Microstructural Evolution of β_2 (NiTi-based) / β' (Ni_2TiAl-based) Two Phase Quaternary Alloys

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Abstract

The microstructural evolution of β_2 (NiTi-based) / β' (Ni_2TiAl-based) two phase alloys has been investigated using transmission electron microscopy, atom probe field ion microscopy, and high-temperature X-ray diffractometry as a function of ageing time. The materials investigated are NiTiAlCr and NiTiAlMo quaternary alloys together with a NiTiAl ternary alloy as a reference. The materials showed supersaturated β_2 single phase microstructures after homogenisation heat treatment at 1200°C for 2hrs, and coherent cuboidal precipitation of β' phase at the early stages of the ageing treatment at 800°C (12mins). Further ageing caused precipitate coarsening and alignment followed by loss of coherence and coalescence (10 hrs for NiTiAlMo and 100hrs for NiTiAl at 800°C). The different rate of changes in morphology between the alloys investigated is discussed in terms of the partitioning behaviour of alloying additions and the resultant changes in lattice misfit.

1. Introduction

Over the last decade, intermetallics such as nickel aluminides and titanium aluminides have been intensively investigated for high temperature applications. However, the combination of good strength and good ductility, which nickel-base superalloys have, has generally been elusive in these intermetallics. Among intermetallics, a NiTi-based alloy having an ordered β_2 phase has reasonable ductility while Ni_2TiAl having the additionally ordered β' phase (Heusler structure) has very good mechanical strength. The crystal structures of the β_2 and β' phases are shown in Fig.1. Substitution of aluminium for a fraction of the titanium in a NiTi alloy can result in the formation of a two-phase NiTi - Ni_2TiAl microstructure. These two phases are expected to form a precipitation hardening system with both good mechanical strength and ductility, which is similar to the conventional fcc γ / $L1_2$ γ' structure of Ni-base superalloys.

The aim of this work is to investigate the microstructural evolution of NiTi-based β_2 / Ni_2TiAl -based β' two phase alloy systems as a function of ageing time. The effect of alloying additions, such as Mo and Cr, on the morphology change of this alloy system are discussed.

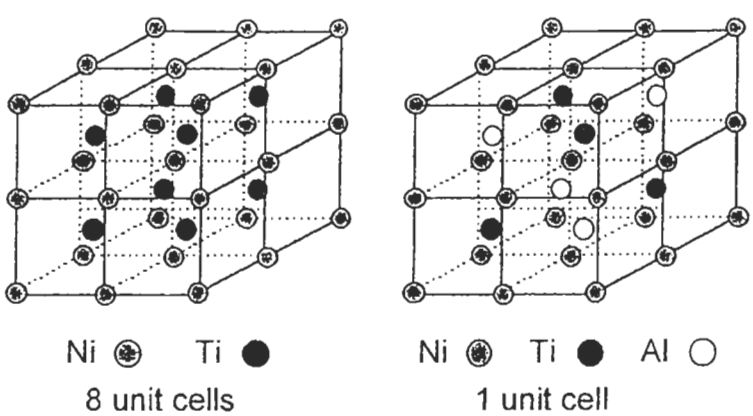

Fig. 1 Schematic illustration of the crystal structure of (a) β_2 and (b) β' phases

2. Experimental

The compositions of alloys investigated in this paper are listed in table 1. These compositions were chosen so that they would have NiTi-based β_2 / Ni_2TiAl -based β' two phase structure under equilibrium conditions. The Al content was chosen on the basis of preliminary mechanical tests reported previously[1]: for ternary $Ni_{50}Ti_{50-x}Al_x$ alloys, $Ni_{50}Ti_{43}Al_7$ has a high yield stress yet still exhibits some ductility and is suitable for solution treatment and precipitation hardening.

Bulk samples were solution heat treated in Ar-sealed quartz tubes at 1200°C for 2hrs and air cooled. These samples were then sectioned for further ageing in Ar-sealed quartz tubes at 800°C for 12mins and 30mins followed by water quenching, and for 1hr, 10hrs and 100hrs followed by air cooling in order to investigate the change in microstructure as a function of ageing time. These heat treated samples were then examined using transmission electron microscopy (TEM) for the observation of microstructures, atom probe field ion microscopy (APFIM) for the determination of phase compositions, and high-temperature X-ray diffractometry (HTXRD) for the determination of lattice misfits between the β_2 and β' phases. The detailed procedure of HTXRD analysis will be described elsewhere.

