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Effect of Ta and Ti on the solidification characteristics of novel γ'-strengthened Co-base superalloys

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ABSTRACT

The effects of Ta and Ti on the microstructure, segregation and solidification path of Co-7Al-8W-base alloy were investigated using directional solidification quenching experiments and isothermal solidification quenching experiments. The results showed that the as-cast microstructure of the Co-7Al-8W alloy (Base alloy) is the γ single phase. The Al element slightly segregates to the interdendritic regions, the W element slightly segregates to the dendritic core, and Co has almost no segregation. The solidification path of the Co-7Al-8W alloy is $L \rightarrow L_1+\gamma \rightarrow \gamma$. With the addition of 1 at.% Ta, there is no change in the segregation of elements, the microstructure and the solidification path of the alloy. The Ta element strongly segregates to the interdendritic regions in the Co-7Al-8W-1Ta alloy. With the addition of 4 at.% Ti, the Ti element strongly segregates to the interdendritic regions, and the segregation of Al and W elements increases. Blocky γ' phase and $(\beta+\gamma')_e$ eutectics form in the interdendritic regions. The solidification path of the Co-7Al-8W-4Ti alloy is $L \rightarrow L_1+\gamma \rightarrow L_2+\gamma+(\beta+\gamma')_e \rightarrow L_3+\gamma+(\beta+\gamma')_e+\gamma' \rightarrow \gamma+(\beta+\gamma')_e+\gamma'$. After the addition of 1 at.% Ta+4 at.% Ti, the segregation of Al, Ta and Ti decreases, while the segregation of W increases. Laves phase, blocky γ' phase and $(\beta+\gamma')_e$ eutectics form in the interdendritic regions. The solidification path of the Co-7Al-8W-1Ta-4Ti alloy is $L \rightarrow L_1+\gamma \rightarrow L_2+\gamma+\text{Laves} \rightarrow L_3+\gamma+\text{Laves}+(\beta+\gamma')_e \rightarrow L_4+\gamma+\text{Laves}+(\beta+\gamma')_e+\gamma' \rightarrow \gamma+\text{Laves}+(\beta+\gamma')_e+\gamma'$. The above results could provide an experimental basis for composition optimization and solidification process control of novel γ'-strengthened Co-base superalloys.

1. Introduction

Co-base superalloys exhibit superior hot corrosion resistance, thermal fatigue resistance and weldability compared with Ni-base superalloys, and they have the potential to be advanced high-temperature structural materials for use in propulsion systems in the aerospace, energy power, and nuclear industries [1]. Conventional Co-base superalloys (Co-Cr-Ni-W-base alloys) are mainly strengthened through solid solution and carbide strengthening. Thus, the applications of the conventional Co-base superalloys at high temperature are restricted due to their inferior high-temperature strength compared to the Ni-base superalloys, which are strengthened by ordered $L1_2$ precipitates (γ'-Ni_3Al phase). Fortunately, Sato et al. [2] discovered a stable ternary γ'-$Co_3(Al,W)$ phase with an $L1_2$ structure in the ternary Co-Al-W system in 2006. In subsequent research, the γ' solvus temperature was reported to be enhanced to higher than 1100 °C by the addition of alloying elements [3]. Therefore, Co-Al-W-base alloys can exhibit long-term stable γ/γ' two-phase microstructures at high temperature and better high-temperature mechanical properties via coherent strengthening and precipitation strengthening. Compared with the conventional Co-base superalloys, the novel γ'-strengthened Co-base superalloys show superior creep and yield strength, similar to those of Ni-base superalloys in the high-temperature region. Recent studies [4,5] have indicated that the single-crystal quinary Co-Al-W-Ta-Ti alloy showed comparable creep properties to the second-generation Ni-base single-crystal superalloys. These results suggested that the Co-Al-W-base alloys were promising as a basis

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for the development of a new class of Co-base superalloys that possess both high-temperature strength and environmental resistance.

Currently, research on novel γ′-strengthened Co-base superalloys is still limited. Compared with Ni-base superalloys, the categories of alloying elements added into Co-Al-W-base alloys are fewer, and there are no commercial alloys. For Ni-base superalloys, many investigations have shown that the interaction of each alloying element has a significant effect on the solidification behaviour. Many studies have been conducted on the solidification path, solidification segregation and eutectic phase formation, which strongly influence the solidification microstructure [6–10] and solidification defects [11–13], such as freckles and shrinkage porosity. For the novel γ′-strengthened Co-base superalloys, however, reports on the solidification behaviour are still limited. Only investigations by Tsunekane et al. [14] and Ding et al. [15] studied the solidification behaviour of Co-Al-W alloy, Co-Al-W-Ta alloy, Co-Al-W-Ti alloy, and Co-Al-W-Ta-Cr alloy. The results showed that the solidification segregation of the Co-Al-W-base alloys was generally lower than that of Ni-base superalloys. However, the solidification behaviour of multi-component Co-Al-W-base alloys is more complex and is associated with multifold intergranular phases, such as β phases, the Laves phase, the γ′ phase, and the μ phase [15–18].

