8.02	1.0	2.43	4.78
67	γ	72.7	18.2	1.29	2.03	5.74
	γ'	81.5	7.32	1.99	5.89	3.32
68	γ	70.4	20.0	1.19	2.79	5.65
	γ'	82.2	4.01	2.14	8.04	3.66

on alloys 67, 68 after aging at 900°C for 144 h. The compositions of the γ and the γ′ phases as determined by quantitative EDS analysis are listed in Table 2. It can be seen that an increase in the Al content causes a decrease in the solubility of Mo and Cr in γ′ and an increase in that of Ti in the γ′ phase.

In order to calculate the lattice parameter mismatch between the γ and γ′ phases it is assumed that the composition of the γ′ phase is independent of the aging temperature. This assumption is justified by the results of some investigators /7/. The composition of the matrix, which changes as a result of the higher γ′ volume fraction at lower aging temperatures, was calculated for each alloy on the basis of the average composition of the alloy and γ′ volume fraction at equilibrium /1/. Then, using expression (3), the elastic parameter r_0 and the critical sphere-to-cube transition parameter, $2a_0$, for each alloy for two aging temperatures were calculated. These parameters are summarized in Table 3. The decrease of the lattice parameter mismatch from a positive value for alloy 66 to negative ones for the others is attributed to a decrease in the content of Mo and Cr in the γ′ and an increase of those of Al and Ti as the overall Al content increases.

SEM micrographs (Fig. 1) illustrate the effect of the lattice parameter mismatch on the γ′ morphology. The γ′ particles tend to change from a spherical to a cubic shape as the absolute value of the lattice parameter mismatch increases due to the ability of the cubic precipitate to reduce strain energy. Spherical particles are randomly oriented in the matrix while cubical particles are strongly aligned along {100} directions.

The kinetics of γ′ phase coarsening were studied in alloys aged at 700°C for periods ranging from 24 to 1100 h. Dark field electron micrographs of the alloys aged for 480 h are shown in Fig. 2. The γ′ particles in the alloy 66 are uniformly distributed, alloy 67 shows some degree of agglomeration, but the spherical shape of the γ′ is still discernible. In alloy 68 the precipitates exhibit the tendency to change from the spherical to the cubic shape.

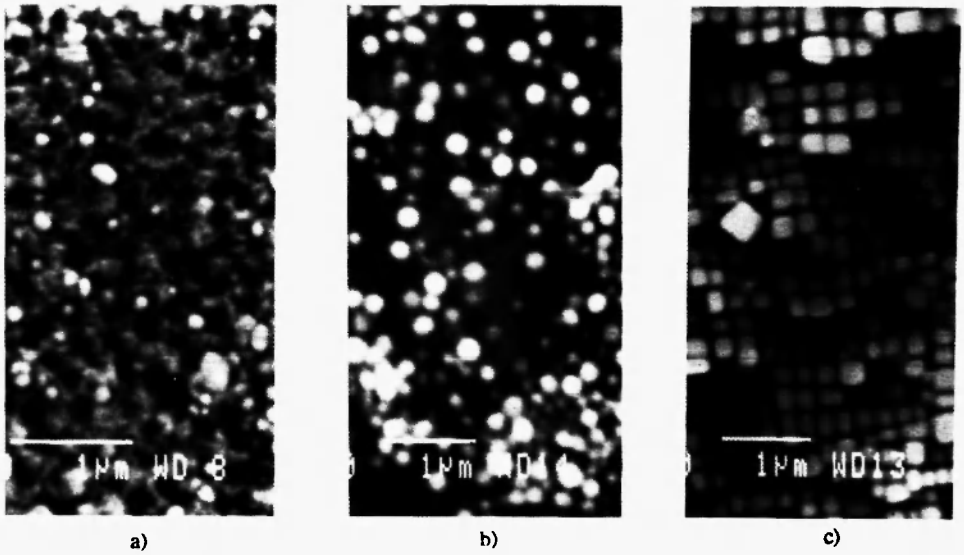
The linear dependence of the mean particle volume $(\bar{a}/2)^3$ on the aging time (Fig. 3) proves that the growth kinetics obey the LSW law. The straight lines were fitted by the least squares method, yielding the rate constant k. The obtained values are listed in Table 4 together with the results obtained by Davies *et al.* /12/ for Ni-Co-Al alloys aged at the same temperature.