TEM samples were prepared by mechanical grinding and twin-jet standard electropolishing using a 10% perchloric acid and 90% acetic acid elctrolyte at about 2°C with an applied voltage of around 30V. TEM studies were performed on a Philips CM200 microscope. For the observation of coherent precipitates at early stages, the dark field imaging technique was applied using the 1/4(111) $L2_1$ lattice reflection.

APFIM samples were prepared by a standard two step electropolishing using a 25% nitric acid and 75% methanol first stage solution and a 3% perchloric acid 97% 2-butoxyethanol second stage solution. APFIM analyses were carried out using an APFIM220 commercial instrument with a sample stage temperature of –243°C (30K) and a pulse fraction of 20%. In field ion microscopy, these coherent precipitates are imaged as bright rectangular regions as shown in fig.2. The phase composition analysis can be conducted either by selected area analysis on the basis of the field ion image such as fig.2, or random area analysis. In this study, the latter method was employed for ease of analysis.

Table 1 Composition of alloys investigated (in atomic %)

	Ni	*Ti*	*Al*	*Mo*	*Cr*
Alloy A	50	42.5	7.5	-	-
Alloy B	49	41.65	7.35	2.0	-
Alloy C	49	41.65	7.35	-	2.0

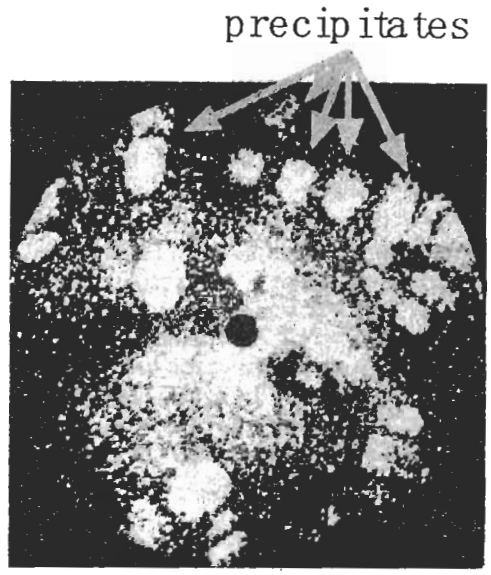

Fig. 2 Field ion micrograph of the NiTiAl-Cr alloy aged for 10hrs at 800°C, showing cuboidal precipitates indicated by arrows. Tip temperature = –243°C(30K), tip voltage = 17.5kV.

3. Results and Discussions

3.1 Microstructural Change as a Function of Ageing Time

TEM micrographs of the morphology of phase decomposition during ageing in the case of the Cr-bearing Alloy C are shown in fig.3. Solution treated material showed uniform fine scale mottling in bright field imaging (fig.3a). After slight ageing for 12mins at 800°C, the dark field image shows fine cuboidal precipitates about 3-5nm in size distributed throughout the matrix (fig.3b). After further ageing for 10hrs, the dark field image shows that the precipitates have coarsened, increasing to about 20nm in size(fig.3c). It is also noted that the precipitates have aligned to form orthogonal platelets on the {100}. After longer ageing for 100hrs the most platelet of precipitates have coalesced and become semi-coherent surrounded by a network of orthogonal dislocations with burgers vectors a_{NiTi}<100> (fig.3d) although some coherent precipitates 30-50 nm in size still remain

