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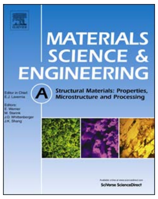

Effect of tungsten concentration on microstructures of Co-10Ni-6Al-(0,2,4,6) W-6Ti (at%) cobalt-based superalloys

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ABSTRACT

The effects of reducing the W concentration (and concomitantly mass density) of Co-10Ni-6Al-xW-6Ti at% Co-based superalloys, with a γ(f.c.c.) plus $\gamma'(L1_2)$ microstructure, is investigated for a series of alloys with W concentrations of 6 at% (baseline alloy), 4 and 2 at% (W-reduced) and 0 at% (W-free). The $\gamma'(L1_2)$ solvus temperature decreases strongly (by 46 °C per 1 at% reduction in W), while the liquidus and solvus temperatures decrease mildly (3–5 °C per 1 at% W reduction) as measured by differential scanning calorimetry. Scanning electron microscopy was used to image phase formation in all alloys. When aging at 900 or 1000 °C for 256 h, the W reduction does not result in the appearance of additional phases within the grains beyond the γ(f.c.c.) and $\gamma'(L1_2)$ phases present in the original alloy. Grain-boundary precipitates are present for all alloy compositions: W-rich or W-free precipitates after aging at 1000 °C, and coarsened $\gamma'(L1_2)$ precipitates after aging at 900 °C. The composition of grain boundary precipitates were measured with energy-dispersive X-ray spectroscopy. Vickers microhardness values decrease with decreasing W content, due to a reduction in $\gamma'(L1_2)$ precipitation and reduced solid-solution strengthening.

1. Introduction

The study of Co-based superalloys strengthened by coherent $\gamma'(L1_2)$-precipitates is accelerating as interest grows for their use in high-temperature structural applications, such as jet-engine turbine blades and discs and turbine blades for land-based natural gas-fired engines for generating electricity. It was long thought that the $\gamma'(L1_2)$-precipitate phase, analogous to the primary strengthening phase in Ni-based superalloys [1–3], could not form in Co alloys [3]. Sato et al. discovered in 2006, however, that a γ(f.c.c.) plus $\gamma'(L1_2)$ two-phase microstructure forms in the Co-Al-W system [4] with a $\gamma'(L1_2)$ composition near $Co_{78}(W_{12.0–12.5}Al_{9.0–10.0})$ when aged at 900 °C [4,5]. Cobalt-superalloys have solidus and liquidus temperatures 50–150 °C higher than conventional Ni-based superalloys [4] and hence they have the potential to surpass the high-temperature capabilities of Ni-based alloys.

However, alloy mass density is a major challenge for most Co-superalloys based on the composition utilized by Sato et al. [4], because W (mass density of 19.3 $g\,cm^{-3}$) is required at high concentrations, 7–10 at% (20–27 wt%), resulting in superalloy mass densities in excess of 9.0 $g\,cm^{-3}$ [6]. By comparison, the mass density of Ni-based superalloys ranges from 8.4 to 9.1 $g\,cm^{-3}$, with the highest values for alloys containing 4–6 wt% W and other high-mass density alloying additions: for example, 6–9 wt% Ta (16.4 $g\,cm^{-3}$) and 3–6 wt% Re (21.0 $g\,cm^{-3}$) [7–9]. The lowest mass densities for Ni-based superalloys are ones with 0 wt% W, with smaller Re (1.5–3.0 wt%) and Ta (6 wt%) concentrations, when 7–10 wt% Mo (10.2 $g\,cm^{-3}$) is added for additional solid-solution strengthening. Therefore, reducing the high W content of Co-superalloys is necessary to match the mass density of current Ni-based superalloys. Makineni et al. [23,24] have developed W-free Co-Ni-Al-Mo-Nb superalloys with a mass density as low as 8.4 $g\,cm^{-3}$, by replacing W with 5 at% Mo (10.2 $g\,cm^{-3}$) and 2 at% Nb (8.6 $g\,cm^{-3}$). The removal of W is accompanied, however, by a strong reduction in the $\gamma'(L1_2)$-precipitate solvus temperature. Depending on Ni content, these alloys have solvus temperatures ranging from 866 °C for alloys containing 0 at% Ni to 990 °C for alloys with 30 at% Ni. Alternatively, Ti has been shown to be an effective substitute for W in Co-Al-W-Ti [10–12] and Co-Ni-Al-W-Ti [15] alloys, increasing the $\gamma'(L1_2)$-solvus temperature and reducing mass density; e.g., 1137 °C and 8.8 $g\,cm^{-3}$, respectively, for a Co-10Ni-5Al-5W-8Ti at% alloy.

