ALLOYING EFFECTS ON HEAT-TREATED MICROSTRUCTURE IN CO-AL-W-BASE SUPERALLOYS AT 1300°C AND 900°C

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Keywords: Co-base superalloys, alloying elements, heat treatment, phase equilibria, secondary phase

Abstract

Two levels of non-refractory (V and Ti) and refractory (Mo, Nb and Ta) alloying elements were added to Co-9Al-10W ternary alloy (at.%, baseline alloy) in order to investigate alloying effects on phase equilibria, microstructural features of γ' phase and secondary phases at 1300°C and 900°C, respectively. It is suggested that refractory alloying additions promoted the precipitation of the μ phase at 1300°C. The phase equilibria changed from γ single-phase region in the baseline alloy to $\gamma+\mu$ two-phase region in quaternary alloys containing high levels of refractory alloying elements (4 at.%) at 1300°C. The μ phase was enriched in W, Mo, Nb and Ta, but depleted in Al, V and Ti. For quaternary alloys with low levels of alloying additions (2 at.%), the γ/γ' two-phase microstructure was observed after aging treatment at 900°C for 50h and 300h, but small amounts of the plate-like DO₁₉ phase precipitated in the matrix of 2Mo and 2Nb alloys. The volume fractions of the γ' phase were at very high level in the range of 74% to 83% in all these experimental alloys. Compared with the baseline alloy, alloying additions did not show the strong effect on γ' morphology, which remained cuboidal after long term aging except Mo addition. For quaternary alloys with high levels of alloying additions after aging at 900°C, the DO₁₉ phase precipitated in addition to γ and γ' phases, as well as the blocky μ phase inherited from the precipitation at 1300°C. There were two types of the DO₁₉ phase: one was plate-like and precipitated in the matrix; the other was blocky and transformed from the previous μ phase. Again, refractory alloying additions (Mo, Nb and Ta) promoted phase transformation for both types of the DO₁₉ phase. The current study is helpful to understand phase equilibria and microstructure in Co-Al-W-base alloys and further develop multi-component γ' -strengthened Co-base superalloys.

Introduction

The successive development of superalloys has been motivated by the demand to enhance the performance and efficiency of gas turbines in aerospace and power-generation industries. Co-base superalloys exhibit superior corrosion, oxidation and wear resistance, but lack in effective precipitation strengthening in comparison with γ' -strengthened Ni-base superalloys [1]. Therefore, they exhibit lower high-temperature capability and relatively limited application in gas turbine industries. In recent years, γ' -Co₃(Al, W) strengthened Co-Al-W-base alloys with higher strength than that of traditional Co- and Ni-base superalloys were reported, and served as the possible candidate for high-temperature structure materials [2-4].

However, according to previous studies, high-temperature strength of this class of Co-base alloys is still significantly lower than that of

advanced Ni-base single crystal superalloys, primarily due to lower γ' solvus temperature [3, 4]. In order to further develop this new class of superalloys as promising structural materials, alloying effects on Co-Al-W-base superalloys were investigated in an attempt to understand and achieve desired high-temperature performance. Ta addition was reported to effectively promote γ' solvus temperature and correspondingly enhance high-temperature strength of Co-Al-W-base alloys [2-5]. Other studies indicated that V, Ti, Nb, Mo, Cr and Ni additions also stabilized γ' phase with higher γ' solvus temperature, but Re and Fe additions showed negative effect on γ' solvus temperature [2-4, 6-8]. In addition to γ' phase stability, the γ' volume fraction and γ/γ' lattice misfit, which is correlated with γ' morphology, have considerable influence on creep resistance of Ni-base superalloys [1, 9]. It was reported that the γ' volume fraction was increased by Ti, Nb, Ta and V additions, but decreased with the additions of Ni, Fe, Cr, Mo, and Re in Co-Al-W-base alloys [6-8]. The γ' morphology changed to spherical and cuboidal with Mo and Ta additions, respectively [2, 10]. However, these studies were quite limited and the effects of alloying additions on γ' volume fraction and morphology under long term heat treatment were rarely reported.

Phase equilibria and microstructural stability at high temperature are quite essential for superalloys, since deleterious phases such as topological-close-packed (TCP) phases may precipitate after long term thermal exposure. According to Co-rich corner of Co-Al, Co-W and Co-Al-W phase diagrams, CoAl-base β phase, Co₇W₆-base μ phase and Co₃W-base DO₁₉ phase may exist in Co-Al-W-base alloys at high temperature, especially the γ/γ' two-phase region was too narrow [2, 11]. The basic crystallography of these phases is listed in Table I. Previous reports indicated that these secondary phases were presented in alloys with relatively high content of W, Re and Mo, and they may probably serve as detrimental precipitates due to their plate-like morphology and refractory-rich compositions [4, 10, 12-14]. On the other hand, alloying elements that enlarge the γ/γ' two-phase region are greatly required to improve microstructural stability, but only Ni addition exhibited positive influence to our current knowledge [7]. Thus, one of these challenges is to understand alloying effect on phase equilibria for desired microstructural stability. To date, there have been limited systematic studies of the influence of alloying additions on phase equilibria and microstructure stability due to initial development stage of Co-Al-W-base superalloys.