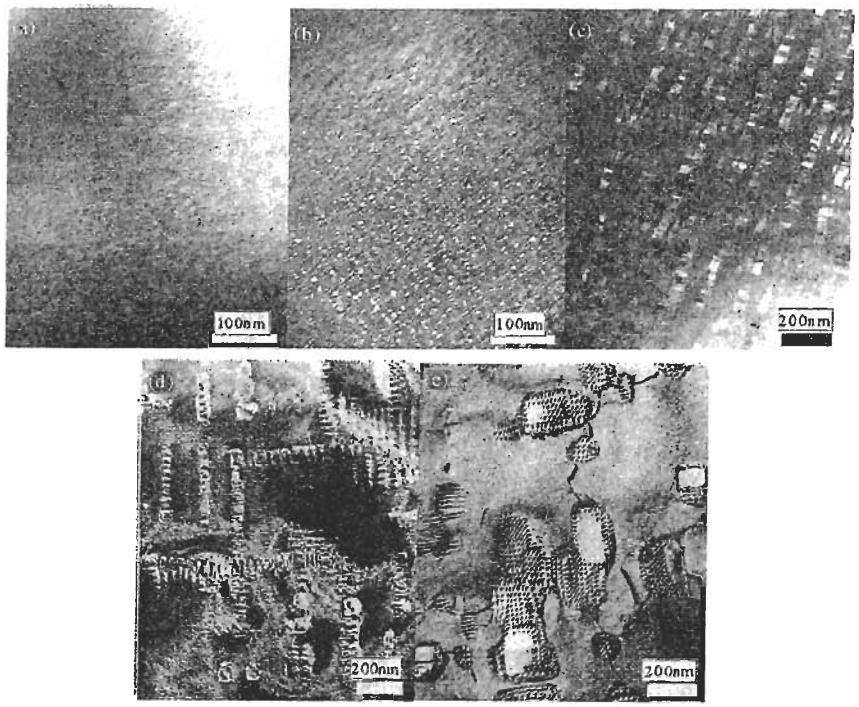

Fig. 3 Development of microstructural morphology during ageing at 800°C in the case of Alloy C. (a) solution treated (bright field) (b) aged 12min (1/4(111)L21 dark field) (c) aged 10hrs (1/4(111)L21 dark field) (d) and (e) aged 100hrs (bright field).

(Fig.3e).

The phase separation occurring during ageing at 800°C observed by TEM as shown in fig.3 can be described as

β_2 supersaturated solid solution $\rightarrow \beta_2 + \beta$'

where phase separation occurs by uniform nucleation and growth of β' precipitates throughout the β_2 matrix. The sequence in the development of morphology of the precipitates is the same in each alloy, however the precipitates in alloy A become semicoherent after 100hrs at 800°C whereas the precipitates in alloy B become semicoherent after only 10hrs at 800°C. It should also be noted that in alloy B, some unidentified precipitates 0.1 ~ 1μm in size were observed even in the as solution-treated sample, which suggests that the Mo content might have exceeded the solubility limit of the β_2 - β' two phase region. It is possible that these additional precipitates might have enhanced the coarsening of the β' precipitates.

3.2 β_2 / β' Composition Analysis

Compositional analysis was carried out using APFIM. The results for alloys A, B and C aged for 10hrs at 800°C are given in Table 2. The precipitates were analysed by random area analysis. For each heat treatment at 800°C, precipitates were clearly observed as distinct increase in the concentration of Al with a resultant decrease in the concentration of Ti. The concentration of Ni was also observed to decrease slightly at the larger precipitates. It is also shown that the alloying elements Mo and Cr both partition into the β_2 matrix.

Fig.4 shows the composition change in the β' precipitates in Alloy C as a function of ageing time. Although some fluctuations are observed, the concentration of each alloying element does not change from the earliest stage of precipitation. This result suggests that precipitation may occur by nucleation and growth rather than spinodal decomposition, however, further investigation will be required to fully elucidate the precipitation mechanism of this alloy system.

