MICROSTRUCTURAL DEVELOPMENT UNDER THE INFLUENCE OF
ELASTIC ENERGY IN Ni-BASE ALLOYS CONTAINING γ' PRECIPITATES

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Abstract

The changes in the size and the distribution of γ' precipitate particles during ageing of some Ni-base alloys were investigated by means of transmission electron microscopy (TEM).

In the alloy system which has smaller lattice misfit and hence smaller elastic energy (e.g. Ni-Cr-Al or Ni-Si-Al), the γ' particles coarsen steadily and the mean particle size $\bar{r}$ at an ageing time t is proportional to $t^{1/3}$. The size distribution of γ' particles does not change during the ageing, and the standard deviation σ of size distribution is practically constant.

In the alloy system which has larger elastic energy (e.g. Ni-Cu-Si), the deceleration of the coarsening of γ' particles occurs during ageing. At the same time, the size distribution of γ' particles becomes sharper gradually, that is, the σ decreases in the course of coarsening.

When the elastic energy is small (e.g. Ni-Cr-Al or Ni-Si-Al), the γ' particles are uniformly (i.e. homogeneously) distributed in the γ matrix. However, when the elastic energy is large (e.g. Ni-Al or Ni-Al-Ti), the γ' particles have a tendency to exhibit non-uniform (i.e. inhomogeneous) distribution in the γ matrix. When the volume fraction of γ' is higher, this tendency is less obvious, that is, the γ' distribution appears uniform, even if the elastic energy is large.

The deceleration of coarsening, the decrease in σ and the formation of non-uniform distribution are the results of elastic interaction energy. When understanding the microstructure of Ni-base superalloys strengthened by γ' particles, we should always take account of the important role of elastic interaction energy.

Introduction

It is well known that the high temperature strength of Ni-base superalloys is a result of a particular microstructure consisting of finely and regularly distributed γ' precipitate particles. Such a microstructure accompanied by desirable properties is almost always in a thermodynamically metastable state because it is usually obtained by interrupting the phase transformation in the course of heat-treatment. Therefore, during further heat-treatment, the favourable microstructure is very likely to develop into a thermodynamically stabler microstructure which has no longer favourable properties in most cases: the individual precipitate particles change their size, shape and distribution to minimize their energy state.

The energy state of the individual coherent particles can be expressed by three energies: surface energy of the particle; elastic strain energy due to the lattice misfit between the particle and the matrix; elastic interaction energy between particles which originates from the overlap of the elastic strain fields around the individual particles. The latter two are known as elastic energy. We have often pointed out the important effects of elastic energy on the morphology of coherent precipitates (1-4). A typical example is the case where the elastic interaction energy plays an essential role in forming various types of γ' precipitate morphology: a single γ' cuboid splits into a pair of parallel small plates or into eight small cuboids in the course of coarsening (1-3). Furthermore, a number of important things which cannot be understood without considering the effects of elastic energy have been reported so far: one example is the structural and/or stability bifurcations (5-7); another is the inhomogeneous (i.e. non-uniform) distribution of precipitate particles (8).

Regarding the change in the size of precipitate particles, the well-known process is the coarsening due to the surface energy of the particle, i.e. "Ostwald ripening". Almost all the conventional theories of precipitate coarsening are based on the theoretical treatment of Ostwald ripening which is widely known as "LSW (Lifschitz, Slyozov and Wagner) theory" (9,10). In such theories, the larger particles coarsen by absorbing the smaller particles to release their excess surface energy, and hence the total energy of the microstructure decreases. Contrary to the conventional theories, our new theory of microstructural stability named "bifurcation" theory (6,7) predicts that in elastically constrained systems, sometimes the smaller particles can grow at the expense of the larger particles to bring a uniform distribution in particle size. Furthermore, it has widely been recognized so far that coherent precipitates are distributed uniformly in the matrix owing to the elastic interaction (11). However, our theoretical calculations predict that coherent precipitates tend to exhibit non-uniform distribution (8). Although a number of attempts are now being made to verify the above two predictions, they leave something to be desired.

