



Novel Co-Ti-V-base superalloys reinforced by L1₂-ordered γ' phase



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ABSTRACT

The influences of alloying elements Al and Ni to a Co-Ti-V master alloy on microstructures, phase stabilities and high-temperature mechanical properties have been investigated. A two-phase microstructure γ/γ' with ultrahigh γ' volume fraction was designed in the Co-Ti-V (master alloy), Co-Ti-V-Al (Al-modified) and Co-Ti-V-Ni (Ni-modified) alloys. Al shows a slight tendency to partition into γ' , while Ni exhibits almost equal distribution between the γ and γ' phases. Al is found to increase the volume fraction and solvus temperature of γ' . The solvus temperatures of γ' in the master alloy, Al-modified and Ni-modified alloys exceed that of Co-9Al-9W alloy (1000 °C) by 91, 112 and 82 °C, respectively. The flow stresses of the designed alloys exhibit an anomalous positive dependence on temperature rising from 600 to 750 °C. The strengths of the master alloy and Ni-modified alloys are not only higher than that of traditional Co-base superalloy MAR-M 302 at the temperature ranging from 700 to 1000 °C, but also comparable with that of the commercial Ni-base superalloy IN-939 between 850 and 1000 °C. In conclusion, the present Co-Ti-V-base alloys reinforced by γ' are suggested as potential candidates for high-temperature utilizations.

1. Introduction

The superalloys, which normally serve in severe industrial environments facing high temperature and pressure, can be generally divided into three classes named as nickel-, cobalt- and iron-base superalloys [1,2]. The melting point of nickel (~1455 °C) is lower compared with that of cobalt (~1495 °C) and iron (~1538 °C) [3,4], and it partly suggests the higher possibility for cobalt- and iron-base superalloys to be utilized at evaluated temperature than Ni-base superalloys. However, the fact is that the Ni-base superalloys reinforced by coherent fcc-ordered Ni₃Al (L1₂ structure) phase [5–8] are more widely utilized in nowadays industries than the other two types. It is believed that the lack of a coherent geometrically close-packed (GCP) phase in cobalt- and iron-base superalloys is the main limitation for their applications [2]. It needs to point out that the cobalt- and iron-base superalloys are still playing a main role in some industrial fields including petrochemical industries, nuclear power plants and gas turbine industries etc. due to some reasons such as the less cost of iron-base superalloys and good resistance to high-temperature hot corrosion (HTHC) of cobalt-base superalloys [2,9].

In recent years, GCP phases were discovered in some Co-base ternary alloys: Co-Al-W [10], Co-Ge-W [11] and Co-Ga-W [12]. The

most attractive aspects are high melting point (T_m) and good mechanical properties shown in Co-Al-W-base alloys [10]. Thus, many studies relating to the Co-Al-W-base alloys were also conducted, for instance, the influence of alloying elements, Ta, Re, Cr, Ti, Nb, Mo, W, Mn, Fe, Ni, V and B, on mechanical properties, volume fraction ($V_{\gamma'}$) and solvus temperature ($T_{\text{solvus-}\gamma'}$) of γ' of Co-Al-W-base alloy were investigated [10,13–19]. Their results suggest a great possibility of producing novel Co-base superalloys reinforced through coherent precipitate to satisfy the increasing severe demands in industries.

However, the γ' phase in Co-Al-W ternary was confirmed to be metastable [20]. Large amounts of nickel need to be incorporated to improve its thermal stability [19]. We, thus, paid attention to other Co-base system, meanwhile noted that apart from the Co-W [21,22] and Co-Al [23,24] systems, the L1₂-ordered phases were also observed in other Co-base systems, such as Co-V [25–27], Co-Ti [28,29] and Co-Ta-Cr [30,31] systems, respectively. Among these Co-base systems, only the γ' phase in Co-Ti system is stable, and exists until its melting point (T_m) [32]. Furthermore, the γ' -Co₃Ti not only shows a low density, but also displays attractive ductility [33–36] which is one of the important factors for practical usages. Disappointedly, the large mismatch between γ and γ' -Co₃Ti and low T_m restrict the applications of the alloys reinforced by γ' -Co₃Ti [29,37]. In our previous work [38], V was found