In the current study, Co-Al-W-base quaternary alloys containing different alloying elements were investigated. Of particular interest was alloying effects on phase equilibria, γ' phase morphology, precipitation of secondary phases and microstructural evolution during aging treatment, as well as transformation temperatures.

Table I. Basic crystallography of β , μ and DO₁₉ phases.

Phase	Strukturbericht symbol	Prototype	Pearson symbol	Space group	Space group number	Example
β	B2	CICs	cP2	Pm $\bar{3}$ m	221	CoAl
μ	D8 ₅	Fe ₇ W ₆	hR13	R $\bar{3}$ m	166	Co ₇ W ₆
DO ₁₉	DO ₁₉	Ni ₃ Sn	hP8	P6 ₃ /mmc	194	Co ₃ W

Experimental Procedures

The nominal compositions and abbreviated names of experimental alloys are listed in Table II. Co-9Al-10W ternary alloy serves as the baseline alloy due to its desired microstructural stability and higher microhardness according to our previous study [13]. Two levels of non-refractory (V and Ti) and refractory (Mo, Nb and Ta) alloying elements were added to the baseline alloy. Ti, Ta and V, mainly γ' -forming elements, as well as Mo and Nb (including Ta), refractory alloying elements referring to their strengthening effects, were selected in the current study. 2 and 4 at.% were named as low and high levels of alloying additions to explore possible difference of their alloying effects, respectively.

Table II. Nominal compositions of experimental Co-Al-W-base superalloys, at.%.

Alloy name	Co	Al	W	V	Ti	Mo	Nb	Ta
Baseline	bal.	9	10	-	-	-	-	-
2V	bal.	9	10	2	-	-	-	-
4V	bal.	9	10	4	-	-	-	-
2Ti	bal.	9	10	-	2	-	-	-
4Ti	bal.	9	10	-	4	-	-	-
2Mo	bal.	9	10	-	-	2	-	-
4Mo	bal.	9	10	-	-	4	-	-
2Nb	bal.	9	10	-	-	-	2	-
4Nb	bal.	9	10	-	-	-	4	-
2Ta	bal.	9	10	-	-	-	-	2
4Ta	bal.	9	10	-	-	-	-	4

Experimental alloys were made from high-purity metals in an arc melting furnace under an argon atmosphere. Alloy buttons with about 20g in weight were alternately melted more than 10 times in order to achieve homogeneous compositions. After arc melting, alloy samples, which were placed in an argon-pressurized quartz tube, were homogenized at 1300°C for 168h (8h and 12h for 2Mo and 4Mo alloys, respectively), and then aged at 900°C for 50~300h to investigate the influence of alloying elements on microstructural evolution. Heat treatments were followed by water quenching, except for the baseline alloy by air cooling.

Microstructural observation of as-cast and heat-treated samples was conducted with an optical microscope and a ZEISS SUPRA 55 field-emission scanning electron microscope (FESEM) in secondary electron (SE) and back-scattered electron (BSE) imaging modes. Differential scanning calorimetry (DSC) was performed using a NETZSCH STA 449C thermal analyzer under high purity argon flow. The transformation temperatures of experimental alloys were determined based on the DSC heating curves with a heating rate of 10 °C/min, including γ' solvus, solidus and liquidus temperatures. The γ' volume fraction was measured by the standard point count method. The volume fraction of secondary phases in heat-treated alloys was measured by the Image-Pro 6.0 software in BSE images. The semi-quantitative and quantitative concentrations of secondary phases were determined by an energy

dispersive spectroscopy (EDS) attached to the FESEM and a JEOL JXA-8800R electron probe microanalyzer (EPMA), respectively. In order to identify these secondary phases, X-ray diffraction (XRD) patterns were obtained from bulk samples by a Rigaku D/max-RB12 diffractometer using Cu K α radiation.