The aims of the present studies are (I) to investigate the changes in the size and the distribution of γ' precipitate particles during ageing of Ni-base alloys by means of transmission electron microscopy (TEM), and (II) to discuss the effects of elastic energy, especially the effects of elastic interaction energy, on the microstructural developments.

Experimental Procedures

The larger is the lattice misfit δ between the particle and the matrix, the larger is the elastic energy. Therefore, the following Ni-base alloys which have different misfits were used in the present studies: Ni-18.2%Cr-6.2%Al ($\delta=0.008$ %), Ni-7.0%Si-6.0%Al ($\delta=0.10$ %), Ni-12.5%Al ($\delta=0.56$ %), Ni-8.0at.%Al-5.0at.%Ti ($\delta=0.65$ %), Ni-36.1%Cu-9.8%Si ($\delta=-1.3$ %) and Ni-47.4%Cu-

Figure 1 - TEM images of γ' precipitate particles in Ni-base alloys with small elastic energy: Ni-18.2%Cr-6.2%Al aged at 1073 K for 86400 s (a), and 691000 s (b); Ni-7.0%Si-6.0%Al aged at 1073 K for 7200 s (c), and for 57600 s (d).

5.0%Si ($\delta=-1.3$ %). All the compositions are given in atomic %. Each alloy was quenched into iced water after homogenizing at a high temperature (i.e. solid solution treatment), and then was aged at a temperature lower than the γ' solvus line. Foil specimens for TEM observations were prepared by electropolishing the aged samples. The changes in the size and the size distribution of γ' particles during ageing were calculated from the TEM images.

Experimental Results

Alloy Systems with Small Elastic Energy

Figure 1 illustrates the TEM images of γ' precipitate particles in the Ni-Cr-Al and the Ni-Si-Al alloys. The shape of the individual particles is spherical and the particles are uniformly and randomly distributed in the γ matrix. Figure 2 illustrates the coarsening kinetics of γ' particles in the Ni-Cr-Al and the Ni-Si-Al alloys aged at 1073 K. It can be seen from this figure that the mean particle size (radius) $\bar{r}$ at an ageing time t is proportional to $t^{1/m}$, and the exponent $1/m$ is 0.33 for the former and 0.32 for the latter. Figure 3 illustrates the changes in the size distribution of γ' particles during ageing of the Ni-Cr-Al and the Ni-Si-Al alloys at 1073 K. The size distribution does not change essentially during coarsening, and the standard deviation σ remains practically constant: the σ is about 0.25 for the former and about 0.27 for the latter.

Figure 2 - Coarsening kinetics of γ' particles in Ni-base alloys with small elastic energy.

Alloy Systems with Large Elastic Energy

Figure 4 illustrates the TEM images of γ' precipitate particles in the Ni-Cu-Si and the Ni-Al alloys. The shape of the individual particles is substantially cuboidal except for the Ni-Al alloy aged for a long time

Figure 3 - Size distribution of γ' particles in Ni-base alloys with small elastic energy: Ni-18.2%Cr-6.2%Al aged at 1073 K (a-c); Ni-7.0%Si-6.0%Al aged at 1073 K (d-f).

Figure 4 - TEM images of γ' precipitate particles in Ni-base alloys with large elastic energy: Ni-36.1%Cu-9.8%Si aged at 823 K for 690000 s (a), and 1200000 s (b); Ni-12.5%Al aged at 973 K for 43200 s (c), 173000 s (d), 346000 s (e), and 1210000 s (f).

($t > 3 \times 10^5$ s). In the Ni-Al alloy, the shape change from cuboid to plate occurs during ageing. Therefore, we must discuss the coarsening behaviour during only the shorter ageings which cause no such serious shape-changes, because we cannot deal with plates on the same basis as cuboids. The half length of the edge of a cuboid is regarded as r value for the cuboid. Furthermore, a prolonged ageing of the Ni-Al alloy brings an extremely non-uniform (i.e. inhomogeneous) distribution of γ' particles, forming clusters. Figures 5 and 6 illustrate the coarsening kinetics and the changes in the size distribution of γ' particles during ageings of the Ni-Cu-Si at 823 K

Figure 5 - Coarsening kinetics (a) and standard deviation σ of size distributions (b) of γ' particles in Ni-base alloys with large elastic energy.