Previous investigations focusing on novel γ′-strengthened Co-base superalloys have shown that Ti and Ta strongly increase the γ′ solvus temperature, high-temperature strength, and creep behaviour [4,5]. Therefore, the quinary Co-Al-W-Ta-Ti alloy, for which the best high-temperature mechanical properties have been reported in previous studies, was investigated in this study. The individual and synergetic effects of Ta and Ti additions on the solidification microstructure, solidification segregation and solidification path of different alloys were mainly focused on. The results could provide a significant reference for composition optimization and production technology formulation of novel γ′-strengthened Co-base superalloys.

2. Experimental procedure

The nominal and actual chemical compositions (at.%) of all investigated alloys are given in Table 1. Based on the Co-7Al-8W ternary alloy, 1 at.% Ta, 4 at.% Ti, and 1 at.% Ta + 4 at.% Ti were added to understand the individual and synergetic effects of Ta and Ti additions on the solidification behaviour. Herein, the alloys will be referred to as the utilized abbreviations (Base alloy, 1Ta alloy, 4Ti alloy, and TaTi alloy, respectively). The ingots of alloys were prepared by vacuum induction melting. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was applied to determine the actual chemical composition.

The solidification path of the investigated alloy was tested via directional solidification quenching experiments. Alloys were cut into bars typically 5 mm in diameter and 100 mm in length. The bars were remelted and directionally solidified in an alumina tube using a high temperature gradient Bridgman furnace. The samples were heated to 1550 °C in an argon atmosphere and held for 15 min to guarantee the uniformity of the melt temperature. Following this, the tube was withdrawn from the chamber at a withdrawal rate of 50 μm/s. After withdrawing a constant length of 50 mm, the tube was quickly removed from the furnace chamber and quenched in Ga-In-Sn liquid metal to obtain a quenching interface.

Isothermal solidification quenching experiments were used to investigate the solidification path in this study. According to the method described in previous studies [19–21], isothermal solidification samples with a size of φ5 × 10 mm were cut from the ingots and embedded into graphite blocks with drilling holes. The samples were surrounded by a mixture of yttrium oxide powder and ethanol. This packaging can protect melts from flow-out and oxidation effectively during melting and solidification. After desiccation, the graphite blocks were heated to 1550 °C and held for 15 min, followed by cooling at ~10 °C/min to different isothermal solidification temperatures. The samples were held at these temperatures for 10 min, followed by water quenching.

The solidification distribution coefficients of the investigated alloy were determined by the point-matrix scanning technique, which was reported in previous studies [22,23]. The specimens were sectioned perpendicular to the growth direction in the dendritic steady growth area. The composition of a 7 by 7 point grid randomly distributed on a representative dendritic structure was measured by an electron probe micro-analyser (EPMA). Considering the back diffusion, the solidification distribution coefficients of each element were determined by fitting the B-F model [24] to the experimental data, as shown in Eq. (1).

$$C_s = C_0k(1\text{-}(1\text{-}2\alpha k)f_s)^{(k-1)/(1-2\alpha k)} \tag{1}$$

where C_s is the composition of the solid; C_0 is the initial composition of the liquid; k is the distribution coefficient; f_s is the fraction solid; and α is the solutal Fourier number, which generally equals 0.01 for superalloys.

Standard metallographic techniques were employed for the preparation of specimens. To reveal the microstructure, specimens were etched with a solution of 10 ml HNO_3+20 ml HCl+170 ml H_2O+10 g $FeCl_3$ and observed with an optical microscope (Nikon LV150). The microstructure at high magnification was observed by a scanning electron microscope (Zeiss Ultra 55). The volume fraction of intergranular phases were determined using the linear intercept method. To obtain the solidus/liquidus temperatures and phase transformation temperatures, differential thermal analysis (DTA) was performed using a NETZSCH STA449C analyser, and the rates of heating and cooling were set as 10 °C/min. The specific temperature points were determined by the tangent method. A Tecnai G220 transmission electron microscope (TEM) was used to analyse the phase structure, and a solution of 10 vol.% $HClO_4$ and 90 vol.% C_2H_5OH was used for twin-jet electron polishing.

Table 1
The nominal and actual chemical compositions of all tested materials (at.%).

Alloy		Co	Al	W	Ta	Ti
Base alloy	nominal	Bal	7	8	–	–
	actual	Bal	7.24	8.34	–	–
1Ta alloy	nominal	Bal	7	8	1	–
	actual	Bal	7.04	8.23	0.92	–
4Ti alloy	nominal	Bal	7	8	–	4
	actual	Bal	6.69	8.29	–	4.00
TaTi alloy	nominal	Bal	7	8	1	4
	actual	Bal	7.11	8.23	0.95	4.01