THE EFFECT OF ELASTIC INTERACTION ENERGY ON THE SHAPE

OF γ' -PRECIPITATE IN NI-BASED ALLOYS

Minoru Doi and Toru Miyazaki

Department of Metallurgical Engineering
Nagoya Institute of Technology
Gokiso-cho, Showa-ku, Nagoya 466
Japan

Summary

The γ' -precipitate particle in Ni-based alloys sometimes splits into a pair of parallel plates (i.e., doublet) or eight small cuboids (i.e., octad) during the growth of the precipitates. Such extraordinary phenomena indicate that the elastic interaction does affect the shape of the individual γ' -particles, to say nothing of the distribution of them. By calculating the energies before and after the split on the basis of a microelasticity theory, we can justify the conception that the elastic interaction between the doublet or the octad formed by the split decreases the total energy by overcoming the increase in surface energy due to the split. The effects of elastic interaction on the shape of γ' -precipitates can well be arranged by introducing the parameter Δ^* which is the ratio of γ/γ' lattice misfit δ to surface energy density γ_s ($\Delta^* = \delta/\gamma_s$).

Introduction

It is well known that the precipitation of coherent γ' -particles plays an important role in the improvement of high temperature strength of Ni-based superalloys. Therefore, one of the important subjects for designing and developing new types of such precipitation-strengthened superalloys is on how to control the morphology of γ' -precipitates by different kinds of heat treatments etc. As for the morphology of precipitates, both the shape and the distribution of them are to be considered in general.

The energy state of every coherent γ' -precipitate particle can be expressed by the following equation:

$$E_{\text{total}} = E_{\text{str}} + E_{\text{surf}} + E_{\text{int}}, \quad (1)$$

where the first term E_{str} is the elastic strain energy which results from the lattice mismatch between the γ' -precipitate and the γ -matrix, and the second term E_{surf} the surface energy (interfacial energy) of the γ' -precipitate. It has widely been recognized so far that the shape of γ' -precipitate

is theoretically given by minimizing the sum of the E_{str} and the E_{surf} . Furthermore, the shape of γ' -precipitate has been considered to vary with the degree of lattice mismatch (1-3); that is, the shape changes from a sphere to a cuboid, a needle or a plate as the lattice mismatch increases.

The third term E_{int} in Eq. (1) is the elastic interaction energy caused by the overlap of the elastic strain fields which accompany the individual coherent γ' -particles. The effect of elastic interaction on the morphology of precipitates has been studied so far (4-8), and it has generally been recognized that the elastic interaction does not influence the shape of the individual particles but has a remarkable effect only on the distribution of them. A feature of the E_{int} between two γ' -particles in γ -matrix is that the E_{int} takes a negative minimum value when the two particles are adjacent to each other along [100] direction (4,7,8). This is the reason why γ' -precipitates are sometimes aligned along [100] direction.

Recently, we have found out an extraordinary phenomenon that a single γ' -precipitate particle splits into plural small particles during the growth of the particle (9,10). We have also explained the phenomenon of split by assuming that the elastic interaction between the particles formed by the split compensates for the remarkable increase in surface energy due to the split (9,10). The phenomenon of split is considered to be a typical example of the effect of elastic interaction on the shape of precipitates.

The aims of the present studies are (i) to obtain the experimental evidence that the elastic interaction plays an important role in the shape-change of coherent γ' -precipitate; that is, whether or not the splits really occur in various kinds of experimental and commercial Ni-based alloys, and (ii) to justify the effect of elastic interaction by the theoretical calculations based on a microelasticity theory.