Figure 6 - Size distribution of γ' particles in Ni-base alloys with large elastic energy: Ni-36.1%Cu-9.9%Si aged at 823 K (a-c); Ni-12.5%Al aged at 973 K (d-f).

and the Ni-Al alloy at 973 K. It can be seen from these figures that the deceleration of coarsening and the simultaneous sharpening of size distribution (i.e. the decrease in σ) occur during ageing of the Ni-Cu-Si alloys. In the Ni-Al alloy, however, the σ value remains constant (≈ 0.21), and the $\bar{r}$ is proportional to $t^{1/3}$: i.e. the deceleration of coarsening does not occur.

Discussions

Coarsening Kinetics and Size Distributions

In the alloy system which has small elastic energy, the coarsening of γ' particles obeys the $t^{1/m}$ law and the $1/m$ value (0.32 or 0.33 in Fig. 2) is practically equal to the value $1/3$ predicted by the LSW theory of Ostwald ripening. However, the size distributions observed in the actual alloy systems with small elastic energy are significantly different from that predicted by the LSW theory. The former is always wider, more symmetric and less peaked than the latter: the observed σ value (0.25 or 0.27 in Fig. 3) is larger than the value 0.215 predicted by the LSW theory. The LSW theory has been modified so far by many investigators to explain the difference between the observed size distribution and the predicted one; many attempts aimed at modifying the LSW theory with respect to the volume fraction of particles (12-17). The results obtained here are in accord with either the LSW theory or the LSW theories modified with respect to the volume fraction. In the alloy systems having smaller elastic energy, the driving force for the coarsening of γ' precipitate particles is their excess surface energy.

A noticeable result obtained in the present studies is that the coarsening of γ' particles is decelerated in the Ni-Cu-Si alloys which have large elastic energy (see Fig. 5-a). This tendency toward deceleration is more obvious when the volume fraction of γ' is higher. Another noticeable result is that the size distribution of γ' particles becomes sharper gradually, i.e. the σ decreases gradually, in the course of coarsening. It should be noted that the deceleration of coarsening and the decrease in σ occur simultaneously. These results suggest the important thing that the sizes of the individual particles become less scattered (i.e. uniform) and the microstructure converges to a particular state if the elastic energy is large and the volume fraction is high: i.e. the unification of particles and the stabilization of a particular microstructure occur.

Stability Bifurcation in γ' -Particle Coarsening

The already well-known theories of particle coarsening, i.e. the LSW or the modified LSW theories, indicate that larger particles continue to coarsen by absorbing smaller particles (hence the microstructure continues coarsening) because the driving force for coarsening is considered to be only the excess surface energy of the particles. As long as we accept the already recognized theories, the unification of particles and the stabilization of a particular microstructure seem incredible. However, if we take account of the new idea named "stability bifurcation" (6,7) in which the elastic energy, and especially the elastic interaction energy plays an essential role, we can clearly explain such unbelievable phenomena.

Figure 7 illustrates the variation in the energy state of a pair of γ' particles as a function of $\bar{r}$ and R (7). The parameter $R \equiv (r_\alpha - r_\beta) / (r_\alpha + r_\beta)$; ($|R| \leq 1$) is used to describe the relative sizes of the paired particles where r_α and r_β are the radii of the paired particles: when $R=0$, the paired particles are identical and take the average size $\bar{r}$; when $R=\pm 1$, only one of the pair exists and takes the maximum size $\sqrt{2} \cdot \bar{r}$. When the $\bar{r}$ is small, e.g. $\bar{r}_1$ in Fig. 7, the state at $R=0$ has the highest energy (indicated by the open

circle ○) and the states at $R=\pm 1$ have the lowest energy (indicated by the solid circles ●); the total energy decreases from ○ to ●, as indicated by the bold arrows (➔). In the Region I, the energy state always decreases toward $R=\pm 1$, and one of the paired particles can coarsen by absorbing the other just like the case predicted by the LSW or the modified LSW theories: the microstructure coarsens to decrease its surface energy and hence its total energy.

