Study on the Precipitation Strengthening in Ni-Al-Cr Alloy System†

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Transmission electron microscopic investigation has been performed concerning the effect of precipitation on the mechanical properties in Ni₃Al- and NiAl-based intermetallics containing various types of fine precipitates. In an L1₂-ordered Ni₃Al alloy with 4 mol. % of chromium and 0.2-3.0 mol % of carbon, fine octahedral precipitates of M₂₃C₆ type carbide, which has the cube-cube orientation relationship with the matrix, appear during aging. Typical Orowan loops are formed in Ni₃Al containing fine dispersions of M₂₃C₆ particles. On the other hand, B2-ordered NiAl hardens appreciably by the precipitation of coherent α -Cr particles. By aging at temperatures around 973 K after solution annealing, fine spherical precipitates appeared homogeneously in the NiAl matrix. The selected area electron diffraction patterns have not revealed any additional extra-spots during aging, because the α -Cr particles have cube-cube orientation relationship and keep perfect coherency with the ordered matrix lattice. Dislocations bypass the particles during deformation. Although the dispersion of α -Cr particles increases the yield strength of NiAl at intermediate temperature, the strength decreases appreciably higher temperatures.

Keywords: L1₂-ordered Ni₃Al, B2-ordered NiAl, Cube-cube orientation relationship, Precipitation.

INTRODUCTION

Much work has been performed to improve the ductility of intermetallics since the finding of the drastic effect of boron to the ductility of Ni₃Al¹. The ductility of intermetallics could also be improved by macrostructural or microstructural control through optimization of chemical compositions, heat treatments or processing. However, it is known that many of the ductilization methods often sacrifice the high temperature strength of the material².

Studies have revealed that the creep strengths of monolithic intermetallics are inferior to advanced single crystal nickel-base superalloys³⁻⁵. Although the intermetallics based on the L1₂-ordered structure are attractive as high temperature structural materials because of their positive temperature dependence of yield strength, "the creep strength anomaly" does not exist in these intermetallics⁴. Large grained B2-ordered NiAl is known to be brittle at room temperature and to have poor creep strength at high temperatures⁵. For NiAl, significant improvements in creep strength were first demonstrated by forming a two phase mixture of NiAl and Ni₂AlTi (Heusler phase), although this mixture is still extremely brittle at room temperature⁶. Therefore, it has been proposed that optimizing

the multi-phase microstructures is necessary to achieve a balance of ductility and high temperature strength. This requires a balance of the compositions of the existing phases, the precipitate volume fraction and the size and distribution of the precipitates by analogy to, for example, the nickel-base superalloys.

The objective of the present work is to investigate various possibilities of precipitation strengthening of Ni₃Al- and NiAl-based alloys and to compare the behaviour of dislocations in these materials.

EXPERIMENTAL

The alloys used in this investigation were materials of 99.9 % Ni, 99.99 % Al and 99.8 % Cr. Carbon was supplied using consolidated Cr₃C₂ of 99.9 % purity. Each alloy button was weighing 30 g. Since weight losses were generally less than 0.15 %, the alloy compositions were considered to be equal to their nominal compositions. Designation of the alloys was based on the chemical composition of each alloy. The ingots were solution annealed at 1563 K for 260 ks (72 h) for NiAl compounds and at 1423 K for 260 ks (72 h) for Ni₃Al compounds in silica capsules. Specimens of 3 mm × 3 mm ×

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53 mm were cut from the ingots and solution annealed for 3.6 ks at 1563 K additionally to obtain maximum super-saturation.

The hardness variations during aging were measured using a micro-Vickers hardness tester. Thin plates of about 0.3 mm thick for transmission electron microscope (TEM) observation were cut from the aged specimens.

RESULTS AND DISCUSSION

Hardness variation during aging: Fig. 1(a-b) show the variation of the Vickers micro-hardness of 72Ni24Al14Cr containing 0.2, 0.5, 1.0, 2.0 and 3.0 mol % of carbon by aging at 973 K (a), 923 and 1073 K (b) after quenching from 1423 K. It should be noted that the variation of hardness is largest for 0.2 and 0.5 mol % carbon doped alloys. It can also be seen that as the content of carbon is larger, the increment of hardness is smaller. This may be explained by considering the strong solid solution hardening for the high carbon containing alloy because a drop in hardness occurs dramatically during aging. According to the reported phase diagrams⁷, the maximum solid solubility of Cr in NiAl is approximately 8 mol % at the eutectic temperature of 1445 K. However some undissolved Cr particles were observed in the NiAl containing 8 mol % of Cr. Fig. 2(a-b) show the variation of hardness of NiAl with different Cr contents during aging at 973 and 1073 K, respectively. The amount of hardening is larger in NiAl containing higher amount of Cr and small in NiAl in which the equal amounts of Ni and Al are replaced by Cr. Greater hardening is obtained in NiAl in which Ni is replaced by Cr.