From Table 4 it can be seen that the γ′ volume fraction does not affect the coarsening rate constant. But the latter is dependent on the lattice parameter mismatch. The effect of the latter on the coarsening rate is correlated with an increase in the interfacial energy resulting from a displacement of the interface atoms from their equilibrium position. The said increase is significant, compared with the very low specific energy of mismatch-free, fully coherent interface. The coarsening rate constant increases linearly with the increase in the specific interfacial energy according to expression (5).

The change in the γ′ volume fraction is reflected in the particle size distribution function, as the particle coalescence proceeds. The effect of that coalescence has been investigated by Davies *et al.* /13/ following the theoretical treatment outlined by Lifshitz and Slyozov /9/, and their modified (LSEM) theory. It is assumed that coalescence occurs instantaneously when two

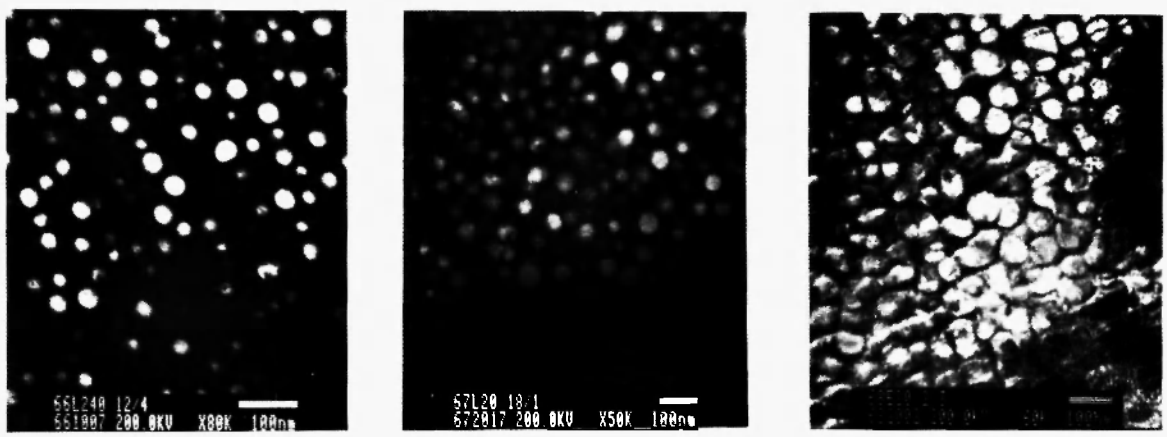
Table 3
Parameters Characterizing γ′ Phase

Alloy	Aging temperature, °C	Volume fraction of γ′,%	Lattice mismatch,ε	Parameter r_0, Å	Transition parameter $2a_0$,Å
66	850	19	0.00095	191	1468
	700	25	0.00045	855	6583
67	900	29	-0.0007	351	2703
	700	35	-0.0009	225	1731
68	900	32	-0.0017	59.5	458
	700	43	-0.0021	40.3	311



a) b) c)

Fig. 1: The effect of Al content and lattice parameter mismatch on the γ′ morphology: (a) alloy 66 (1.5 wt.% Al) aged for 168 h at 850°C, ε = 0.000095; (b) alloy 67 (3 wt.% Al) aged for 144 h at 900°C, ε = -0.0007; (c) alloy 68 (4.5 wt.% Al) aged for 144 h at 900°C, ε = –0.0017.



a) b) c)

Fig. 2: γ′ precipitates after aging at 700°C for 480 h: (a) in alloy 66 (1.5 wt.% Al); (b) in alloy 67 (3 wt.% Al); and (c) in alloy 68 (4.5 wt.% Al).