However, when the $\bar{r}$ is large, e.g. $\bar{r}_2$ in Fig. 7, the energy state takes a minimum at $R=0$ (indicated by the rectangular □): the total energy decreases toward $R=0$, as indicated by the open arrows (➡). As the $\bar{r}$ becomes large, the elastic interaction energy becomes dominant as compared with the surface energy. The appearance of the energy minimum at $R=0$ is a result of the elastic interaction energy between the paired particles. It is clear from Fig. 7 that in the shadowed Region II, smaller particles can coarsen by absorbing larger particles to decrease the energy state, which is opposite to the LSW or the modified LSW theories. According to the above bifurcation theory, no wonder the deceleration of coarsening and the sharpening of size distribution (the decrease in σ), i.e. the unification and the stabilization of microstructure, occur.

It is also clear from the present discussions that the deceleration of coarsening is a result of the change in driving force for coarsening, i.e. the change from the mechanism controlled by surface energy to that by elastic interaction energy. The equation $\bar{r}=K \cdot t^{1/m}$ is usually used to describe the coarsening kinetics. When the coarsening rate changes, we usually take account of only the change in $1/m$. However, we had better conclude that not the exponent $1/m$ but the K should change during ageing, which results in the deceleration of coarsening and the decrease in σ . Here we should remember the coarsening behaviour of γ' particles in the Ni-Al alloy (see Fig. 5). Although the elastic interaction in the Ni-Al alloy

Figure 7 - Variation in the energy state of a pair of γ' particles as a function of the average particle size $\bar{r}$ and the parameter R .

system is strong, the coarsening of γ' particles is not decelerated but obeys the $t^{1/3}$ law when their size distribution and hence the σ do not change. This fact clearly supports the above idea that the exponent $1/m$ is always constant ($=1/3$) and a constantly varying K brings a constantly varying coarsening-rate, i.e. the deceleration of coarsening.

Inhomogeneous Distribution of γ' Particles

The third noticeable result is that the γ' particles in the Ni-Al alloy have a tendency to exhibit an extremely non-uniform distribution in the matrix, as shown in Figs. 4-e and -f. This tendency is more obvious when the volume fraction of γ' is lower: e.g. in the Ni-Al-Ti alloy during reversion, the γ' particles are locally distributed forming clusters in the γ matrix. The present results agree with our result obtained by theoretical calculations (8) that such a non-uniform distribution is energetically stabler than the uniform distribution. Even if the elastic interaction is strong, however, the higher is the volume fraction, the less obvious is the tendency toward non-uniform distribution. The distribution of γ' particles appears uniform when their volume fraction is high.

Summary and Conclusions

We have been believing for very long that the precipitate coarsening proceeds steadily and never slows down to converge to a particular state. We have also been believing that the coherent precipitates are uniformly distributed in the matrix owing to the effect of elastic interaction energy and never have the tendency toward clustering. However, the present results are just the opposite and clearly urge us to change the already well-known ideas on the development of microstructure containing coherent precipitates. It is an effect of elastic interaction energy that the γ' precipitates become uniform in their size to converge to a particular microstructure in a stable state (desirable effect). It is another effect of elastic interaction energy that the γ' precipitates become non-uniform in their distribution to form clusters (undesirable effect).

The present studies clearly show that the elastic interaction energy has remarkable effects on the microstructural developments, in other words, on the instability of the desirable microstructure accompanied by good properties. Of course, it is very important for the practical use whether such a desirable microstructure is stable or unstable during further heating. When understanding the microstructures and hence the properties of Ni-base superalloys strengthened by γ' precipitate particles, we should not neglect the important role of elastic energies.