Results

Low levels of alloying additions

The microstructure of ternary (baseline alloy) and quaternary alloys with low levels of alloying additions was examined by using the BSE mode via SEM after solidification and heat treatment at 1300°C. Figures 1 (a1)~(f1) show the typical microstructure of these experimental alloys after solidification, presenting the dendritic structure in the as-cast condition. As exhibited in Figure 1(a1), no eutectic structure was formed in the interdendritic regions of the baseline alloy. There was no apparent change in the interdendritic regions by 2V addition (Figure 1(b1)), whereas 2Ti addition promoted the formation of small amounts of eutectic pools with dark-contrast in the interdendritic regions (Figure 1(c1)). For quaternary alloys with refractory alloying elements, trace amounts of bright-contrast eutectic structure were observed in the interdendritic regions by 2Mo addition (Figure 1(d1)), and relatively large amounts of the eutectic structure with the same contrast existed in 2Nb and 2Ta alloys, exhibited in Figures 1(e1) and (f1). The dark-contrast phase in 2Ti alloy contained high levels of Al and Ti, presumably β phase, and the bright-contrast phases in alloys with refractory alloying additions were enriched in W, Mo, Nb and Ta, suggesting μ phase. XRD did not identify these eutectic structures because of their limited amounts.

Figures 1 (a2)~(f2) show typical microstructure of these experimental alloys after heat treatment at 1300°C for 168h, exhibiting that the dendritic structure disappeared and the eutectic structure was completely dissolved into the γ matrix. Trace amounts of bright-contrast precipitates ($V_f \sim 0.05\%$) were found to exist in the γ matrix of the baseline alloy (Figure 1(a2)), and no secondary phase was observed in the 2V and 2Ti alloys, shown in Figures 1(b2)~(c2). Figures 1(d2)~(f2) exhibit that 2Mo, 2Nb and 2Ta additions slightly increased the volume fraction of bright-contrast precipitates ($V_f < 2\%$) in the matrix. The composition analyses using SEM-EDS indicated that these bright-contrast phases were enriched in refractory alloying elements (W, Mo, Nb and Ta) with the depleted content of Al, and therefore considered as μ precipitates. According to microstructural observation and the narrow γ/γ' two-phase region in most Co-Al-W-base alloys, these experimental alloys in the current study were regarded as γ single-phase alloys with small amounts of the μ phase after heat treatment at 1300°C, in order to investigate the influence of alloying elements on γ/γ' two-phase microstructure after the following aging treatment at 900°C was employed.

The γ/γ' two-phase microstructure was achieved in these experimental alloys after heat treatment at 900°C. In addition to γ/γ' phases, the μ phase, inheriting from the precipitation at 1300°C,

Figure 1. Typical microstructure of baseline and quaternary alloys with low levels of alloying additions after solidification and heat treatment at 1300°C for 168h and then aging treatment at 900°C for 50~300h, respectively.

(a1)~(a4) baseline

(b1)~(b4) 2V

(c1)~(c4) 2Ti

(d1)~(d4) 2Mo

(e1)~(e4) 2Nb

(f1)~(f4) 2Ta

was observed in the matrix of certain alloys, while some plate-like phases precipitated in 2Mo and 2Nb alloys (images not shown), possibly the DO₁₉ phase based on morphology and composition results. It should be pointed out that the images of γ/γ' microstructure were taken away from these secondary phases. Figures 1 (a3)~(f3) are SEM images in the SE mode, showing the typical γ/γ' microstructure in the matrix of six alloys after aging for 50h. The γ' precipitates were found to be cuboidal in the baseline alloy, as shown in Figure 1(a3). Nearly cuboidal γ' precipitates were observed in 2V alloy (Figures 1(b3)), and the γ' phase exhibited cuboidal morphology in 2Ti alloy, shown in Figures (c3). For quaternary alloys containing refractory alloying elements, the γ' morphology was nearly cuboidal in 2Mo alloy (Figure 1(d3)), like that in 2V alloy, but it remained cuboidal in 2Nb and 2Ta alloys (Figures 1(e3) and (f3)) compared to the baseline alloy. Figures 1(a4)~(f4) show γ/γ' two-phase microstructure of these experimental alloys after heat treatment at 900°C for 300h. There was no apparent difference in the γ' morphology after aging treatment between 50h and 300h in these experimental alloys, whereas the γ' size was obviously increased due to coarsening.

Table III summarizes microstructural characteristics of γ' precipitates in these experimental alloys after aging treatment at 900°C for 50h and 300h, including the morphology and volume fraction. It is worthy to note that the volume fractions of the γ' phase were at very high levels in the range of 74% to 83% for all these ternary and quaternary alloys after aging treatment for 50h. Correspondingly, the results in Table III indicate little change in γ' morphology and volume fraction in these experimental alloys after long term aging treatment (300h).

Table III. Morphology and volume fraction of γ' precipitates in ternary and quaternary alloys with low levels of alloying additions after aging heat treatment at 900°C for 50h and 300h.

