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Cobalt-Base High-Temperature Alloys

J. Sato, T. Omori, K. Oikawa, I. Ohnuma, R. Kainuma, K. Ishida*

We have identified cobalt-base superalloys showing a high-temperature strength greater than those of conventional nickel-base superalloys. The cobalt-base alloys are strengthened by a ternary compound with the $L1_2$ structure, γ' $Co_3(Al,W)$, which precipitates in the disordered γ face-centered cubic cobalt matrix with high coherency and with high melting points. We also identified a ternary compound, γ' $Ir_3(Al,W)$, with the $L1_2$ structure, which suggests that the Co-Ir-Al-W–base systems with $\gamma + \gamma'$ $(Co,Ir)_3(Al,W)$ structures offer great promise as candidates for next-generation high-temperature materials.

Cobalt and nickel have the face-centered cubic (fcc) structure at high temperature, with melting points of 1768 and 1728 K, respectively. However, the most fascinating heat-resistant alloys are the Ni-base superalloys, which are used, for example, in aircraft engines, industrial gas turbines, reactors, and the chemical industry (*1*). The main reason why Co-base alloys have not found widespread usage is their lower strength compared with that of Ni-base alloys, but they have been studied for a long time (*2*). With the development of Ni-base superalloys strengthened by the ordered γ' $Ni_3(Al, Ti)$ phase, the possibilities of precipitation hardening using geometrically close-packed phases that have the form of A_3B have been extensively investigated. Two types of geometrically close-packed phases have been reported in Co-base alloys: Co_3Ti with the $L1_2$ structure (*3*, *4*) and ordered fcc Co_3Ta (*5*, *6*). Although the effect of various alloying elements on the stability and morphology of the γ' Co_3Ti phase has been investigated, the usefulness of the γ' phase is restricted to temperatures below 1023 K (*4*). In the case of Co_3Ta, the ordered fcc phase is metastable and readily converts to the stable hexagonal close-packed (hcp) structure Co_3Ta (*6*). Furthermore, the lattice parameter mismatches of these phases in Co-base alloys are usually more than 1.0%, which is not as useful for strengthening as the geometrically close-packed phases in Ni-base superalloys, where mismatches typically vary from –0.1 to + 0.5% (*2*). Geometrically close-packed phase strengthening has thus not been used in commercial Co-base superalloys.

In determining the phase diagram of the Co-Al-W ternary system, we found a stable ternary compound with the $L1_2$ structure, which has the form $Co_3(Al, W)$, designated as γ'. Figure 1A shows a transmission electron micrograph of Co-9Al-7.5W (atomic %) annealed at 1173 K for 72 hours after solution treatment at 1573 K for 2 hours. The cuboidal phase homogeneously precipitates in the γ(A1) matrix, which is very similar to the morphology observed in Ni-base superalloys. The selected area electron diffraction pattern of the same sample is also shown in Fig. 1B, where the crystal structure of the γ' phase is confirmed as being the $L1_2$ ordered structure and the cuboidal γ' precipitates align along the <001> directions. The compositions of the matrix and that of the precipitate were determined using a field emission electron probe microanalyzer (FE-EPMA). The composition of cuboidal precipitates observed in Fig. 1A is the ternary compound $Co_3(Al,W)$, where the composition of Al and W has an almost equiatomic ratio. In the geometrically close-packed A_3B compound, the stable Co_3W phase with the DO_{19} structure appears in the Co-W binary system (*7*). Although no stable compound of Co_3Al is formed in the Co-Al binary system, the formation of an ordered Co_3Al phase has been reported (*8*, *9*). Recently, the metastable Co_3Al phase with the $L1_2$ structure, which is formed in the Co-14Al alloy annealed at 873 K for 24 hours, was observed by our group (*10*). It can be said, therefore, that metastable Co_3Al γ' is stabilized by alloying with W. Ternary compounds of $Co_3(Al, Cr)$ or $Co_3(Al, Mo)$ have not been reported.

Figure 2, A and B, show isothermal section diagrams determined experimentally in the present study, as well as recent data (*11*) on the Co-W binary system at 1173 and 1273 K, respectively. The γ' phase is stable at 1173 K but metastable at 1273 K. The thermal stability of the γ' phase and the effect of alloying were investigated by differential scanning calorimetry (DSC). Figure 3A shows the DSC curves on heating, where the solvus temperature was determined from the endothermic peak, as indicated by arrows. The DSC curve of Waspaloy [Ni-21Cr-2.5Mo-13Co-2.9Al-3.5Ti-0.3C (atomic %)], a widely used commercial Ni-base superalloy, is also shown. The solvus temperatures of the γ' phase in the Co-Al-W ternary system is ~1263 K, which corresponds well with the phase diagram, as shown in Fig. 2. The addition of Ta stabilizes the γ' phase such that the solvus temperature is ~1373 K, and this value is higher than that of Waspaloy.