Table 2 Averages of atom probe analyses of phase compositions after 10h at 800°C

Alloy name	*Phase*	*Ni*	*Ti*	*Al*	*Mo*	*Cr*
Alloy A[2]	b_2	50.9	43.1	6.0	-	-
Alloy A[4]	b'	48.4	30.2	21.4	-	-
Alloy B	b_2	50.2	41.9	5.9	2.0	-
Alloy B	b'	44.2	34.2	20.9	0.7	-
Alloy C	b_2	48.5	43.6	6.0	-	1.9
Alloy C	b'	45.9	30.7	22.9	-	0.5

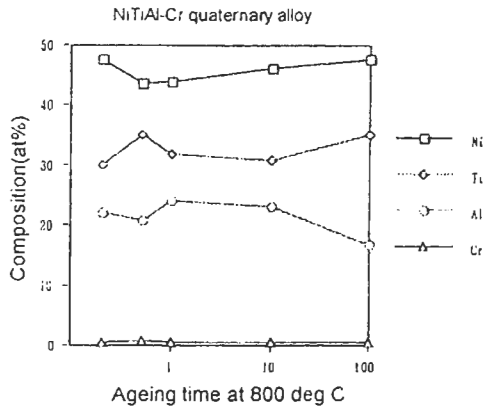

Fig. 4 Composition change of precipitates as a function of ageing time in Alloy C.

3.3 β_2 / β' Lattice Misfit

The lattice misfit between the two phases affects the microstructural evolution during ageing since the lattice misfit strain is a major contribution to the interface energy.
The lattice misfit is defined as

$$\Delta a = \frac{a_{precipitate} - a_{matrix}}{a_{matrix}}$$

Since the lattice misfit is a strong function of temperature, high temperature X-ray analysis was used to determine the lattice misfit at the ageing temperature of 800°C. This gave lattice misfits for the alloys A, B and C as roughly −1.53, −1.46 and −1.28% respectively. It is also possible to measure the lattice misfit from the spacing of interfacial dislocations round the semi-coherent precipitates. From the TEM observations at room temperature of the dislocation networks around precipitates in materials aged for 100hrs the lattice misfits of alloys A, B and C were calculated roughly as −1.65[2], −1.5 and −1.4%, respectively. Overall the HTXRD analysis and TEM observations showed good quantitative agreement. It is concluded that the lattice misfit at 800°C is smallest in Cr-bearing alloy C and largest in ternary alloy A. The small discrepancies may be attributed to the fact that the sample may not have reached equilibrium due to the relatively short holding time (12mins) at 800°C before HTXRD analysis.
From the HTXRD results, the change in lattice misfit is mainly caused by the change in the β_2 lattice parameters. Since the Cr atoms partition into the β_2 phase, it is expected that Cr atoms are likely to substitute for the Ti sublattice in the β_2 crystal structure. The addition of Cr atoms thus decreases the lattice parameter of the β_2 phase since Cr has smaller atomic radius than Ti. Accordingly, the negative lattice misfit was decreased. Mo is expected to have similar but less pronounced effect in reducing lattice misfit due to the larger atomic radius than Cr (Cr < Mo < Ti). Therefore the Cr-bearing alloy C has the smallest lattice misfit and maintains coherency for the longest ageing period. It is thus concluded that Cr addition is more effective in stabilizing the β' precipitates. However, the lattice misfit of −1.3 ~ −1.4% is still too large compared with that of γ / γ' Ni-base superalloys which usually have lattice misfits less than 0.5%. Increased amounts of Cr additions together with alloying additions of other elements should be attempted in order to reduce the lattice misfit further.

4. Conclusions

The microstructural evolution of β_2 / β' two phase alloys were investigated and the following results were obtained.

1. The sequence of precipitation is in the following order: β_2 supersaturated solid solution → cuboidal coherent precipitation of β' phase → semi-coherent precipitation of β' phase.
2. Both Mo and Cr have preference to partition into the β_2 matrices in this study.
3. The lattice misfit is smallest in the NiTiAlCr alloy. The NiTiAl-Mo comes next and NiTiAl ternary alloy has the largest lattice misfit.
4. NiTiAl-Mo alloy started losing coherency after 10hrs ageing at 800°C while NiTiAlCr alloy still maintained coherency. This is partly caused by the larger lattice misfit of Mo bearing alloy and partly because excessive addition of Mo over the solubility limit. It is thus expected that Cr addition is more effective in improving the mechanical properties of this alloy system.
5. The composition of precipitates doesn't change from the early stage of precipitation, to the semi-coherent coarsening, which suggests that precipitation might occur by nucleation and growth rather than spinodal decomposition.

Acknowledgments

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References

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