Experimental Procedures

Eleven kinds of Ni-based alloys were used in the present studies, as follows: Ni-12%Al, Ni-12%Si, Ni-11%Ti, Ni-7%Si-7%Al, Ni-10%Al-4%Si, Ni-8%Al-5%Ti, Ni-40%Cu-6%Si, Ni-20%Cr-10%Al, Ni-18%Cr-5%Si, and commercial super-alloys of Inconel 700 and Nimonic 115. All compositions are given in atomic %. A rod-shaped single crystal of each alloy about 11 mm in diameter was prepared by a Bridgman technique. Thin discs about 1 mm in thickness whose faces were parallel to (100) were spark-cut from each rod-shaped single crystal. After homogenizing at a high temperature, each disc was slowly cooled in a furnace to the temperature just below the γ' -solvus, and then held at that temperature for suitable times. Thin foil specimens for transmission electron microscope (TEM) observations were prepared by electro-polishing the discs thus aged. A JEOL JEM-200A electron microscope was used at the accelerating voltage of 200 kV to observe the morphological changes of the γ' -precipitates during their growth. A Mitsubishi MELCOM-COSMO 700III/MP computer was used for the numerical calculations of the energetically stable shape of the γ' -precipitate.

Experimental Results on the Split

When the Ni-12%Al alloy is slowly cooled in a furnace to 1133 K (just below the γ' -solvus) after homogenizing at 1473 K and then aged at 1133 K for a short time, coherent γ' -particles in cuboidal shape appear sparsely and randomly in the γ -matrix. During the growth of the particles by further ageing at 1133 K, the shape of the individual γ' -particles changes to a

Figure 1 - TEM image of γ' -precipitate doublets (pairs of parallel plates) in Ni-12at.%Al alloy aged at 1133 K (just below the γ' -solvus) for 144000 sec subsequent to a furnace cooling from 1473 K (homogenizing) to 1133 K.

distinctive one, as illustrated in Fig. 1. In this figure, a number of pairs of parallel plates which are separated by a narrow crevice filled with γ -matrix, can be seen here and there in the matrix. The paired γ' -plates are in face-face configuration and the crevice between them is parallel to $\{100\}$. Such a pair of γ' -plates is considered to be formed by the split of a cuboidal γ' -particle during its growth, as follows: first, a rod of γ -matrix is formed near the center of the γ' -cuboid (see Fig. 2(a)); then the rod widens along one of the $\{100\}$ planes (see Fig. 2(b)); and finally, the rod reaches the side surface of the γ' -particle (see Fig. 2(c)), which results in the completion of the split into a pair of parallel plates, i.e., a doublet. This type of split is also observed in Ni-11%Ti, Ni-40%Cu-6%Si and Ni-18%Cr-5%Si alloys.

Figure 2 - TEM images of γ' -precipitates in Ni-12at.%Al alloy aged at 1133 K for 72000 sec subsequent to a furnace cooling from 1473 K to 1133 K, illustrating the progressive split of a single cuboid into a doublet.

Figure 3 - TEM image of the groups of eight γ' -cuboids in Ni-12at.%Si alloy aged at 1103 K (just below the γ' -solvus) for 72000 sec subsequent to a furnace cooling from 1473 K (homogenizing) to 1103 K.

When the Ni-12%Si alloy is aged at 1103 K (just below the γ' -solvus) subsequent to a furnace cooling from 1473 K (homogenizing) to 1103 K, another type of distinctive shape-change occurs in the cuboidal γ' -particles which are sparsely and randomly distributed, as illustrated in Fig. 3. Although each of the unit assemblies of γ' -particles distributed here and there in the γ -matrix is viewed to be a group of four cuboids, TEM observations of many foil specimens whose faces are not parallel to $\{100\}$ show that the unit assembly is really a group of eight cuboids, i.e., an ogdoad. It can be considered from Fig. 4 that such a unit assembly is formed by the split of a single γ' -cuboid into eight small cuboids, as follows: first, the center of each side surface of a γ' -cuboid, i.e., $\{100\}$, is depressed by the γ -matrix (see Fig. 4(a)); then the depression (γ -matrix) extends towards the center

Figure 4 - TEM images of γ' -precipitates in Ni-12at.%Si alloy aged at 1103 K for 36000 sec subsequent to a furnace cooling from 1473 K to 1103 K, illustrating the progressive split of a single cuboid into eight small cuboids.