Fig. 1. Variation of microhardness of Ni₂₄Al₁₄Cr containing 0.2, 0.5, 1.0, 2.0 and 3.0 mol.% of carbon by aging at (a) 973 K, (b) 923 K and 1073 K after quenching from 1423 K

Aging structure: Huetter and Stadelmaier⁸ showed that there is considerable solubility of carbon in Ni₃Al. When the carbon atoms occupy the octahedral interstices of Ni₃Al, it represents the cubic perovskite of Ni₃AlC. The degree of carbon stoichiometry is not unity but $x = 0.29$ when the stoichiometry is expressed in terms of Ni₃AlC _{x} ⁹. Therefore it can be said that the solid solubility of carbon in Ni is 4.8 mol % of aluminum is included in nickel. This solubility is a little higher than the solubility of carbon in nickel without aluminum, which has been reported to be around 2.5 mol % at the eutectic temperature⁹.

Fig. 3(a) shows the microstructure of the Ni₂₄Al₁₄Cr_{0.5}C (mol %) alloy aged at 973 K for 1.08 Ms (300 h). The corresponding selected-area electron diffraction pattern shown in

Fig. 2. Variation of hardness of NiAl-Cr by aging at 973-1173 K after quenching from 1423 K

Fig. 3. Transmission electron micrographs of Ni₂₄Al₁₄Cr_{0.5}C. Alloy aged at (a) 973 K for 1.08 Ms (300 h) and (b) 1073 K for 108 ks (30 h) showing the precipitation of M₂₃C₆ carbide

Fig. 3 indicates that the precipitate is not a perovskite-type carbide but an M₂₃C₆-type carbide and has the orientation relationship (100)-M₂₃C₆ parallel to [100]- γ and [001]-M₂₃C₆ parallel to [001]- γ with a lattice parameter of about 1.06 nm which is approximately three times as large as that of Ni₃Al⁹. By aging at higher temperatures or for longer periods, the precipitates grow into rods lying parallel to $\langle 100 \rangle$ of the matrix as shown in Fig. 3(b). Fig. 4 shows the high resolution

Fig. 4. High resolution electron micrograph of $M_{23}C_6$ carbide formed by aging at 973 K for 360 ks (100 h). BD = [110]

image of the interface between the $M_{23}C_6$ precipitate and the matrix observed along the [110] direction of the matrix.

It can be seen that an almost perfect matching of {111} planes of the matrix and $M_{23}C_6$ is kept at the interface as proposed by Beckitt and Clark¹⁰ for $M_{23}C_6$ in a stainless steel.

Fig. 5(a-b) show the precipitates formed in $Ni_{42}Al_8Cr$ aged at (a) 973 K for 3.6 ks (1 h/peak-aged) and (b) at 1223 K for 360 ks (100 h), respectively, after quenching from 1563 K. Precipitation of α -Cr particles occurs quickly even during quenching from 1563 K to iced-brine. By aging at higher temperatures, the binodal distribution of α -Cr particles disappears as shown in (b). The corresponding SAED pattern taken from the [100] lattice direction of the matrix is shown in Fig. 5(c).

Fig. 5. Transmission electron micrographs of precipitates in $Ni_{42}Al_8Cr$ aged at (a) 973 K for 3.6 ks (1 h) and (b) 1223 K for 360 ks (100 h) with the corresponding selected area electron diffraction pattern (c) taken from [100] lattice direction of the B2-NiAl matrix

Fig. 6 shows a high resolution image of the interface between the α -Cr precipitate and B2-ordered NiAl in $Ni_{44}Al_6Cr$ aged at 973 K for 360 ks (100 h).

Fig. 6. High resolution electron micrograph of $Ni_{44}Al_6Cr$ aged at 973 K for 360 ks (100 h)

High temperature strength: Fig. 7 shows the temperature dependence of the yield stress of polycrystalline $Ni_{24}Al_4Cr_{0.5}C$ solution annealed at 1423 K for 260 ks (72 h) and aged at 973 K for 1.08 Ms (300 h/peak aged). For comparison, the temperature dependence of the yield stress of polycrystalline $Ni_{19}Al_4Cr$ with and without carbon doping, annealed at 1423 K for 260 ks (72 h) and tested under the same condition is also shown. In Fig. 7 the data of the temperature dependence of the yield stress of binary Ni-24.1 %Al alloy polycrystals obtained by Noguchi *et al.*¹¹ is also shown for comparison. It is obvious that the strength of the alloy containing $M_{23}C_6$ carbide is higher than those of the precipitate-free alloys over the whole temperature range investigated.

