A New Co-Base Superalloy Strengthened by γ' Phase

Chuanyong Cui, Dehai Ping, Yuefeng Gu and Hiroshi Harada

High Temperature Materials Center, National Institute for Materials Science, Tsukuba 305-0047, Japan

A γ’ strengthened Co-base superalloy with enhanced high temperature properties has been newly developed and the microstructure is mainly composed of a γ/γ’ (fcc/L1₂) structure. The cuboidal γ’ phase is formed with a bimodal distribution and is suggested to play the role of precipitation hardening. [doi:10.2320/matertrans.47.2099]

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1. Introduction

Cobalt superalloys are widely used in industrial and aircraft turbines for vane and combustor sections because of their intrinsic properties such as good stress-rupture parameters, excellent hot corrosion and oxidation resistance and superior thermal fatigue resistance. In industrial practice, most of Co-base superalloys are used in the as-cast state.1) The microstructure of conventional as-cast Co-base superalloys mainly consists of a continuous face-centered cubic (fcc) matrix and a variety of carbides (M6C, M7C3 and MC). The strengthening mechanisms utilized in the conventional Co-base superalloys are principally a balance of refractory element solid-solution hardening and carbides precipitation hardening. However, it has been pointed out that low-temperature ductility decreases greatly as a consequence of secondary carbide precipitation during service exposure in a temperature interval of 650–927°C.2,3)

The formation of γ’ phase with L1₂ structure is substantially difficult in Co-base alloys since the chemical and crystallographic stability are affected by a lattice mismatch, which is required to be less than 1%.3) In addition, Co3Al, an analog of the equilibrium intermetallic phase Ni3Al, is missing in the Co-Al phase diagram,4) because it is metastable phase and exists only at high pressure.5) Recently, the metastable Co2Al is reported to be stabilized by alloying with W.6) On the other hand, a γ’-type Co3Ti phase does exist in the Co-Ti phase diagram.7) The efforts to utilize Co3Ti strengthening in Co-base alloy have been unsuccessful owing to the fact that the Co3Ti phase has a low solution temperature (815–872°C), and also tends to precipitate in cellular form with large mismatch, leading to poor high-temperature properties.8)

Recently, we have successfully developed a γ’ strengthened Co-base superalloy with enhanced high temperature properties by adding a high amount of Ti. In this study, the microstructure, partitioning behavior of alloying elements and mechanical properties of this new Co-base superalloy are presented.

2. Experimental

The nominal composition of the present alloy is listed in Table 1. An ingot, weighing about 25 g, was prepared by arc-melting and re-melted at least ten times to ensure the compositional homogeneity. The ingot was heat-treated at 1100°C for 2 hours (followed by quenching in oil) then at 650°C for 24 hours (air cooling), and finally at 760°C for 16 hours (air cooling). After mechanical polishing and chemical etching in a Kalling reagent (100 ml HCl, 100 ml CH3OH and 50 g CuCl2), the samples were examined in a Philips XL30 scanning electron microscope (SEM) operated in a back-scattered electron (BSE) image mode. Thin foils for TEM observations were prepared by a standard twin-jet electropolishing method in a solution of 23% perchloric acid and 77% acetic acid at about –40°C and examined in a Philips CM200 transmission electron microscope (TEM) operated at 200 kV.

Square rods of approximately 0.2 mm × 0.2 mm × 10 mm were cut from the ingot by electron discharge machining (EDM). These rods were then electropolished to sharpen needle-shape specimens for field ion microscope (FIM) observation and three dimensional atom probe (3DAP) analysis. FIM was performed at –208°C with neon as the imaging gas. The atom probe FIM analyses were performed at 20% pulse fraction and a pulse repetition rate of 1500 Hz with a residual neon gas pressure of 2 × 10⁻⁵ Pa. The micro-Vickers hardness of various phases were determined by a Vickers hardness tester under 25 g load. The data were averaged from 12 points for each phase. Compression specimens with 3 mm in diameter and 6 mm in height were cut by the EDM. The compression tests were performed on a Shimadzu AG-50KNI testing machine in vacuum at a nominal strain rate of 2.5 × 10⁻⁴ s⁻¹ from room temperature to 1100°C.

3. Results

Figure 1 shows the compressive yield strengths of the present alloy as a function of temperature. For comparison, the yield strengths of intermetallic Co-20 at%Ti,9) Ni-base superalloy U720Li,9) Co-base superalloys FSX-414 and MAR-M50910) are also included. Compared with either the intermetallic or other Co-base superalloys, the present alloy
shows a much higher strength at temperatures above 700°C. Even at 980°C, the yield strength is still 475 MPa, which is about 3 times higher than that of Co-base superalloy MAR-M509, and twice that of intermetallic Co-20at%Ti and U720Li.

Detailed microstructural investigations were carried out to understand the occurrence of the enhanced strength at high temperatures. Figure 2 shows a typical BSE image revealing a platelet phase with tens of micrometer in length and a high density of cuboidal phase with several hundreds of nanometer in diameter embedded in the matrix phase. Measured from two BSE images using the Image-Pro Plus (IPP) for windows, the volume fraction of the cuboidal phases was estimated to be about 35%. The platelet phase was identified to be a (Ni(1-x)Co_x)3Ti phase (hexagonal structure with a ~ 0.51 nm and c ~ 1.25 nm) and will be reported in detail elsewhere.