Figure 5 - TEM images of γ' -precipitates in Ni-7at.%Si-7at.%Al alloy aged at 1273 K (just below the γ' -solvus) for 14400 sec (a) or for 21600 sec (b) subsequent to a furnace cooling from 1523 K (homogenizing) to 1273 K. The γ' -particles remain spherical and never split into plural particles.

of the cuboid and simultaneously widens along $\{100\}$ (see Fig. 4(b)); and finally, a group of eight cuboids is formed. This type of split is also observed in Ni-10%Al-4%Si and Ni-8%Al-5%Ti alloys.

The phenomena of splits mentioned above take place only when the volume fraction and hence the density of γ' -particles keep low. All the γ' -particles that are sparsely and randomly distributed in the γ -matrix, however, do not split into plural particles. When the Ni-7%Si-7%Al alloy is aged at 1273 K (just below the γ' -solvus) immediately after a furnace cooling from 1523 K (homogenizing) to 1273 K, the spherical γ' -particles appear and grow in the γ -matrix (see Fig. 5(a)). During the growth of the particles by further ageing at 1273 K, the particles remain spherical and never split into plural particles, as illustrated in Fig. 5(b). In the case of the Ni-20%Cr-10%Al alloy also, the γ' -spheres never split into plural particles.

Explanation of the Split on the Basis of a Microelasticity Theory

Judging from the usual conception that the shape of the individual γ' -particles can theoretically be explained by the sum of the elastic strain energy E_{str} and the surface energy E_{surf} , it is improbable that a single precipitate particle should split into plural small particles because of a remarkable increase in the E_{surf} . Such an extraordinary phenomenon of split, however, can be explained by introducing the following concept, which opposes the usual conception widely recognized: the elastic interaction has a remarkable effect on the shape of the individual γ' -particles. In this section, the above conception newly introduced will be examined by applying a microelasticity theory to the cases of the splits in the Ni-Al and the Ni-Si alloys.

In the case of the Ni-Al alloy, the following two things are assumed: (i) there exists a γ' -particle (volume V) which is a single inhomogeneous ellipsoid of revolution in an infinite γ -matrix which is elastically anisotropic; (ii) the single γ' -particle splits into two small ellipsoidal γ' -particles (volume $V/2$). The total energies for the states before and after the split. i.e., $E^{(1)}$ and $E^{(2)}$, respectively, can be expressed by the following two equations:

$$E^{(1)} = V \cdot E_{\text{incl}}(P) + S(P) \cdot \gamma_s \quad (2)$$

and

$$E^{(2)} = 2 \cdot \frac{V}{2} \cdot E_{\text{incl}}(P) + 2 \cdot S'(P) \cdot \gamma_s + E_{\text{int}}^{\alpha\beta}(P), \quad (3)$$

where P is the aspect ratio of the ellipsoid; $E_{\text{incl}}(P)$ the elastic strain energy of the ellipsoid; $S(P)$ and $S'(P)$ the surface areas of the ellipsoids before and after the split, respectively; γ_s the surface energy density of the ellipsoid; $E_{\text{int}}^{\alpha\beta}(P)$ the elastic interaction energy between the two ellipsoids formed by the split. According to the theoretical basis explained in our previous paper (9), the values of $E^{(1)}$ and $E^{(2)}$ can be calculated. The numerical values of the eigen strain (stress free strain) e^{T*} , i.e., γ/γ' lattice misfit δ ($\delta = (a_{\gamma'} - a_{\gamma})/a_{\gamma}$, where $a_{\gamma'}$ and a_{γ} are the lattice parameters of γ' -precipitate and the γ -matrix, respectively), the γ_s and the elastic constants of γ -matrix and γ' -precipitate, i.e., C_{ij} and C_{ij}^* , respectively, are necessary for the calculations. The values used here are as follows (as regards the source of each value, refer to (9)): $e^{T*} = 0.00563$; $\gamma_s = 0.0142 \text{ J/m}^2$; $C_{11} = 11.24 \times 10^4 \text{ MN/m}^2$, $C_{12} = 6.27 \times 10^4 \text{ MN/m}^2$, $C_{44} = 5.69 \times 10^4 \text{ MN/m}^2$; $C_{11}^* = 16.66 \times 10^4 \text{ MN/m}^2$, $C_{12}^* = 10.65 \times 10^4 \text{ MN/m}^2$, $C_{44}^* = 9.92 \times 10^4 \text{ MN/m}^2$.