In order for Co-based superalloys to be adopted in the aerospace

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industry, they must have densities at least as low as conventional Ni-based superalloys. Tungsten (19.3 g cm^{-3}) is the highest density element in Co-based superalloys and therefore understanding the role of W in γ′($L1_2$)-precipitation (and thus strength) is critical to the long-term success of these alloys. Pyczak et al. has shown that reduction of W in the ternary Co-Al-W system significantly reduces γ′($L1_2$)-precipitate volume fraction where reducing W from 11 to 8 at% leads to a drop in volume fraction from 73% to 34% [14]. Furthermore, for the same decrease in W yielded a drop in γ′($L1_2$)-solvus temperature from 1036 to 960 °C [14]. The present research investigates the effect of decreasing W content, up to its complete removal, in a series of Co-10Ni-6Al-xW-6Ti at% alloys (x = 6, 4, 2, 0). The intent of the present work is to build off on current understanding of W in the Co-Al-W ternary system [14,16] by investigating the higher order Co-Ni-Al-W-Ti system. Co-Al-W was alloyed with Ti [10–12] and Ni [15] because both of these additions are known to stabilize the γ′($L1_2$) two-phase microstructure. By replacing W with Ni and Ti, the overall alloy density will be reduced while maintaining strength. The microstructural stability of the γ′($L1_2$)-precipitate phase is investigated employing isothermal aging treatments at 900 and 1000 °C for 256 h. Phase compositions of γ′($L1_2$)-precipitates and grain boundary (GB) precipitates are measured utilizing energy-dispersive X-ray spectroscopy (EDS). Room temperature Vickers microhardness measurements are utilized to compare mechanical properties. This work aims to further the understanding of low W Co-based superalloys and the role of W on the precipitation kinetics of the γ′($L1_2$) phase.

2. Experimental methods

Button ingots of ~ 50 g were produced with nominal compositions of Co-10Ni-6Al-xW-6Ti at% (x = 6, 4, 2, 0), which correspond to Co-10Ni-3Al-xW-5Ti wt% (x = 19, 13, 6, 0). The alloys are herein denoted as 6W, 4W, 2W and 0W, respectively, with their concentrations given in at%. The alloys were produced using high purity Co (99.9%), Al (99.999%), Ni (99.995%), Ti (99.995%) and a Co-10Ni-9Al-9W cast master alloy arc-melted under a partial Ar atmosphere; the ingots were flipped four times between each melting step to guarantee a homogenous distribution of the constituent elements. Bulk compositions were measured using inductively-coupled plasma atomic-emission spectroscopy (ICP-AES) using ~ 1 g samples (Table 1).

The 0W, 2W and 4W alloys were homogenized in a high-vacuum furnace at 1200 °C for 24 h followed by furnace cooling. Due to a higher W content, the 6W alloy was homogenized at a higher temperature, 1240 °C for 24 h, and then furnace-cooled. The samples utilized to investigate the high-temperature stability of the γ′($L1_2$)-precipitates were wrapped in a Ta foil and encapsulated in quartz tubes, which were flushed with Ar and evacuated, then aged at 900 °C or 1000 °C for 256 h, and quenched into ice water. The 900 °C and 1000 °C aging temperatures were chosen to match Pyczak et al.'s study on the effect of W in a ternary Co-Al-W alloy [14]. Similarly, the 256 h aging time was chosen to be comparable to the 200 h used by Pyczak et al. and is sufficiently long to observe the precipitation and potential decomposition of the γ′($L1_2$)-phase.

Vickers microhardness measurements were performed at ambient temperature utilizing a Struers Duramin-5 microhardness tester, with an applied load of 1 kg and a dwell time of 5 s. Measurements were made across multiple grains on samples that were polished to a 1 µm finish.

Table 1
Bulk compositions of Co-10Ni-6Al-xW-6Ti at% alloys as measured by ICP-AES. Data for Co-10Ni-6Al-6W-6Ti is taken from Ref. [13].