Alloy	Aging time, h	γ' precipitate morphology	γ' volume fraction, %
Baseline	50	cuboidal	77.3
	300	cuboidal	81.2
2V	50	nearly cuboidal	77.9
	300	nearly cuboidal	79.2
2Ti	50	cuboidal	82.4
	300	cuboidal	76.0
2Mo	50	nearly cuboidal	74.1
	300	nearly cuboidal	74.4
2Nb	50	cuboidal	81.2
	300	cuboidal	76.7
2Ta	50	cuboidal	78.3
	300	cuboidal	80.7

High levels of alloying additions

Figure 2 presents BSE images, showing the typical microstructure of as-cast and heat-treated baseline alloy and quaternary alloys with 4 at.% alloying additions. It should be noted that Figures 2(a1) and (a2), taken from the baseline alloy, were again shown here to be convenient for comparison. All as-cast alloys exhibited the dendritic structure, presented in Figures 2(a1)~(f1). There was no eutectic structure in the interdendritic regions of the baseline alloy (Figure 2(a1)), but trace amounts of bright-contrast particles and moderate amounts of eutectic pools with dark-contrast were observed in the interdendritic regions of alloys containing 4V and 4Ti additions, as shown in Figures 2(b1) and (c1), respectively. Meanwhile, significant amounts of eutectic structure with

bright-contrast existed in the interdendritic regions of 4Mo, 4Nb and 4Ta alloys (Figures 2 (d1)~(f1)). Composition analyses from EDS results indicate that the bright phases mainly contained refractory alloying elements (W, Mo, Nb and Ta), but the dark-contrast phase in 4Ti alloy was enriched in Al and Ti, implying β phase. The XRD results identified the bright-contrast phase as μ phase in 4Mo, 4Nb and 4Ta alloys (data not shown), whereas no more information was obtained about the dark-contrast phase in 4Ti alloy.

Figures 2(a2)~(f2) show the typical microstructure of secondary phases in the γ matrix after as-cast alloys were heat-treated at 1300°C for 168h, exhibiting that the dendritic structure disappeared and the eutectic structure was dissolved. Figure 2(a2) shows trace amounts of the bright-contrast phase ($V_f < 0.05\%$) existed in the γ matrix of the baseline alloy. For quaternary alloys, there were limited amounts of bright-contrast phases ($V_f < 2\%$) in 4V and 4Ti alloys (Figures 2(b2)~(c2)), and significant amounts of bright-contrast particles ($V_f > 7\%$) in 4Mo, 4Nb and 4Ta alloys, shown in Figures 2(d2)~(f2). The EPMA composition results and volume fraction of these secondary phases at 1300°C are listed in Tables IV and V, respectively. Figure 3(a) shows the XRD results of 4Mo, 4Nb and 4Ta alloys and μ phase was identified to coexist with γ phase in these experimental alloys. Combined with composition results (Table IV), the bright-contrast phases in 4Mo, 4Nb and 4Ta alloys were confirmed as the μ phase, and the bright phases in 4V and 4Ti alloys were presumed as the μ phase based on EPMA results.

Figures 2 (a3)~(f3) and (a4)~(f4) show the typical microstructural evolution of secondary phases after thermal exposure at 900°C for 50h and 300h, respectively. Besides γ and γ' primary phases, the main consideration was taken to examine secondary phases in these experimental alloys, such as the μ phase inherited from homogenization treatment. For example, Figures 2(a3)~(a4) focus on the μ phase instead of γ/γ' primary phases in the baseline alloy, presenting that the μ phase was almost unaltered in the baseline alloy after both short and long term aging. Although blocky μ particles remained unchanged in 4V alloy after aging for 50h (Figure 2(b3)), they were partially consumed by the plate-like phase with the gray-contrast when the prolonged heat treatment was employed (Figure 2(b4)). The same case occurred in 4Ti alloy under the same aging conditions (Figures 2(c3)~(c4)). Figures 2(d3)~(f3) and (d4)~(f4) present that an obvious solid phase transformation occurred in quaternary alloys containing refractory alloying elements, involving the μ phase and a new phase with gray-contrast. In 4Mo alloy, the plate-like phase with gray-contrast precipitated densely in the matrix with the unchanged μ phase after aging for 50h, as shown in Figure 2(d3). After aging for 300h, besides the plate-like precipitates, some gray precipitates developed through the μ phase (Figure 2(d4)). In 4Nb alloy, gray-contrast plate-like precipitates were observed in the matrix, and some blocky precipitates with the same contrast formed surrounding the μ phase after annealing for 50h (Figure 2(e3)). The density of the plate-like phase increased significantly, and the volume fraction of blocky precipitates was obviously enhanced by consuming the μ phase after heat treatment for 300h, shown in Figure 2(e4). In the matrix of 4Ta alloy, there were no plate-like precipitates, but a gray-contrast phase was found to envelop the μ phase after aging treatment for 50h (Figure 2(f3)). Figure 2(f4) suggests that the phase transformation for increasing the gray phase with decreasing the μ phase in volume fraction was enhanced after aging for 300h, and some of the plate-like phase preferentially

Figure 2. Typical microstructure of baseline and quaternary alloys with high levels of alloying additions after solidification and heat treatment at 1300°C for 168h and then aging treatment at 900°C for 50~300h, respectively.

