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Phase equilibria in Co-rich region of Co−Ti−Ta system

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Abstract: The phase equilibria in Co-rich region of Co−Ti−Ta system were studied. The microstructure and XRD analysis together with EDS determination show that $L1_2$ type Co_3Ti phase and Laves_C36_Co_3Ta phase get equilibrium with α-Co phase from 1 000 to 1 200 °C. The Co_3Ti phase possesses a solubility of Ta higher than 10%, and the addition of Ta stabilizes the Co_3Ti phase. The isothermal sections of the Co−Ti−Ta system in the Co-rich region at 1 000, 1 100 and 1 200 °C were constructed according to the result.

Key words: $L1_2$ type intermetallic compound; phase equilibrium; Co−Ti−Ta; Co-based superalloys

1 Introduction

The development of superalloys has been driven by the demand to increase the operating temperature of gas turbines in power plants and aircraft engines, thus a higher thermodynamic stability of the γ' phase is obviously more important. Ta is an important alloying element in both Co-based and Ni-based superalloys, and it has been known that Ta can stabilize the γ' phase [1−5]. However, both γ'-Ni_3Ta and γ'-Co_3Ta are not stable, thus, a quantitative thermodynamic description for Ta in stabilizing the γ' phase is not available.

The $L1_2$ type intermetallic compound Co_3Ti is the only binary stable γ' phase in the commercial Co-based superalloys. In many systems, Ta can substitute Ti and exhibits a relatively large solubility region [6−8]. If Ta can substitute Ti in the γ'-Co_3Ti phase, then according to thermodynamic analysis [9−11], the thermodynamic stability of the metastable γ'-Co_3Ta phase can be estimated.

On the other hand, the information for Co−Ti−Ta system is very limited [12]. Recently, XU et al [13] have studied the phase equilibria in Co−Ti−Ta system at 950 °C and established the phase relationship between α-Co, Co_3Ti and Co_7Ta_2 phases in the Co-rich region. The result is important for the alloy design of the Co-based superalloys, but it is not enough to understand the overall phase relationship in the Co-rich region, especially to establish a critical temperature dependence of the phase stability on the γ' phase. Therefore, in this work, a systematic experimental study was done to the Co-rich Co−Ti−Ta alloys at 1 000, 1 100 and 1 200 °C to reveal the effect of Ta on the thermodynamic stability of the Co_3Ti phase, to determine the Co_3Ti phase composition accurately and to establish a reliable phase relationship in the Co-rich region.

The constitute binary systems of Co−Ti and Co−Ta have both been thermodynamically studied before. The Co−Ti system has been thermodynamically assessed by DAVYDOV et al [14]. In the Co-rich region, there is a peritectic reaction of $L+\alpha$-Co$\leftrightarrow$$Co_3Ti$ at 1 181.5 °C, and Co_3Ti gets equilibrium with α-Co at low temperature. The binary Co−Ta system has been critically assessed by LIU and CHANG [15] and HARRL et al [16]. In the Co-rich region, the two assessments have no much difference, and both claim that the intermetallic compound Co_7Ta_2, which gets equilibrium with α-Co, decomposes into α-Co and a Laves_C36 phase Co_3Ta at about 950 °C.

2 Experimental

To establish an overall phase relationship in the Co-rich region, alloys with different Co contents in the composition range of Co−$Co_{80}Ti_{20}$−$Co_{80}Ta_{20}$ (molar fraction, %, the same as below) were designed. The desired alloys were prepared by high purity metals of

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Co (99.99%), Ti (99.9%) and Ta (99.9%). The pure metals were melted in an arc furnace under high purity argon atmosphere using a non-consumable tungsten electrode. The buttons were remelted 3 times to improve their homogeneity. The cast alloys were annealed in the quartz tubes evacuated up to 0.3×10^{-3} Pa at 1 200 °C for 4 h and subsequently quenched into cold water. The alloys for phase equilibrium study at 1 000 and 1 100 °C were further annealed at 1 000 and 1 100 °C for 168 and 72 h, respectively, followed by quenching.

The equilibrated Co−Ti−Ta alloys were first examined using optical microscopy. The microstructures and compositions were then analyzed by scanning electron microscopy (SEM) with the assistance of energy dispersive spectroscopy of X-ray (EDS) on a HITACHI S3400N under an accelerating potential of 20 kV. The phase constituents were determined by X-ray diffraction (XRD) on a Philips PW3040/60 diffractometer using Cu K_α radiation, at a high tension of 40 kV and 40 mA.

3 Results and discussion

3.1 Equilibrium phase constituents

The backscattering electron (BSE) images of the typical alloys annealed at different temperatures are shown in Figs. 1 and 2. Figure 1(a) shows the microstructure of the $Co_{85}Ti_3Ta_{12}$ alloy annealed at 1 200 °C for 4 h. The alloy apparently consists of two phases, the black matrix and the gray precipitated phase. The XRD analysis shows that the matrix is α-Co phase with disordered FCC structure, and the precipitated phase is Laves_C36 phase, denoted as Co_3Ta.