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References

1. M. Doi, and T. Miyazaki, "The Effect of Elastic Interaction Energy on the Shape of γ' -Precipitate in Ni-Based Alloys," Superalloys 1984, ed. M. Gell, C. S. Kortovich, R. H. Bricknell, W. B. Kent and J. F. Radavich (Warrendale, PA: The Metallurgical Society, 1984), 543-552.
2. M. Doi, T. Miyazaki, and T. Wakatsuki, "The Effect of Elastic Interac-

- tion Energy on the Morphology of γ' Precipitates in Nickel-based Alloys," Materials Science and Engineering, 67 (1984) 247-253.
3. M. Doi, T. Miyazaki, and T. Wakatsuki, "The Effects of Elastic Interaction Energy on the γ' Precipitate Morphology of Continuously Cooled Nickel-base Alloys," Materials Science and Engineering, 74 (1985) 139-145.
 4. M. Doi, and T. Miyazaki, " γ' Precipitate Morphology Formed under the Influence of Elastic Interaction Energies in Nickel-base Alloys," Materials Science and Engineering, 78 (1986) 87-94.
 5. W. C. Johnson, and J. W. Cahn, "Elastically Induced Shape Bifurcations of Inclusions," Acta Metallurgica, 32 (1984) 1925-1933.
 6. T. Miyazaki, K. Seki, M. Doi, and T. Kozakai, "Stability-bifurcations in the Coarsening of Precipitates in Elastically Constrained Systems," Materials Science and Engineering, 77 (1986) 125-132.
 7. T. Miyazaki, M. Doi, and T. Kozakai, "Shape Bifurcations in the Coarsening of Precipitates in Elastically Constrained Systems," Proc. Int. Symp. on Non Linear Phenomena in Materials Science, Aussoia, September 1987 [in printing].
 8. M. Doi, M. Fukaya, and T. Miyazaki, "Inhomogeneity in a Coherent Precipitate Distribution Arising from the Effects of Elastic Interaction Energies," Philosophical Magazine, (1988) [in printing].
 9. I. M. Lifshitz, and V. V. Slyozov, "The Kinetics of Precipitation from Supersaturated Solid Solutions," Journal of Physics and Chemistry of Solids, 19 (1961) 35-50.
 10. C. Wagner, "Theorie der Alterung von Niederschlägen durch Umlösen (Ostwald-Reifung)," Zeitschrift für Elektrochemie, 65 (1961) 581-591.
 11. A. J. Ardell, R. B. Nicholson, and J. D. Eshelby, "On the Modulated Structure of Aged Ni-Al Alloys," with an Appendix "On the Elastic Interaction between Inclusions," Acta Metallurgica, 14 (1966) 1295-1309.
 12. A. J. Ardell, "The Effect of Volume Fraction on Particle Coarsening: Theoretical Considerations," Acta Metallurgica, 20 (1972) 61-71.
 13. A. D. Brailsford, and P. Winblatt, "The Dependence of Ostwald Ripening Kinetics on Particle Volume Fraction," Acta Metallurgica, 27 (1979) 489-497.
 14. C. K. Davies, P. Nash, and R. N. Stevens, "The Effect of Volume Fraction of Precipitate on Ostwald Ripening," Acta Metallurgica, 28 (1980) 179-189.
 15. J. A. Marqusee, and J. Ross, "Theory of Ostwald Ripening: Competitive Growth and Its Dependence on Volume Fraction," Journal of Chemical Physics, 80 (1984) 536-543.
 16. P. W. Voorhees, and M. E. Glicksman, "Solution to the Multi-Particle Diffusion Problem with Applications to Ostwald Ripening — I. Theory," Acta Metallurgica, 32 (1984) 2001-2011.
 17. Y. Enomoto, M. Tokuyama, and K. Kawasaki, "Finite Volume Fraction Effects on Ostwald Ripening," Acta Metallurgica, 34 (1986) 2119-2128.