(a1)~(a4) baseline

(b1)~(b4) 4V

(c1)~(c4) 4Ti

(d1)~(d4) 4Mo

(e1)~(e4) 4Nb

(f1)~(f4) 4Ta

Table IV. EPMA composition results of the secondary phases in the baseline and quaternary alloys with high levels of alloying additions after heat treatment at 1300°C for 168h and then aging treatment at 900°C for 300h, respectively, at.%.

Alloy	1300°C/168h	900°C/300h
	μ	DO ₁₉
Baseline	Co-2.3Al-40.8W	-
4V	Co-1.5Al-39.4W-1.9V	Co-1.5Al-19.0W-2.8V
4Ti	Co-1.7Al-40.5W-1.5Ti	Co-1.2Al-19.6W-2.4Ti
4Mo	Co-2.5Al-32.6W-3.6Mo	Co-2.6Al-15.7W-8.6Mo*
4Nb	Co-3.4Al-18.1W-9.0Nb	Co-0.6Al-14.4W-7.0Nb
4Ta	Co-2.8Al-18.2W-11.6Ta	Co-0.7Al-14.1W-10.1Ta

*EDS composition results

Figure 3. XRD results of 4Mo, 4Nb and 4Ta alloys after heat treatment at (a) 1300°C for 168h and then aging treatment at (b) 900°C for 300h, respectively.

Table V. Volume fraction (V_f) of μ phase in experimental alloys after heat treatment at 1300°C for 168h, %.

Alloy	Baseline	2V	2Ti	2Mo	2Nb	2Ta
V_f	0.05	0	0	1.6	1.6	0.8
Alloy	4V	4Ti	4Mo	4Nb	4Ta	
V_f	1.6	1.2	7.7	12.2	16.7	

precipitated near the μ phase. It should be noted that all the plate-like precipitates in 4Mo, 4Nb and 4Ta alloys exhibited evident orientation relationship with the matrix. The composition results of the gray-contrast phase in these experimental alloys after heat treatment at 900°C for 300h are also listed in Table IV. It is

indicated that the gray-contrast phase was enriched in refractory alloying elements (W, Mo, Nb and Ta), but contained lower content of Al, V and Ti.

Figure 3(b) shows XRD results of 4Mo, 4Nb and 4Ta alloys after long term heat treatment at 900°C. In addition to γ , γ' and μ phases, peaks of the DO₁₉ phase were identified. Therefore, the gray-contrast phase was the DO₁₉ phase. It is worth noting that diffraction peaks of the μ phase became weaker compared with those after heat treatment at 1300°C (Figure 3(a)). This is in agreement with the microstructural observation that the μ phase decreased and DO₁₉ phase increased in volume fraction during heat treatment at 900°C in 4Mo, 4Nb and 4Ta alloys (Figure 2).

Transformation temperature

Table VI lists the γ' solvus, solidus and liquidus temperatures of ternary and quaternary alloys with low levels of alloying additions after heat treatment at 1300°C and then aging treatment at 900°C for 50h. In order to determine the γ' solvus temperatures more accurately, aged alloys were employed instead of as-cast ones. It was 1029°C in the baseline alloy. The addition of 2V decreased the γ' solvus temperature by 32°C, but 2Ti addition increased it by 36°C. A slight negative influence of 2Mo addition was presented on γ' solvus temperature, while 2Nb addition promoted the thermal stability of the γ' phase by about 20°C. It is inconsistent with some reports that γ' solvus temperature was increased by V and Mo additions [6, 8], possibly resulting from the composition deviation or different baseline alloy. Among all these alloying elements, Ta addition showed the most positive effect on γ' solvus temperature, which was 1100°C for 2Ta alloy. Compared with the baseline alloy, the solidus temperatures were decreased in some extent by the additions of alloying elements, and Ti and Nb additions showed the most negative effect on the solidus temperatures. The baseline alloy exhibited the highest liquidus temperature at 1476°C, but it was decreased in some extent under various alloying additions.

Table VI. γ' solvus, solidus and liquidus temperatures of the baseline and quaternary alloys with low levels of alloying additions after heat treatment at 1300°C and then aging treatment at 900°C for 50h, °C.