In the case of the Ni-Si alloy, it is assumed that a γ' -particle (volume V) which is a single inhomogeneous ellipsoid of revolution exists in an infinite γ -matrix which is elastically anisotropic and the single γ' -particle splits into eight small ellipsoidal γ' -particles (volume $V/8$). In this case also, the total energy before the split can be expressed by Eq. (2). The energy state after the split, i.e., $E^{(8)}$, is expressed as follows (10):

$$E^{(8)} = 8 \cdot \frac{V}{8} \cdot E_{\text{incl}}(P) + 8 \cdot S''(P) \cdot \gamma_s + E_{\text{int}}^{(8)}(P), \quad (4)$$

where $S''(P)$ is the surface area of the individual ellipsoids after the split; $E_{\text{int}}^{(8)}(P)$ the elastic interaction energy between the eight ellipsoids formed by the split. The numerical values of the e^{T*} and the γ_s used for the Ni-Si alloy are -0.0030 and 0.0111 J/m^2 , respectively (11). The values of C_{ij} and C_{ij}^* for the Ni-Al alloy are used in place of those for the Ni-Si alloy because the values of them at the ageing temperature, i.e., 1103 K, have not been known. Although the use of such approximate values may rise some uncertainties in the energy states calculated, the stable shape thus predicted is not replaced by such other shapes as are to be predicted otherwise (12).

In the case of the Ni-Al alloy, the $E_{\text{int}}^{\alpha\beta}(P)$ is calculated for the doublet as two-body problem. In the case of the Ni-Si alloy, however, the approximate value of the $E_{\text{int}}^{(8)}$ can only be calculated because of the many-body problem. The total sum of the respective elastic interaction energies which are calculated for every different pairs taken from the eight particles is to be regarded as the approximate value of the $E_{\text{int}}^{(8)}$ (10).

According to the procedures hereinbefore mentioned, the changes in the energy state of γ' -particles before and after the splits are calculated for the Ni-Al and the Ni-Si alloys, and the results are illustrated in Fig. 6. The abscissa of each figure indicates the size of the single γ' -particle before the split. It can be seen from Fig. 6(a) that the $E^{(1)}$ is lower than

Figure 6 - Comparisons between the energy states of γ' -precipitates before splits ($E^{(1)}$) and after splits ($E^{(2)}$, $E^{(8)}$). $E^{(2)}$ or $E^{(8)}$ becomes lower than $E^{(1)}$ with increasing the particle size, which results in the split. It is the elastic interaction that makes the energy states lowered (e.g., $D \rightarrow D'$) by overcoming the increase in surface energy (e.g., $D \rightarrow D''$).

the $E^{(2)}$ when the particle size is small but that the $E^{(2)}$ decreases below the $E^{(1)}$ with increasing the particle size. This calculation indicates unquestionably that as the γ' -particle in the Ni-Al alloy grows, the energetically stable shape is changed from a single to a doublet. It is clear from Fig. 6(b) that the stable shape of the γ' -particle in the Ni-Si alloy is changed from a single to a group of eight small particles, i.e., an octad, as the particle grows. It is the elastic interaction that makes the total energy greatly decreased and hence causes the split. From the usual conception that only the sum of the E_{str} and the E_{surf} in Eq. (1) governs the shape of the individual γ' -particles (that is, the E_{int} is omitted), it follows that the total energy is remarkably increased by the increase in surface area (and hence in the E_{surf}) which accompanies the split; e.g., from D to D'' in Fig. 6(b). However, the elastic interaction really contributes to the determination of the stable shape of the γ' -particles, which results in the decrease in the total energy by overcoming the increase in the E_{surf} even if the split takes place; e.g., from D to D' in Fig. 6(b). It is fully convinced from the above that in order to decrease the total energy of the system, the γ' -particle does split into plural small particles when it grows to a certain size.