Table 4

Coarsening Rate Constants for Alloys Aged at 700°C

Alloy	Volume fraction of γ′	Lattice mismatch,%	k x 10^{-30} m^3/sec
Ni-9.3Co-11.8Al*	0.16	0.45	14.6
Ni-9.5Co-12.6Al*	0.24	0.45	17.88
Ni-21.7Co-13.4Al*	0.31	0.4	11.07
66	0.25	0.045	2.49
67	0.35	0.09	3.36
68	0.43	0.21	6.05

*Results of Davies et al. [12]

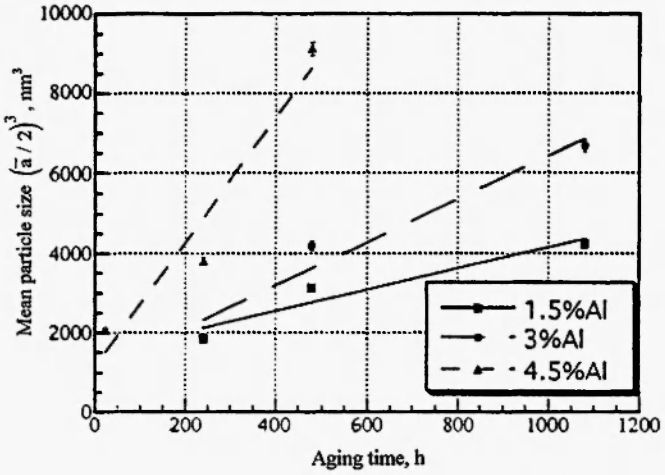


Fig. 3: The mean γ′ particle volume $(\bar{a}/2)^3$ as a function of aging time at 700°C.

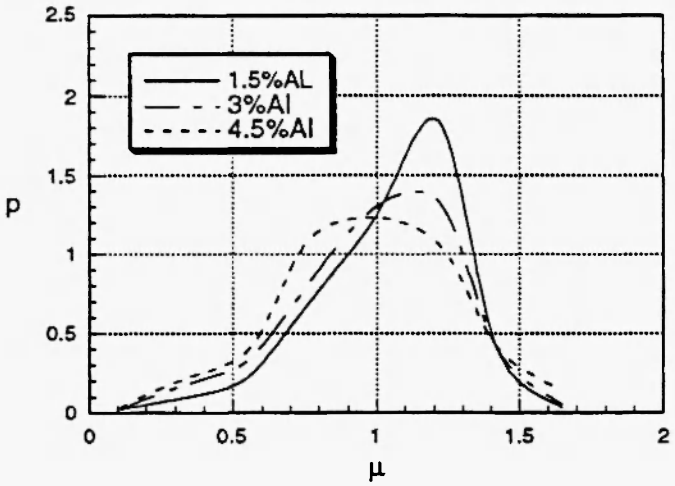


Fig. 4: Normalized particle size distribution for alloys aged for a long time at 700°C. P is the probability and μ is the normalized linear particle size.

particles collide, so that two particles are removed from the smaller size range of the distribution and one is added to the larger size ranges. Therefore, as the Al content increases, the coalescence at a defined aging time is more advanced and hence the particle distribution becomes broader and more symmetrical, as can be seen in Fig. 4.

SUMMARY

The results of this work can be summarized as follows:

1. The γ-γ′ lattice mismatch depends on the partitioning of the elements between the γ and γ′ phases. The increase of Al content from 1.5 wt.% to 4.5 wt.% promotes the Ti solubility in the γ′ phase and decreases the Mo and Cr solubility therein. As a result, the lattice mismatch changes from a positive to a negative value while increasing in absolute value which, in turn, affects the growth kinetics.
2. The γ′ particle morphology was correlated to lattice parameter mismatch between the γ and γ′ phases: with increasing mismatch, transition from spherical to cubic shape occurs at smaller particle size. The critical parameter of the transition from spherical to cubic shape was calculated. The correspondence of the observed morphology with the calculated critical transition parameter was found. The spherical γ′ particles were found randomly oriented in the matrix, while the cubic particles exhibit some degree of alignment along the {100} directions.
3. γ′ particle growth is a diffusion-controlled process obeying the Lifshitz-Slyozov-Wagner (LSW) law. The coarsening rate constant depends on the matrix/particle lattice parameter mismatch, which is responsible for an increase in the γ-γ′ interface energy. The higher the lattice mismatch (in absolute value), the higher the growth rate.
4. It was found that the particle size distribution depends on the γ′ volume fraction, which is in accord with the Lifshitz-Slyozov encounter modified (LSEM) theory.

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