Alloy	γ' solvus	Solidus	Liquidus
Baseline	1029	1459	1476
2V	997	1443	1472
2Ti	1065	1408	1468
2Mo	1018	1440	1468
2Nb	1047	1405	1464
2Ta	1100	1412	1455

Discussion

In order to achieve desired high-temperature properties under extremely severe conditions, more than ten alloying elements were introduced during continuous alloy development of advanced multi-component superalloys [1, 9]. In addition to γ/γ' phases, however, complex chemical compositions might lead to possible existence of secondary phases, which generally decreased microstructural stability and mechanical behavior of superalloys. Thus, the relationship of alloy chemistry and microstructure is of primary importance to assure an optimum combination of properties. In the current study, Co-Al-W-base quaternary alloys were investigated to understand phase equilibria and microstructure with various alloying additions.

Phase equilibria at 1300°C and 900°C

In the Co-rich corner of Co-Al and Co-W binary systems at 1300°C, γ phase coexists with CoAl-base β phase and Co_7W_6 -base μ phase, respectively [11]. Previous studies reported that alloys containing high levels of W content exhibited μ precipitates in the matrix of Co-Al-W ternary system at 1200°C and 1300°C [12, 13, 15]. The baseline alloy in the current study contained trace amounts of the μ phase ($V_f \sim 0.05\%$) and thus can be regarded as γ single-phase alloy after heat treatment at 1300°C. 2V and 2Ti additions showed no influence on the precipitation of secondary phases, but high levels of them introduced small amounts of the μ phase ($V_f < 2\%$) in the matrix of 4V and 4Ti alloys. For refractory alloying elements (Mo, Nb and Ta), low levels of alloying additions resulted in the formation of the μ phase with the similar limited levels ($V_f < 2\%$), and high levels of alloying additions (4 at.%) strongly affected the precipitation of the μ phase with large volume fraction ($V_f > 7\%$). It can be summarized that the quaternary alloys with negligible amounts of the μ phase, namely 2V, 4V, 2Ti, 4Ti, 2Mo, 2Nb and 2Ta alloys, were considered to be γ single phase alloys, and alloys with high levels of refractory alloying elements (4Mo, 4Nb and 4Ta alloys) were clearly in the $\gamma+\mu$ two-phase field at 1300°C.

According to phase equilibria at 900°C, although the equilibrium phase field of the γ' phase did not exist in binary systems, new compound γ' - $\text{Co}_3(\text{Al}, \text{W})$ formed in Co-Al-W ternary system [2]. In the current study, the γ/γ' two-phase microstructure was observed in all experimental alloys after heat treatment at 900°C for 300h, coupled with the μ phase and/or the DO_{19} phase in certain alloys, respectively. The μ phase appeared to be not thermodynamically stable at 900°C referring to the isothermal section in the Co-rich corner of Co-Al-W ternary system at 900°C [2]. It inherited from the precipitation at 1300°C and gradually transformed into the DO_{19} phase due to slow diffusion of refractory alloying elements. Different from the unequilibrated μ phase, the DO_{19} phase is stable and probably presented when the content of W is relatively high, since the γ/γ' two-phase field was very narrow [2]. The current microstructural observation indicated that DO_{19} phase did not exist in the baseline alloy, and only high levels of V and Ti additions resulted in the negligible amounts of the DO_{19} phase. However, 2Mo and 2Nb additions promoted the formation of plate-like DO_{19} phase in the matrix, and high levels of refractory alloying additions played an effective role in increasing the volume fraction of DO_{19} precipitates. Therefore, the γ/γ' two-phase region located in 2V, 4V, 2Ti, 4Ti and 2Ta alloys at 900°C, while $\gamma+\gamma'+\text{DO}_{19}$ three phases were stable in 2Mo, 2Nb, 4Mo, 4Nb and 4Ta alloys. Based on the current results, it is indicated that

non-refractory alloying elements possessed limited influence on the phase equilibria, but refractory alloying additions strongly affected phase constituents in Co-Al-W-base alloys.

The phase equilibria in experimental alloys at 1300°C and 900°C are summarized in Table VII. Unlike non-refractory alloying elements (V and Ti), the present study suggests that refractory alloying additions (Mo, Nb and Ta) strongly influenced the thermodynamics of Co-Al-W-base alloys by promoting the formation of μ and DO_{19} phases. It is also revealed that current alloying elements did not exhibit positive effects on enlarging the $\gamma+\gamma'$ two-phase region like Ni [7]. The additions of refractory alloying elements must be carefully optimized in order to generate γ/γ' two-phase alloys and avoid the possible precipitation of μ and DO_{19} phases. On the other hand, recently, Kobayashi et al suggested that the γ' phase was metastable at 900°C and γ , β and DO_{19} phases were thermodynamically in equilibrium using diffusion couple experiments [12]. Therefore, more investigation is necessary to find effective alloying additions to enlarge γ/γ' two-phase region and provide reliable database of phase equilibria for further developing Co-Al-W-base alloys.