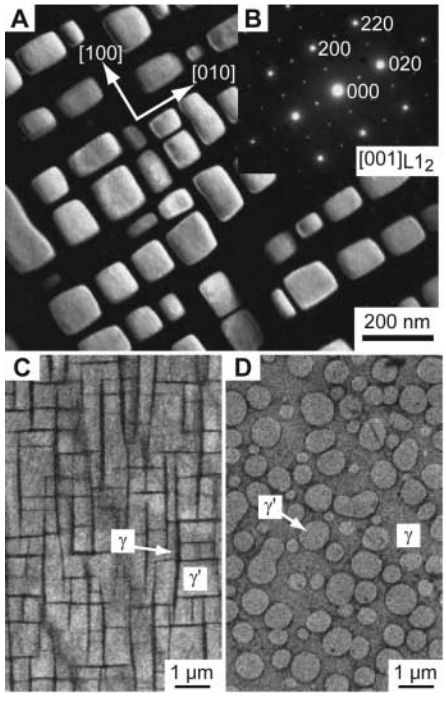

Fig. 1. Electron micrographs of Co-9Al-7.5W alloy annealed at 1173 K for 72 hours. (**A**) Dark-field image. (**B**) Selected area diffraction pattern. (**C** and **D**) Field emission scanning electron micrographs of Co-8.8Al-9.8W-2Ta (C) and Co-8.8Al-9.8W-2Mo (D) annealed at 1273 K for 1 week.

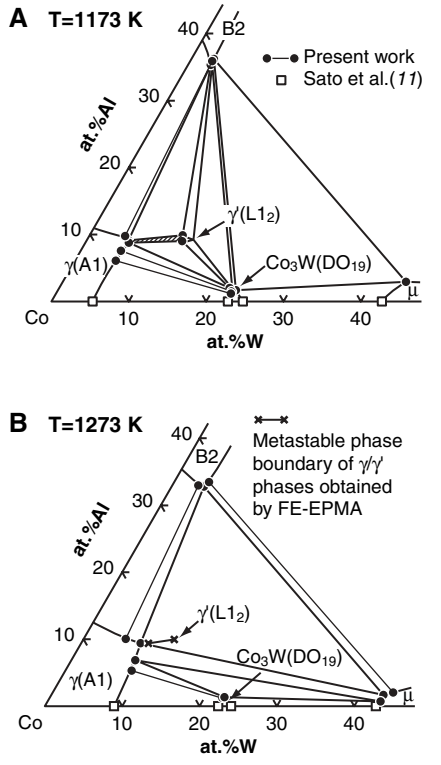

Fig. 2. Isothermal section diagrams of the Co-Al-W ternary system in the Co-rich portion at (**A**) 1173 K and (**B**) 1273 K.

Department of Materials Science, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan.

*To whom correspondence should be addressed. E-mail: ishida@material.tohoku.ac.jp

The addition of Nb or Ti shows a similar effect. It can also be seen from Fig. 3A that the melting temperatures of Co-Al-W–base alloys are ~1673 K, which is 50 to 100 K higher than those of Ni-base superalloys (*12*). Figure 3B shows the temperature variation of Vickers hardness of the $\gamma + \gamma'$ structure for Co-9.2Al-9W and Co-8.8Al-9.8W-2Ta aged at 1073 K for 24 hours after solution treatment at 1573 K for 2 hours. Aging treatment of Waspaloy was carried out at 1118 K for 24 hours and 1033 K for 16 hours after solution treatment at 1353 K for 4 hours. The hardness of the $\gamma + \gamma'$ structure of the Co-9.2Al-9W alloy is very similar to that of Waspaloy. The addition of Ta increases the hardness, which might be due to the stabilization of the γ' phase up to 1373 K. The 0.2% compressive proof strengths of Co-9.2Al-9W and Co-8.8Al-9.8W-2Ta alloys are 473 and 674 MPa at 1143 K, respectively, as compared with 520 MPa for the 0.2% tensile proof strength of Waspaloy (*12*). These data correspond well with the results for high-temperature hardness in Fig. 3B.

Semiquantitative analyses of the partition behavior of various alloying elements between the γ and γ' phase were also carried out by EPMA. The results show that Mo, Ti, Nb, V, and Ta distribute to the γ' phase rather than the γ phase and stabilize the γ' phase, whereas Fe, Mn, and Cr tend to distribute to the γ phase, which is similar to the case of Ni-base superalloys (*13*, *14*). It is notable that Ni is almost equally distributed in the γ and γ' phases and substitutes for more than 50% of the Co with the rise in the solvus temperature of the γ' phase. For instance, the γ' solvus temperature of Co-20Ni-10Al-10W-2Ta is ~1423 K. Because the partition coefficient between the γ and γ' phases depends on the composition and temperature, as in the case of Ni-base superalloys (*13*), more systematic studies are required.

