Changes in precipitates and dispersed particles during heat treatment in a mechanically alloyed Ni base super alloy

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Abstract

Changes in precipitates and dispersed particles during heat treatments in *MA6000*, a mechanically alloyed oxide-dispersion strengthened (ODS) nickel base superalloy is studied. There are at least four kinds of particles in as-received *MA6000*. $M_{23}C_6$ type carbides dissolve before the onset of recrystallisation temperatures. The other more stable particles are Ti-rich particles, Y-Al and Y-Al-Zr particles. Ti-rich particles can exist temperatures in excess of 1160 ℃, but coarsening takes place relatively rapidly. The Y-Al and Y-Al-Zr particles are more thermally stable. Although they slightly increase in size during annealing, it is not clear whether this represents coarsening or reaction to form garnets.

There is no direct evidence that the coarsening of particles significant with regard to the onset of recrystallisation.

1. Introduction

It is reported that yttrium oxide in ODS alloys is not as stable as had originally anticipated [1,2,3]. Furthermore, it is expected to be found carbides, nitrides and oxides because the alloy contains many carbide, nitride and oxide forming elements [1]. It is, however, not certainly cleared that the effect of the changes in particles on recrystallisation. The purpose here is to investigate any changes in the size, the distribution and chemical composition of precipitates and dispersed particles as a function of the heat treatment, in order to clarify their effects on recrystallisation behaviour. Hence, the investigation focuses on comparisons of the microstructure before and after recrystallisation.

2 Experimental Method

The detailed alloy processing route is given elsewhere [5], the chemical composition (wt.%) is:

$$Ni\text{-}0.06C\text{-}14.96Cr\text{-}4.44Al\text{-}2.28Ti\text{-}1.97Ta\text{-}1.96Mo\text{-}3.91W\text{-}0.13Zr\text{-}0.08Si\text{-}1.49Fe\text{-}1.08Y_2O_3$$

Specimens were machined from the as-extruded and hot-rolled bar of only the 'intermediate' region within the cross-section of the bar (Fig.1). As noted in earlier research, the recrystallisation behaviour has so strong dependence on the specimen extracted regions, that specimens must be taken very carefully [5]. The specimens were heat treated using computer controlled resistance furnaces. A reproducible etch for metallographic data and carbon extracted replicas was obtained by the controlled etching using an mixture of $CuCl_2$/HCl/ethanol at 25 ℃ for 30 sec. Carbon extraction replicas were taken from the etched surfaces.

A transmission electron microscopy (TEM) with an energy dispersive X-ray analyser (EDX) was carried out to observe microstructure and carbon replicas, and to identify the chemical compositions of particles. X-ray diffraction of extracted phases was also carried out.

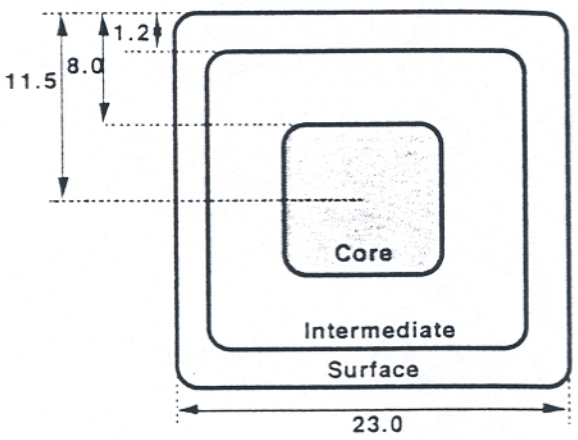

Fig. 1 Illustration of the surface, intermediate and core specimens extracted from as received *MA6000* bar.The extraction direction is normal to the plane of the diagram.

3. Results

3.1 As-received specimens

Examples of the EDX results from finer particles in as-received specimens are shown in Fig. 2. There are essentially four kinds of particles which can be distinguished by their chemistry and the X-ray diffraction analysis of extracted phases. They are; Type A: Cr-rich ($M_{23}C_6$ carbides), Type B: Ti-rich (TiC, TiN), Type C: Y-Al and Type D: Y-Zr-Al. (three kinds of mixed Y_2O_3-Al_2O_3 oxides; $Y_3Al_5O_{12}$, $Y_4Al_2O_9$, and $YAlO_3$ hexagonal).

Type A particles are typically several hundred nm in diameter, although a small number of finer (< 50 nm) particles could also be found. More than half of particles within the size range 50 - 200 nm were of type B. Approximately a quarter of the small particles (< 50 nm) are of type B, the rest being type C and D.