Table VII. Phase equilibria in experimental alloys at 1300°C and then aging treatment at 900°C, respectively.

Alloy	1300°C	900°C
Baseline	γ^*	$\gamma+\gamma'^{**}$
2V	γ	$\gamma+\gamma'$
2Ti	γ	$\gamma+\gamma'$
2Mo	γ^*	$\gamma+\gamma'+\text{DO}_{19}^{**}$
2Nb	γ^*	$\gamma+\gamma'+\text{DO}_{19}^{**}$
2Ta	γ^*	$\gamma+\gamma'^{**}$
4V	γ^*	$\gamma+\gamma'^{**}$
4Ti	γ^*	$\gamma+\gamma'^{**}$
4Mo	$\gamma+\mu$	$\gamma+\gamma'+\text{DO}_{19}^{**}$
4Nb	$\gamma+\mu$	$\gamma+\gamma'+\text{DO}_{19}^{**}$
4Ta	$\gamma+\mu$	$\gamma+\gamma'+\text{DO}_{19}^{**}$

* including trace amounts of the μ phase

** including the metastable μ phase

Volume fraction and morphology of γ' phase

It is well known that γ' phase is the primary strengthening phase for alloys containing $\gamma+\gamma'$ two-phase microstructure, like Ni-base superalloys. Their creep resistance mainly depends on the volume fraction of γ' precipitates. In the present work, the γ' volume fraction in the baseline alloy was 77.3%, and it remained at very high levels in the range of 74% to 83% under various alloying additions after thermal exposure at 900°C for 300h without the appearance of γ' rafting (Figure 1 and Table III). Although previous studies indicated that γ' volume fraction was increased with Ti, Nb, Ta and V additions but decreased with Mo addition [6, 8], no obvious influence of alloying additions on γ' volume fraction was observed in the current quaternary alloys, compared to the baseline alloy with such a high level of γ' volume fraction. On the other hand, it was reported that the longest creep life occurred when the volume fraction of γ' phase was in the range of 65% to 70% in both 900°C/392MPa and 1100°C/137MPa in Ni-base single crystal superalloys [16]. In contrast, the appropriate γ' volume fraction for superior creep properties of Co-Al-W-base alloys has not been reported, but Titus et al revealed that alloys containing a high γ' volume fraction exhibited better creep properties compared with

alloys with low volume fraction of γ' precipitates at 900°C/241~310 MPa [17].

It is well accepted that creep resistance was also affected by γ/γ' lattice misfit, which has its close relationship with γ' morphology, especially in Ni-base single crystal superalloys [1, 9]. Previous investigation indicated that spherical γ' precipitates resulted from a near zero misfit, while the cuboidal morphology of γ' phase correlated with lattice misfit deviated from zero [18]. It was reported that the temperature capability of Ni-base single crystal superalloys was improved by changing the lattice misfit towards more negative [19]. Recent investigation indicated that Co-Al-W-base alloys with cuboidal γ' precipitates had the comparable creep rate to Ni-base superalloy IN713C at 850°C and single-crystal alloy René N4 at 900°C [6, 17]. In this study, the γ' morphology in the baseline alloy was cuboidal, and no apparent influence was observed by alloying additions except the nearly cuboidal γ' phase in 2V and 2Mo alloys. These results show good agreement with γ' morphology reported by previous studies [2-6, 13, 20]. To date, among limited creep studies in Co-Al-W-base superalloys, the effects of lattice misfit and some other factors (such as γ' size and alloy chemistry) on creep resistance of Co-Al-W-base alloys have not been investigated yet. Therefore, more investigation is required to understand their creep resistance and behavior for further practical applications of Co-Al-W-base alloys.

Precipitation and composition of μ phase

In addition to the effective strengthening phases in the matrix and/or grain boundaries like γ' phase and carbides, it is possible to promote the formation of undesirable secondary phases during heat treatment or more commonly during service as alloying additions exceed the solubility of the γ matrix, among which TCP phases are most notable [1, 9]. μ phase is one common type of TCP phases and generally precipitated due to excessive content of Cr and refractory alloying elements [1, 9]. In the current study, it precipitated at 1300°C as an equilibrium phase coexisting with γ phase. Trace amounts of μ phase were observed in the baseline alloy and limited amounts of this phase existed in 4V, 4Ti, 2Mo, 2Nb and 2Ta alloys, while large amounts of μ phase were present under high levels of refractory additions. Its morphology was blocky. The composition results indicated that the μ phase was evidently enriched in W, Mo, Nb and Ta, but depleted in Al, V and Ti. Although the μ phase existed at 900°C in the early stage, it inherited from the precipitation at 1300°C and was considered to be a metastable phase. As the aging time was extended, the volume fraction of μ phase gradually decreased (Figures 2 and 3) due to lower diffusion coefficients of refractory elements and it would ultimately disappear.