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to increase the T_m of the alloy containing γ' -Co₃Ti, and V-modified Co-Ti-V ternary alloy also shows the moderate strength. Meanwhile, according to other researchers' work, V was also confirmed to raise the γ' -Co₃Ti's yield stress corresponding to T_p [39] (T_p : the upper critical temperature relating to positive temperature dependence of strength) and to solid-solute into γ' -Co₃Ti phase with a large solubility (20 at. %) [40]. Therefore, the Co-Ti-V ternary system is suggested as the potential sub-system for developing novel Co-base superalloys.

The primary objectives of the present work focusing on the Co-Ti-V-base alloys are: (1) to study the microstructure evolution; (2) to investigate the alloying behavior of elements Al and Ni; (3) to examine the phase stabilities of γ and γ' ; (4) to exploit the high-temperature mechanical properties. The obtained results will provide important information for the development of the novel Co-base superalloys.

2. Experimental procedures

High purity cobalt (99.9 wt %), vanadium (99.7 wt %), titanium (99.9 wt %), aluminum (99.9 wt %) and nickel (99.9 wt %) were utilized for preparing the cast ingots (Co-5Ti-15V (2X) (in at.%) where 2X is added as outer percentage of master alloy (Co-5Ti-15V), (X = Al and Ni)) which are respectively defined as MA, 2Al and 2Ni, as listed in Table 1 where the details of the heat treatments on these alloys are also provided. The alloys annealed at 800 °C for different times t ($t = 1, 6, 9, 24, 47, 69, 94, 136, 160, 184$ h) after homogenization at 1100 °C for 24 h are designated as MAHt, 2AlHt and 2NiHt (t indicates the annealing time with the unit of hour), respectively.

Some steps for preparing the samples investigated are summarized as follows: (1) the grinding machine was used to remove the oxide layer of cobalt, while the vanadium was cleaned by dilute HF solution; (2) the refractory element was melted with a certain amount of cobalt by arc melting under high purity argon atmosphere to form the alloys with lower T_m ; (3) the vacuum induction furnace was employed to prepare the cast ingots under high purity argon atmosphere; (4) the ingots, weighted around 400 g, were cut into the shape with dimension of $\phi 6 \text{ mm} \times 9 \text{ mm}$ by wire-cutting machine, and cylindrical ingots were slightly polished, sealed in quartz capsules filled with argon gas before heat treatment; (5) the samples were quickly quenched into ice water after the heat treatment.

The transmission electron microscope (TEM) was employed to identify the crystal structure of the γ' phase, and the foil specimens for TEM analyses were prepared through twin jet electropolishing in a solution of HClO₄ (8 vol %) + CH₃COOH (72 vol %) + CH₃CH₂OH (vol. 12%) + HOCH₂CH₂OH (vol. 8%). A field emission scanning electron microscope (FE-SEM) and electron probe microanalyzer (EPMA) were introduced to observe the microstructures of the Co-Ti-V-base alloys, and the alloys for FE-SEM observations were mechanically polished, then etched in a solution of HCl (vol. 50%) + HNO₃ (vol. 50%) for a few seconds. Since the distribution of the alloying elements strongly affects the high-temperature strength, creep resistance, and γ' stability in superalloys, the partitioning behaviors of Al and Ni are thus desired to be evaluated. Normally used cold-rolling [11,12,15,19] was conducted on MAH94, 2AlH94 and 2NiH94 alloys, then, the cold-rolled alloys were annealed at 800 °C for 744, 406 and 704 h respectively to obtain the alloys with coarsened precipitates for composition analyses. The compositions of coarsened γ and γ' phases were measured by a