The lattice parameters of the γ and γ' phases of Co-9.2Al-9W alloy heat-treated at 1173 K were determined by room temperature x-ray diffraction at 0.3580 and 0.3599 nm, respectively. The lattice parameter mismatch is thus 0.53%, which is similar to that of Ni-base superalloys. The lattice parameter mismatch affects the morphology of the precipitate, because the mismatch is the driving force in the growth and coalescence of γ' particles. Figure 1, C and D, show field emission electron scanning micrographs of a typical $\gamma + \gamma'$ structure of Co-8.8Al-9.8W–base alloy annealed at 1273 K, where the addition of 2 atomic % Ta and Mo changes the morphology and the volume fraction of the γ' phase. The volume fraction of the γ' phase is increased by the addition of Ta, which is due to the increase in solvus temperature, as shown in Fig. 3. The spherical γ' phase shown in Fig. 1D suggests that the γ/γ' interface is coherent and stable. These findings suggest that the alloy design of Co-Al-W–base superalloys can be achieved under a wide variety of conditions, as is the case for the Ni-base superalloys.

The present Co-Al-W alloys exhibit very good hot workability. Because the melting temperatures of Co-Al-W–base alloys are higher than those of conventional Ni-base superalloys (Fig. 3), hot-working could be carried out in a wider temperature range than was possible in the Ni-base alloys, although new Ru-containing nickel superalloys with higher melting temperatures have been reported (*15*).

The $\gamma + \gamma'$ structure also shows good mechanical properties at room temperature. The tensile properties of Co-9.2Al-9W heat-treated at 1173 K for 1 hour after hot-rolling are as follows: 0.2% proof and tensile strengths of 737 and 1090 MPa, respectively, with 20% elongation; these are comparable with the tensile properties of Ni-base superalloys such as Waspaloy, with 0.2% proof and tensile strengths of 795 and 1275 MPa, respectively, and 25% elongation (*12*).

We note a ternary compound, γ' $Ir_3(Al,W)$, with the $L1_2$ structure. Figure 4 shows the electron micrograph of a dark-field image and the selected area diffraction pattern of Ir-10Al-10W alloy annealed at 1573 K for 72 hours, which confirms that the γ' phase with the $L1_2$ structure finely precipitates. The high-temperature hardness of Ir-10Al-10W and Ir-20Co-10Al-10W alloys annealed at 1573 K for 24 hours is shown in Fig. 3B, where high hardness is maintained even at 1273 K. Because Ir has a melting temperature of 2720 K and the fcc γ phase in the Co-Ir binary system shows a complete solid solution, the Ir-Al-W and Co-Ir-Al-W–base systems with $\gamma + \gamma'$ $(Co,Ir)_3(Al,W)$ structures offer great promise as candidates for next-generation high-temperature materials (*16*).

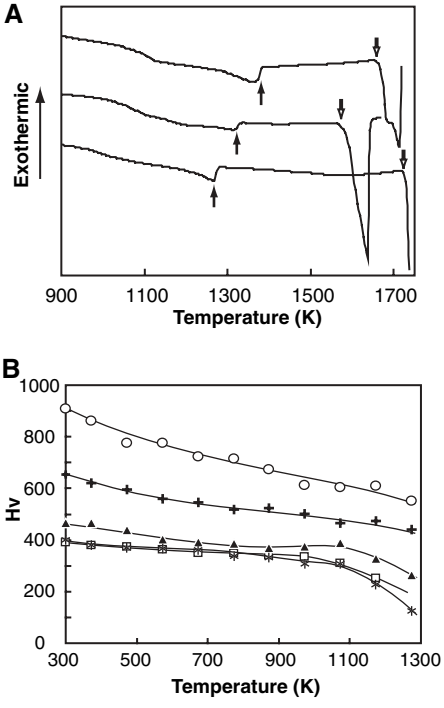

Fig. 3. (**A**) DSC curves. (Top) Co-8.8Al-9.8W-2Ta; (middle) Waspaloy; (bottom) Co-9.2Al-9W. (**B**) High-temperature Vickers hardness. (○) Ir-20Co-10Al-10W, (+) Ir-10Al-10W, (*) Co-9.2Al-9W, (▲) Co-8.8Al-9.8W-2Ta, (□) Waspaloy.

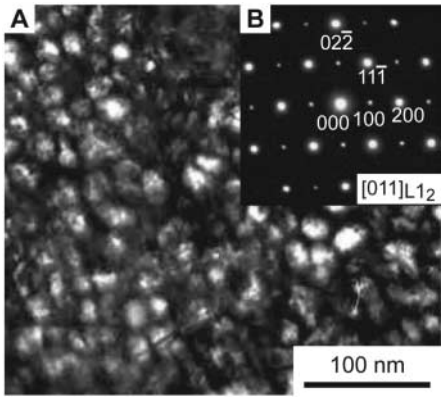

Fig. 4. Electron micrographs of Ir-10Al-10W alloy annealed at 1573 K for 72 hours. (**A**) Dark-field image. (**B**) Selected area diffraction pattern.

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