Fig. 7. Temperature dependence of the yield stress of polycrystalline $Ni_{24}Al_4Cr$, $Ni_{24}Al_4Cr_{0.5}C$, $Ni_{19}Al_4Cr$ and $Ni_{19}Al_4Cr_{0.5}C$ alloys aged at 973 K for 1.08 Ms (300 h) after solution annealed at 1423 K for 260 ks (72 h)

The strength of B2 compound strongly depends on the composition¹²⁻¹⁴. Pascoe and Newey¹⁴ investigated the deformation behaviour of polycrystalline binary NiAl of various compositions and revealed strong temperature dependence of the yield stress typical alloys. The strength as well as the temperature dependence changed largely by changing the stoichiometry of NiAl. The minimum strength is obtained at the stoichiometric composition and the deviation from stoichiometry increases the strength of NiAl.

Fig. 8 shows the temperature dependence of the yield strength of Ni₄₂Al₈Cr with various aging conditions. For comparison, the temperature dependence of the monolithic NiAl with different stoichiometry is shown in the figure. The strength of NiAl-Cr decreases gradually with increasing temperature and approaches to the strength level of monolithic NiAl with non-stoichiometry.

Fig. 8. Temperature dependence of compressive yield strength of NiAl-Cr. Data for the binary NiAl are included

Dislocation-particle interaction: Fig. 9 shows $g = 220$ weak beam dark field image of the deformation induced dislocations in Ni₂₄Al₄Cr_{0.5}C aged at 973 K for 1.08 Ms (300 h) and deformed about 3 % at 573 K. Straight dislocations lying parallel to the $[ps10\ 220]$ direction of the matrix are screw in nature. It is evident that the dislocations bypass the carbide particles leaving loops surrounding them. Fig. 10 shows a dislocation introduced by 3 % deformation of the same alloy at 1173 K. We can see immediately a different morphology of dislocations from that observed at lower deformation temperatures.

Fig. 11 is a $g = 002$ dark field weak-beam image of dislocations in Ni₄₂Al₈Cr aged at 973 K for 1.08 Ms (300 h) and deformed 3 % in compression at 1173 K. The α -Cr particles should have grown during testing, since the testing temperature is higher than the aging temperature. The present observation is in contrast to the case of Ni₃(Al,Ti) with

Fig. 9. Dark field micrograph showing the Orowan bypassing process in Ni₂₄Al₄Cr_{0.5}C aged at 973 K for 1.08 Ms (300 h) and deformed 3 % at 573 K

Fig. 10. TEM weak-beam image showing the dislocation attracted to the interface. The specimen was aged at 973 K for 1.08 Ms (300 h) and deformed 3 % at 1173 K

Fig. 11. Dark field image of dislocations in Ni₄₂Al₈Cr aged at 973 K for 1.08 Ms (300 h) and deformed 3 % in compression at 1173 K

disordered g dispersoids¹⁵, where dislocations cut through the dispersoids at any stage of aging and to the case presented by Arzt *et al.*^{16,17}, where the dislocation surmounts the dispersoid by climb and adheres to the departure side of the dispersoid.

Fig. 12 is a bright field image of dislocations in Ni₄₂Al₈Cr aged at 1173 K for 1.08 Ms (300 h) and deformed 3 % at 1173 K. Pairs of dislocation loops marked by arrows seems to be formed by bypassing involving cross-slip at the particles¹⁸.

It is presumed that the modulus hardening might make the most important contribution to the strengthening of NiAl with α -Cr particles. It is therefore unable to estimate the shear modulus from bulk crystals. The NiAl-Cr system should be one of the ideal case to test the modulus hardening theories since the shear moduli of α -Cr and β -NiAl are already known. The absence of the attractive interaction between the particles

Fig. 12. Dislocations in Ni₄₂Al₈Cr aged at 1173 K for 1.08 Ms (300 h) and deformed 3 % at 1173 K

and dislocations might explain the serious loss of strength of NiAl-based intermetallics with increasing temperatures.

Conclusion

M₂₃C₆ precipitates nucleate in the matrix and also at the dislocations as octahedral bounded by {111} interfaces. The shape of the precipitates is not always equilateral, but tetragonal or elongated octahedral ones appear during aging. After prolonged aging or by aging at higher temperatures, the precipitates adopt a rod-like morphology elongated parallel to the <100> directions and HRTEM revealed that a nearly perfect coherency is retained between the M₂₃C₆ and matrix lattices at their interface. Typical age-hardening and over age softening occurs by the fine precipitation of α -Cr in NiAl by aging after

quenching from higher temperatures. Dislocations by pass the particles during high temperature deformation. Attractive interaction has not been detected at α -Cr dispersoids in NiAl.

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