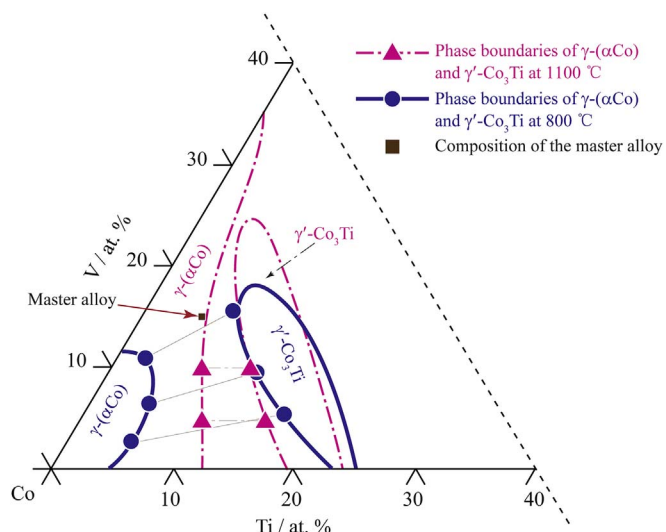


Fig. 1. Phase equilibria in the Co-rich corner of the Co-Ti-V ternary system at 800 and 1100 °C [38].

field-emission electron probe microanalyzer (FE-EPMA). Besides, the phase transition temperatures were examined by differential scanning calorimetry (DSC) under argon atmosphere at a heating rate of 10 °C/min. The compression tests with the strain rate of $1.0 \times 10^{-4} \text{ s}^{-1}$ at the temperature ranging from room temperature to 1000 °C were performed through a Thermecmaster Z machine. Hardnesses of the alloys were measured using a hardness testing machine (MVK-H1, Akashi) under the load with 0.5 kg.

3. Results and discussions

3.1. Composition design and microstructure control

According to our previous reported results [38], 800 and 1100 °C were selected for annealing and homogenization respectively in the present work. Fig. 1 shows the γ -(α Co) + γ' -Co₃Ti phase equilibrium at 800 °C (solid lines) and 1100 °C (dotted lines). It is seen that the solubility of V in γ' -Co₃Ti and γ -(α Co), and Ti in γ -(α Co) increase with the temperature rising from 800 °C to 1100 °C. In order to obtain the Co-Ti-V ternary alloy with γ/γ' two-phase microstructure, as well as to achieve a high volume fraction of the strengthening phase γ' -Co₃Ti, the alloy with a composition of Co-5Ti-15V (at. %) was, thus, designed using the information indicated in Fig. 1, and defined as master alloy (MA).

Fig. 2(a) shows the morphology of single γ phase of the MA alloy homogenized at 1100 °C for 24 h, while Fig. 2(b), the bright-field TEM image (BFI), displays the uniform two-phase γ/γ' microstructure of the MA alloy annealed at 800 °C for 184 h after high-temperature homogenization (MAH184). These results agree well with the phase relationship indicated in Fig. 1. Fig. 2(c)-(d) show a selected area diffraction pattern (SADP) and a dark-field TEM image (DFI) obtained from the MAH184 alloy, respectively. The homogeneously distributed irregular cuboidal precipitates are proved to be with L1₂-ordered structure using the superlattice reflections, 110 and 010, seen in

Table 1

The designation of the alloys investigated and the relating heating processes.

Designation	Heat-treatment process
MA, 2Al, 2Ni	As-cast
MAH1,6,9 ... 184	Obtained from the MA alloy annealed at 800 °C for different times (1, 6, 9, 24, 47, 94, 136, 160, 184 h) after homogenization at 1100 °C for 24 h
2AlH1,6,9 ... 184	Obtained from the 2Al alloy annealed at 800 °C for different times (1, 6, 9, 24, 47, 69, 94, 136, 160, 184 h) after homogenization at 1100 °C for 24 h
2NiH1,6,9 ... 184	Obtained from the 2Ni alloy annealed at 800 °C for different times (1, 6, 9, 24, 47, 69, 94, 136, 160, 184 h) after homogenization at 1100 °C for 24 h

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