The current results also suggest that refractory alloying elements promoted the formation of the μ phase, and high levels of them strongly increased the volume fraction of μ phase. Although no study has been reported for the effect of μ phase on high temperature mechanical properties of Co-Al-W-base superalloys, the composition results of the μ phase suggest that it absorbed refractory alloying elements from the matrix and thus would be detrimental to high temperature performance. Therefore, in practice, the contents of refractory alloying elements need to be carefully balanced to avoid the formation of μ phase.

Precipitation and morphology of DO₁₉ phase

Like μ phase, the Co₃W-based DO₁₉ phase is derived from Co-W binary system and expected to precipitate in the matrix with high levels of W content in Co-Al-W ternary system [2]. Present research showed two types of DO₁₉ precipitates in morphology, plate-like and blocky shape. The plate-like DO₁₉ phase precipitated as a result of the decomposition of γ matrix at 900°C, and their preferential orientation should be similar to that in previous studied Co-20W alloy, resulting from a (0001)_{hcp}//(111)_{fcc}, [1120]_{hcp}//[110]_{fcc} [21]. In contrast, the blocky DO₁₉ precipitates were transformed from the μ phase by consuming refractory alloying elements, since the composition difference between the μ and DO₁₉ phases corresponded to normal downhill diffusion process (Table IV). Based on these results, it is indicated that refractory alloying elements strongly promoted the precipitation of the DO₁₉ phase. The effect of DO₁₉ phase on high temperature mechanical properties has not been investigated in Co-Al-W-base superalloys yet. However, its plate-like morphology and high levels of refractory alloying elements content implied the deleterious effect on mechanical behavior. According to the present results, it is suggested that refractory alloying elements must be carefully controlled to prevent the formation of DO₁₉ phase for an optimum microstructure and mechanical properties.

Conclusions

The influence of non-refractory alloying elements (V and Ti) and refractory alloying elements (Mo, Nb and Ta) on high-temperature phase equilibria, γ' phase and secondary phases as well as transformation temperatures were investigated in the current study. The following conclusions can be drawn:

1. High levels of refractory alloying elements (4 at.%) strongly promoted the formation of μ phase at 1300°C. These quaternary alloys were located in $\gamma+\mu$ two-phase equilibrium region, while the other alloys were considered to be γ single-phase alloys with negligible amounts of the μ phase. The μ phase contained high levels of W, Mo, Nb and Ta, but was depleted in Al, V and Ti.
2. The γ/γ' two-phase microstructure was generated in all experimental alloys containing low levels of alloying additions (2 at.%) after aging at 900°C, and the volume fractions of the γ' phase were at very high levels in the range of 74% to 83%. Compared with the baseline alloy, alloying additions did not show strong effects on γ' morphology, which remained cuboidal or nearly cuboidal after long term aging.
3. For quaternary alloys with refractory alloying additions after aging at 900°C except 2Ta alloy, the DO₁₉ phase precipitated in addition to γ and γ' phases, as well as the blocky μ phase, which inherited from the precipitation at 1300°C. The $\gamma+\gamma'+\text{DO}_{19}$ equilibrium phase field was located in 2Mo, 2Nb, 4Mo, 4Nb and 4Ta alloys. And the γ/γ' two-phase microstructure existed with negligible amounts of the DO₁₉ phase in 2V, 2Ti, 2Ta, 4Ti and 4V alloys.
4. There were two types of morphology of DO₁₉ phase: one was plate-like and precipitated in the matrix; the other was blocky

morphology and transformed from the previous μ phase. It is suggested that refractory alloying additions (Mo, Nb and Ta) promoted the phase transformation for DO₁₉ phase.

5. Compared with the baseline alloy, Ta, Ti and Nb additions showed stronger effect on promoting γ' phase stability by increasing γ' solvus temperature in the order: Ta>Ti>Nb, while V and Mo additions presented negative effect on γ' solvus temperature.

Acknowledgments

The authors would like to acknowledge useful discussions with Y.R. Zheng. The financial support provided by the National Natural Science Foundation of China (Grant No.: 50771012), Aviation Science Foundation of China (Grant No.: 2009ZF74) and New Century Excellent Talents in University, Chinese Ministry of Education (Grant No.: NCET-06-0079) are gratefully acknowledged.

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