Classification of the Effects of Elastic Interaction on the Splits

The discussions in the preceeding section clearly indicate that whether the split occurs during the growth or not depends on the difference between the elastic interaction energy and the surface energy in magnitude. The phenomena of splits are assumed to be well arranged by introducing some parameters which are able to express such a difference. In fact, the phenomena of splits can well be arranged by using the parameter Δ which is the ratio of the density of elastic interaction energy to the γ_s (10). However, they can also be arranged successfully by introducing a new parameter Δ^* , which is the ratio of the γ/γ' lattice misfit δ to γ_s (i.e., $\Delta^* = \delta/\gamma_s$), as illustrated in Fig. 7. In this figure, the abscissa indicates the absolute value of Δ^* introduced in place of Δ , and the ordinate indicates the particle sizes at which the γ' -particles split (the sizes are experimentally obtained in the present studies). The introduction of Δ^* is considered to

Figure 7 - Relationship between the particle sizes at which the splits occur and the parameter Δ^* . The Δ^* is the ratio of γ/γ' lattice misfit δ to surface energy density γ_s ($\Delta^* = \delta/\gamma_s$) and has a distinctive advantage of the simplicity of predicting the morphology of γ' -precipitates.

be very suitable for arranging the effects of elastic interaction. Although there are no significant differences between the use of Δ and Δ^* , the Δ^* is by far the better of the two because the density of elastic interaction energy in the Δ cannot be calculated so easily (10).

It is clear from Fig. 7 that the effects of elastic interaction on the splits are grouped into the three categories as follows: (I) when the elastic interaction is weak, i.e., $|\Delta^*| < 0.2$, the γ' -precipitate remains spherical during the growth and never splits into plural particles; (II) when the elastic interaction is intermediate, i.e., $0.2 < |\Delta^*| < 0.4$, the single cuboidal γ' -precipitate splits into a group of eight small cuboids, i.e., an ogdoad; (III) when the elastic interaction is strong, i.e., $0.4 < |\Delta^*|$, the single cuboidal γ' -precipitate splits into a pair of parallel plates, i.e., a doublet. Furthermore, the size at which the split occurs becomes smaller as the elastic interaction becomes stronger, i.e., with increasing $|\Delta^*|$. The essentially same discussions as the above can be made by using the Δ , over which the Δ^* has a distinctive advantage in the practical use (10).

Prediction of the Morphology of γ' -Precipitates by Using the Δ^*

An interesting and valuable point which is evident from Fig. 7 is that the morphology of γ' -precipitates can easily be predicted only if the value of Δ^* is known. The lattice parameters of the γ' -precipitate and the γ -matrix, i.e., $a_{\gamma'}$ and a_{γ} , respectively, are obtained from the chemical composition of the alloy in question with the method proposed by Watanabe and Kuno (13). By using those values, the value of δ is given by the equation $\delta = (a_{\gamma'} - a_{\gamma})/a_{\gamma}$ and hence the value of Δ^* is obtained by the

Table III. Stress Rupture Properties of LRO26

Temperature (°F)	Stress (psi)	Life (hrs)	Elongation (%)	Reduction in Area (%)
1300	70,000*	576.0	7.2	8.1
1300	75,000**	298.4	5.7	14.3
1400	50,000	73.5	6.9	9.1
1400	50,000	68.1	5.2	8.0
1500	40,000	18.3	11.1	14.7
1500	40,000	16.7	9.7	15.5
1700	5,000	44.6	92.9	97.2
1700	5,000	109.9	51.8	92.4

* 503.5 hours at 50,000 psi before overloading.