3.2 Continuous Heating Experiments

Type A particles were found in the specimens heated up to 1090 ℃ but not in specimens heated to higher temperatures. Types B, C and D particles were observed in all heat treated specimens (for example Fig. 3). TiC and TiN decreased changed to Ti(C,N) during heating. The garnets also changed giving the dominant yttrium containing phases as both hexagonal and perovskite $YAlO_3$, with lesser quantities of $Y_3Al_5O_{12}$, $Y_4Al_2O_9$.

A comparison of the size distributions before and after recrystallisation revealed that the number of the small particles decreased, but other size ranges were not significantly altered (Fig. 4).

Fig.2 Particles for the as-received specimen in a carbon extraction replica. Relative atomic percent ratio for the metallic elements in the marked particles are

A: $Cr_{80\text{-}90}$-$Mo_{5\text{-}10}$-$Ni_{5\text{-}10}$-$W_{5\text{-}10}$

B: $Ti_{90\text{-}95}$-$Cr_{0\text{-}5}$-$Ta_{0\text{-}10}$

C: $Y_{40\text{-}60}$-$Al_{40\text{-}60}$

D: $(Y\text{-}Zr)_{40\text{-}60}$-$Al_{40\text{-}60}$

Fig.3 Particles in a carbon extraction replica from the continuous heating experiment, at 1230 ℃ recrystallised and water quenched. Relative atomic percent ratio for the metallic elements in the marked particles are

B: $Ti_{90\text{-}95}$-$Cr_{0\text{-}5}$-$Ta_{0\text{-}10}$

C: $Y_{40\text{-}60}$-$Al_{40\text{-}60}$

D: $(Y\text{-}Zr)_{40\text{-}60}$-$Al_{40\text{-}60}$

3.3 Isothermal Annealing The annealing temperatures 1160 and 1180 ℃ are greater than the $M_{23}C_6$ dissolution temperature (≈1100 ℃), so that type A particles are absent. None of the heat-treatments produced even partial recrystallisation. Types B, C and D particles are found at all stages of the heat treatments. The particle size distributions in the isothermally annealed specimens are very different from the data for the continuously heated specimens, with clear evidence for particle coarsening (Fig. 5). However, no abnormal grain growth could be found even in specimens annealed for as long as 3000 min. at 1160 ℃, but the grain structures did coarsen (grain size is 1.0 μm). This is in spite of large changes in the particle size distributions.

Fig. 6 illustrates the fraction of Ti-rich particles within a particular size range (approximately 20 - 40 nm) as a function of annealing time. The fraction of Ti-rich particles gradually decreases with increasing time. From these results, it is concluded that another contribution forwards that drop in the number density of particles comes from the dissolution of small Ti-rich particles.

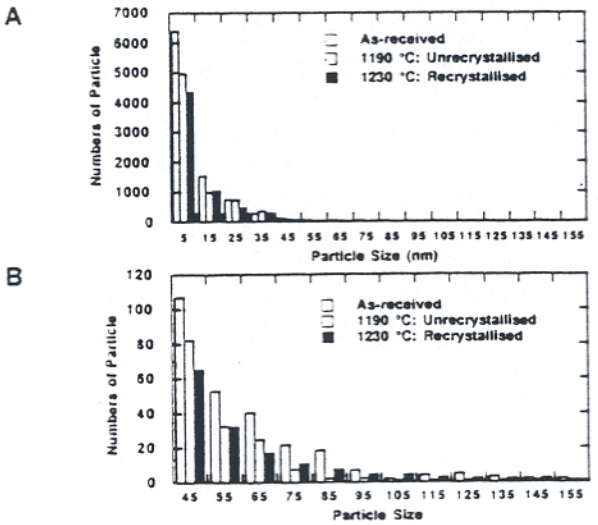

Fig.4 Comparison of particle distributions for the continuously heated specimens.
A: Number of particles as a function of particle size
B: Same as A, but detail of large size area.

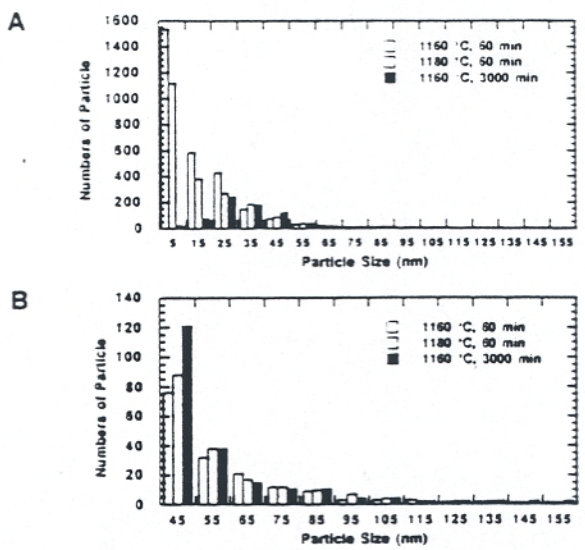

Fig.5 Comparison of particle distributions for the isothermally heated specimens.
A: Number of particles as a function of particle size
B: Same as A, but detail of large size area.