Figure 3(a) is a bright field TEM image, showing the cuboidal phase with the corresponding selected area electron diffraction (SAED) pattern. Electron diffraction analysis suggested that the matrix could be identified as a disordered fcc γ phase; and the cuboidal phase as the γ' phase with a L12-ordered Co3Ti structure. The SAED pattern reveals typical γ/γ' diffraction spots from a [100]γ zone axis. The dark field image (Fig. 3(b)), which was taken using the superlattice reflection of the γ' phase, clearly reveals that a bimodal distribution of cuboidal-like γ' phase formed in the matrix. A large cuboidal γ' has a size of several hundreds nanometers to several micrometers, while the average size of the smaller one is about 40 nm. For clarity, the large cuboidal γ' is designated as the γ'1 and the fine one as the γ'2 phase. Measured from this image using IPP, the volume fraction of γ'2 was estimated to be about 5%.

The partitioning behavior of the alloying elements between the γ and γ' phases was carefully analyzed by using three-dimensional atom probe (3DAP). Figure 4(a) shows the elemental mappings of the alloying elements (Co, Ni, Ti, Cr, Al, Mo and W) in a volume of 24 nm x 24 nm x 200 nm. Each dot represents a single atom in the mapping. The Ti-enriched regions corresponded to the γ' (γ'2) phase, while the Ti-depleted regions corresponded to the γ phase. It is clear that the elements Co and Cr are enriched in the γ phase, Ti, Al and Ni are enriched in the γ' phase, while the Mo and W are almost uniformly distributed in the γ and γ' phases. In order to evaluate the partitioning behavior of the solute elements more quantitatively, concentration depth profiles of Co, Ni, Ti, Cr, Al, Mo, and W in the γ and γ' regions...
determined from a selected volume are shown in Figure 4(b). This profile was obtained by analyzing a small subset volume (10 nm × 10 nm × 26 nm) across the γ/γ' interfaces as shown in Figure 4(a). The selected volume is chosen so that the interfaces are nearly perpendicular to the selected subset. The dashed lines clearly indicate the phase boundaries. The compositional profiles across the γ/γ' interfaces were always found to be sharp with no evidence of long-range composition gradient. The above 3DAP analysis also clearly revealed the two phases with the following compositions: γ (Co ≈ 61, Ni ≈ 14, Ti ≈ 3, Cr ≈ 18, Mo ≈ 1.5, W ≈ 0.5, at%), γ' (Co ≈ 39, Ni ≈ 36, Ti ≈ 15, Cr ≈ 4, Al ≈ 4, Mo ≈ 1.5, W ≈ 0.5, at%).

4. Discussion

It turned out that the present alloy mainly consists of γ/γ' two phase with a fcc/L12 structure. The γ' phase was actually (Co, Ni)2Ti that was stabilized by the high Ni content (>30 at%). This kind of coherent precipitation, which formed due to the addition of Ni, was also observed in an Fe-base alloy A-286.12) The Ni addition was suggested to suppress the formation of a hexagonal-close-packed (hcp) Co phase at low temperature. The bimodal distribution of cuboidal γ' can be rationalized in the following way. Particle γ'1 was formed during the cooling of the arc-melting process, and it was normally stable at the following aging treatment. While particle γ'2 was formed in the supersaturated matrix during quenching and following aging treatment.

The compression tests clearly showed that the present alloy had higher yield stress than other Co-base superalloys at high temperature. The strength increase may be attributed to the following two independent factors: (1) the effect of solid-solution hardening of γ; (2) the effect of precipitation hardening by particles, γ' and the platelet phase ((Ni0.3-Co0.7)3Ti). As for the factor (1), it is known that the refractory elements Cr and W are the major solid-solution strengtheners for the FSX-414 and MAR-M509.21) The Cr and W contents are 29.0 and 7.0 mass% in FSX-414, 23.5 and 7 mass% in MAR-M509, respectively. However, the Cr and W contents in the present alloy are significantly lower than those in FSX-414 and MAR-M509. Thus, the solid-solution hardening of γ may not contribute greatly to the increased strength. As for the factor (2), it is known that the volume fraction and size of L12 γ' phase significantly affect the strength of Ni-base superalloy.13) Ni-base superalloy reaches a maximum strength at a particular volume fraction of γ'.14) In the present alloy, the volume fraction of the γ' measured by IPP was approximately 40% (γ'1 ≈ 35%, γ'2 ≈ 5%). The strength increase is mainly due to the precipitate hardening by the high volume fraction of γ'. As for the effect of the platelet phase, no strength data on the platelet phase is reported in the literature, thus we measured the Vickers hardness of various phases. The Vickers hardnesses of the γ matrix, γ'1 and the platelet phase were measured to be 460, 490 and 540, respectively. Thus, the platelet phase may be beneficial to the strength increase. However, the exact effects of this phase on mechanical property are still under study.

5. Conclusions

The microstructure, elemental distribution and compression properties of the new Co-base superalloy have been examined:

1) The microstructure was a typical of γ/γ' with a fcc/L12 structure. The cuboidal γ' phase precipitated with a bimodal distribution.

2) Cr and Co were enriched in the γ, while Ti, Al and Ni were enriched in the γ'. W and Mo were more or less uniformly distributed in the γ and γ'.

3) Higher yield stress was mainly attributed to the precipitation hardening of the γ' phase.

REFERENCES

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