Alloy	Concentration (at%)				
	Co	Ni	Al	W	Ti
10Ni-6Al-0W-6Ti	78.1	10.0	5.8	–	6.2
10Ni-6Al-2W-6Ti	75.9	10.0	5.9	2.0	6.1
10Ni-6Al-4W-6Ti	73.9	10.1	5.7	3.9	6.2
10Ni-6Al-6W-6Ti	71.6	10.1	5.2	6.7	6.4

Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDS) composition measurements were recorded using a Hitachi S-3400N-II SEM equipped with an Oxford INCAx-act SDD EDS detector. The samples used for SEM imaging were polished to a 1 µm finish and imaged in an unetched condition. The volume fraction, ϕ, for γ′($L1_2$)-precipitates was measured by the line-intercept method [17] on SEM images recorded near a {100}-type plane. Differential scanning calorimetry (DSC) experiments were performed under He to measure the γ′($L1_2$)-solvus temperatures of the 0W, 2W, and 4W alloys aged at 900 °C for 16 h. Single cycle experiments at a heating rate of 5 °C min^{-1} were used to identify the γ′($L1_2$)-solvus, solidus, and liquidus temperatures during heating. All data for the 6W alloy, with the exception of the 900 °C micrographs and microhardness measurements, were taken from our prior work [13].

3. Results and discussion

3.1. Microstructure

After 256 h of aging at 900 °C (Fig. 1), the 2W, 4W and 6W alloys form a γ(f.c.c.) plus γ′($L1_2$) microstructure, while only a single-phase γ(f.c.c.) microstructure is present in the W-free (0W) alloy. The 4W and 6W alloys contain large volume fractions (58 ± 5 and 73 ± 2%, respectively) of highly-aligned cuboidal γ′($L1_2$)-precipitates most of which, in the 6W alloy, are coalesced and form lath-shaped structures. The 2W alloy aged at 900 °C contains aligned γ′($L1_2$)-precipitates, but at a much smaller volume fraction (19 ± 2%) than the 4W and 6W alloys, which have coarsened in the < 100 > -type direction to form elongated precipitates. The morphological evolution of the γ′($L1_2$)-precipitates at 900 °C in the 4W and 6W alloys is comparable from what has been observed in the Co-Al-W system [14] where the γ′($L1_2$)-precipitates retain their cuboidal shape. The elongated round γ′($L1_2$)-precipitates observed in the 2W alloy is more comparable to Co-Al-W-Ti alloys aged at 1000 °C for 1000 h [11]. The volume fraction of the Co-Ni-Al-W-Ti samples drops 13.5% per one at% W, which matches almost exactly the 13% per one at% W measured in the Co-Al-W system by Pyczak et al. [14] (aged at 900 °C) and 14% per one at% W measured by Ooshima et al. [16] (aged at 850 °C).

After 256 h of aging at 1000 °C, only the 4W and 6W alloys exhibit a γ(f.c.c.) plus γ′($L1_2$) microstructure, while the 0 W and 2W alloys consist of only a single–phase γ(f.c.c.). The 4W and 6W alloys aged at 1000 °C have smaller γ′($L1_2$) volume fractions than when aged at 900 °C: 27 ± 4 and 37 ± 2% compared to 58 ± 5 and 73 ± 2%, respectively (Table 2). The γ′($L1_2$) precipitates are larger in the alloys aged at 1000 °C than at 900 °C, indicative of coarsening, (Ostwald Ripening) and are rounded rather than cuboidal. The precipitates in both the 4W and 6W alloys are highly coalesced, forming large precipitates formed from multiple smaller precipitates. Small volume fractions of the Co-24W-5Ni-1Al-13Ti phase, with a needle-like morphology (which typically correspond to the $D0_{19}$-Co_3W phase) were found in the grain interior of the 4W (~3 vol%) and 6W (~1–2 vol%) alloys aged at 1000 °C, which are visible in Fig. 2. No phases other than the γ(f.c.c.), with and without γ′($L1_2$)-precipitates, were observed at grain interiors for the remainder of the alloys and aging conditions. The morphological evolution of the γ′($L1_2$)-precipitates at 1000 °C in the 4W and 6W alloys is comparable to Co-Al-W-Ti alloys aged at 1000 °C for 1000 h [11]. The volume fraction of the Co-Ni-Al-W-Ti samples drops only 5% per 1 at% W which is lower than the samples aged at 900 °C as well as the 13% and 14% per 1 at% W measured in the Co-Al-W system aged at 900 °C [14] and 850 °C [16].