4. Discussion

Coarsening and dissolution take place during heat treatments, so that grain boundary pinning forces must decrease due to the heat treatment. The Zener pinning force P_r for particles of radius r is [5]:

$$P_p = C_1 V_M \sigma r \sum N_r \quad (4.1)$$

where C_1 is a constant whose magnitude depends on the details of the pinning process, r is the particle radius, V_M is the molar volume ($\approx 7.1\times10^{-6}$ m^3 mol^{-1}), and σ is the boundary energy per unit area. N_r is the number of particles per unit area which were measured from carbon replica TEM micrographs.[4]. The driving force for secondary recrystallisation ΔG_s is given by

$$\Delta G_s \approx V_M \sigma / R \quad (4.2)$$

where R is the average grain size of the recrystallised microstructure [5].

Calculations of P_p and ΔG_s were carried out using reasonable values of $C_1 = \pi$ and $\sigma = 0.6$ J m^{-2}, and using measured values of R and r. Measured N_r values are much greater than in reality because the extraction process exaggerates the number density. Therefore, only a comparison of trends can be done. Figs. 7 shows the results. The pinning force decreases rapidly but the driving force does not. The pining

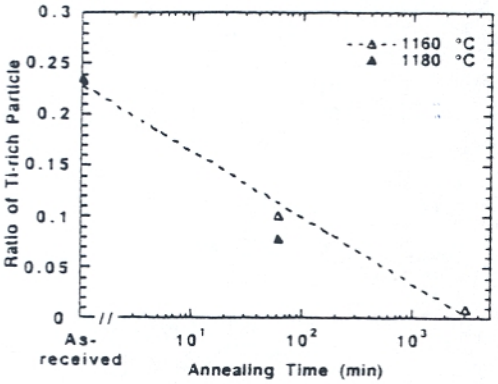

Fig.6 Fraction of Ti-rich particles within a particular size range (20 - 40 nm) as a function of annealing time, during isothermal heating experiments.

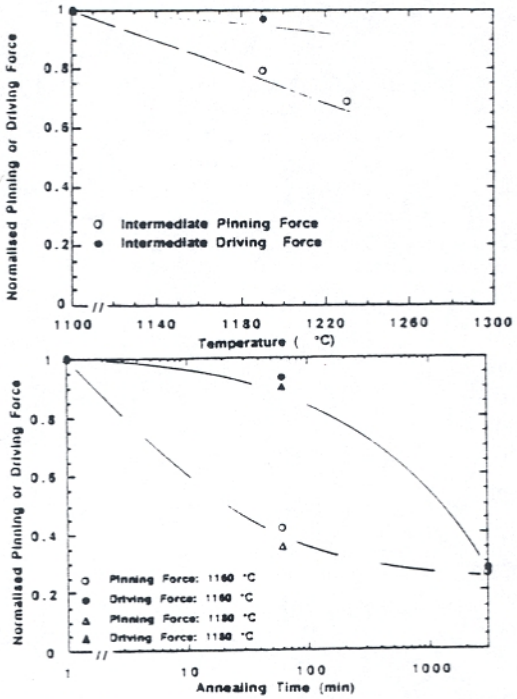

Fig.7 Pinning force and driving force for recrystallisation calculated using measured distributions and size. The pinning force and driving force of the as-received intermediate specimens are taken to be unity.
A: Continuous heating
B: Isothermal heating

force significantly decreases during isothermal annealing, but this does not stimulate recrystallisation.

For example, in the intermediate specimens, after annealing at 1160 ℃ for 60 min., the pinning force becomes much smaller but the sample nevertheless does not recrystallise.

5. Conclusions

There are at least four kinds of particles in as-received *MA6000*. $M_{23}C_6$ type carbides dissolve well before the onset of recrystallisation temperatures. The other more stable particles are Ti-rich particles, Y-Al and Y-Al-Zr particles. The Ti-rich particles are probably Ti(C,N) or mixed Ti(C,N) and Ta(C,N). Y-Al and Y-Al-Zr particles are in fact are of a variety of possible garnets. Ignoring $M_{23}C_6$, the rather larger (50-150 nm) particles are mainly Ti-rich and the smaller particles (< 50 nm) are mainly Y-Al or Y-Al-Zr. Ti-rich particles can exist temperatures in excess of 1160 ℃, but coarsening takes place relatively rapidly. The Y-Al and Y-Al-Zr particles are more thermally stable. Although they slightly increase in size during annealing, it is not clear whether this represents coarsening or reaction to form garnets.

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