** 266.2 hours at 58,000 psi before overloading.

Figure 8: SEM Photo of LRO26 room temperature fractures

Discussion

The feasibility of melting, atomizing to powder and consolidation of the LRO26 alloy to high density preforms presented no difficulty. Normal vacuum melting techniques were applied and only limited consolidation trials were necessary to achieve high density preforms. Fabrication by extrusion and hot rolling was accomplished with initially chosen hot working parameters. Ease of fabrication was attributed to the single phase fcc structure and high ductility.

Structural examination of the LRO26 material showed a uniform non-segregated fully austenitic (fcc) matrix with what appears to be small dispersed carbides and inclusions. Beside the three major elements (Co, Fe, V) the material contained substantial amounts of aluminum, titanium and silicon along with normal residuals of carbon, oxygen and nitrogen. The aluminum and titanium were intentional and aimed at keeping minor impurities out of the grain boundaries. The silicon was unintentional and the result of a high level in the ferro-vanadium. These additional elements may be responsible for the lower than anticipated critical temperature observed. More work on melt practice and residual elements appears warranted.

References

- (1) E. von Hornbogen, and M. Roth, "Die Verteilung kohärenter Teilchen in Nickellegierungen," Zeitschrift für Metallkunde, **58** (1967) pp. 842 - 855.
- (2) W. T. Loomis, J. W. Freeman, and D. L. Sponseller, "The Influence of Molybdenum on the γ' Phase in Experimental Nickel-Base Superalloys," Metallurgical Transactions, **3** (1972) pp. 989 - 1000.
- (3) A. Kelly, and R. B. Nicholson, "Precipitation Hardening," pp. 149 - 391 in Progress in Materials Science Volume 10, B. Chalmers, ed.; Pergamon Press, Oxford, 1963.
- (4) 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) pp. 1295 - 1309.
- (5) E. Seitz, and D. de Fontaine, "Elastic Interaction Energy Calculations for Guinier - Preston Zones in Al - Cu and Cu - Be," Acta Metallurgica, **26** (1978) pp. 1671 - 1679.
- (6) H. Yamauchi, and D. de Fontaine, "Elastic Interaction of Defect Clusters with Arbitrary Strain Fields in an Anisotropic Continuum," Acta Metallurgica, **27** (1979) pp. 763 - 776.
- (7) W. C. Johnson, and J. K. Lee, "Elastic Interaction Energy of Two Spherical Precipitates in an Anisotropic Matrix," Metallurgical Transactions A, **10A** (1979) pp. 1141 - 1149.
- (8) T. Miyazaki, H. Imamura, H. Mori, and T. Kozakai, "Theoretical and Experimental Investigations on Elastic Interactions between γ' -Precipitates in a Ni-Al Alloy," Journal Of Materials Science, **16** (1981) pp. 1197 - 1203.
- (9) T. Miyazaki, H. Imamura, and T. Kozakai, "The Formation of " γ' " Precipitate Doublets" in Ni-Al Alloys and Their Energetic Stability," Materials Science And Engineering, **54** (1982) pp. 9 - 15.
- (10) M. Doi, T. Miyazaki, T. Wakatsuki, and T. Kozakai, "The Effect of Elastic Interaction Energy on the Morphology of γ' -Precipitates in Ni-Based Alloys," to be published.
- (11) P. K. Rastogi, and A. J. Ardell, "The Coarsening Behavior of the γ' Precipitate in Nickel-Silicon Alloys," Acta Metallurgica, **19** (1971) pp. 321 - 330.
- (12) T. Miyazaki, K. Nakamura, and H. Mori, "Experimental and Theoretical Investigations on Morphological Changes of γ' Precipitates in Ni-Al Single Crystals during Uniaxial Stress-Annealing," Journal Of Materials Science, **14** (1979) pp. 1827 - 1837.
- (13) R. Watanabe, and T. Kuno, "Alloy Design of Nickel-Base Precipitation Hardened Superalloys," Transactions Of The Iron And Steel Institute Of Japan, **16** (1976) pp. 437 - 446.