The two-phase region of (α-Co+Co_3Ta) covers a relatively large composition range in the Co-rich region at temperatures from 1 000 to 1 200 °C. Figures 1(b) and (c) show the microstructures of the $Co_{76}Ti_5Ta_{19}$ and $Co_{85}Ti_3Ta_{12}$ alloys annealed at 1 100 and 1 000 °C, respectively, which are both in the two-phase equilibrium between α-Co and Co_3Ta. One difference between them is that the volume fraction of the α-Co phase in the $Co_{76}Ti_5Ta_{19}$ alloy is very small (see Fig. 1(b)), hence the composition of 5% Ti and 19% Ta should be close to the phase boundary of (α-Co+Co_3Ta)/Co_3Ta. Figures 1(a) and (c) show the microstructure of $Co_{85}Ti_3Ta_{12}$, and in the latter image, the precipitated Co_3Ta phase grows apparently during the further heat treatment at 1 000 °C for 168 h after annealing at 1 200 °C for 4 h. XU et al [13] detected the phase equilibrium between α-Co and Co_7Ta_2 phase at 950 °C. The Co_7Ta_2 phase decomposes into α-Co and Co_3Ta just at about 950 °C according to the binary Co−Ta phase diagram [15], thus a two-phase equilibrium between α-Co and Co_3Ta is obtained at 1 000 °C in the Co−Ta side.

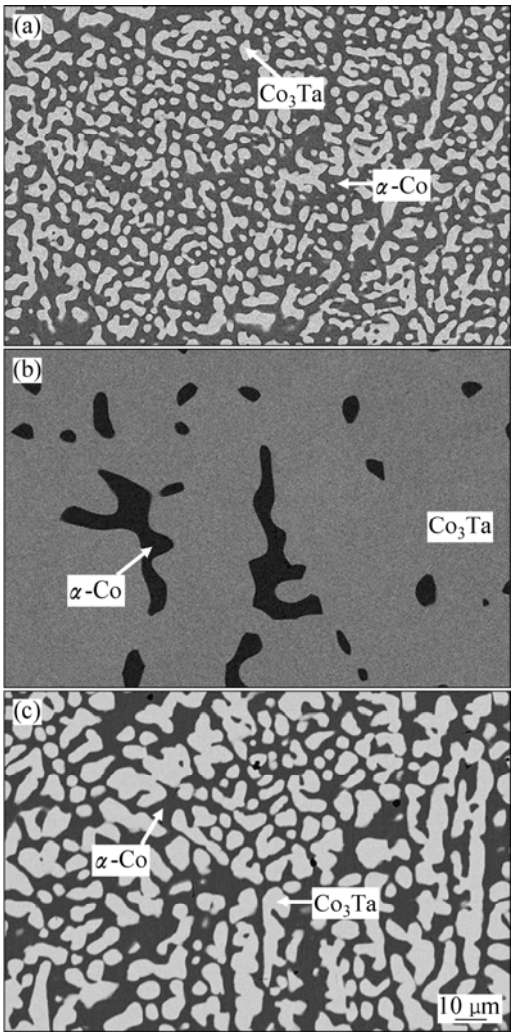

Fig. 1 SEM images of $Co_{85}Ti_3Ta_{12}$ alloy annealed at 1 200 °C for 4 h (a), $Co_{76}Ti_5Ta_{19}$ alloy annealed at 1 100 °C for 72 h after heat treatment at 1 200 °C for 4 h (b) and $Co_{85}Ti_3Ta_{12}$ alloy annealed at 1 000 °C for 168 h after heat treatment at 1 200 °C for 4 h (c)

With the increase of Ti, the Co−Ti−Ta alloys leave from the (α-Co+Co_3Ta) two-phase region. Figure 2 shows the microstructures of the $Co_{76}Ti_{12}Ta_{12}$ and $Co_{73}Ti_{16}Ta_{11}$ alloys annealed at 1 100 °C for 72 h after heat treatment at 1 200 °C for 4 h. The first alloy enters into a three-phase region, consisting of dark α-Co phase, grey Co_3Ta phase and another dark grey Co_3Ti phase, based on the XRD analysis results. The latter alloy with more addition of Ti has no α-Co phase, and the alloy is located in a two-phase region of (Co_3Ta+Co_3Ti). The phase constitution of the alloys annealed at 1 000 °C is almost the same as that annealed at 1 100 °C, however, those of alloys with higher Ti content annealed at 1 200 °C are different. At about 1 180 °C, a peritectic reaction $L+\alpha\text{-Co}\longleftrightarrow Co_3Ti$ occurs in the binary Co−Ti system [3], thus the Co−Ti−Ta alloys with higher Ti content have liquid at 1 200 °C first at the phase boundaries.

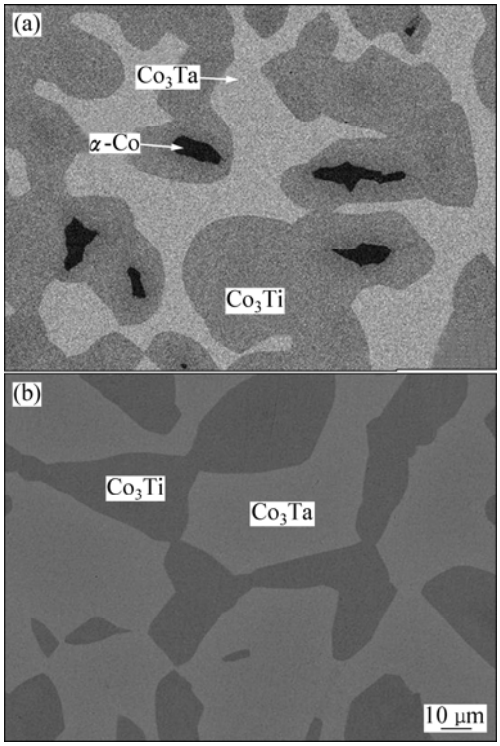

Fig. 2 SEM images of alloys annealed at 1 100 °C for 72 h after heat treatment at 1 200 °C for 4 h: (a) $Co_{76}Ti_{12}Ta_{12}$ alloy; (b) $Co_{73}Ti_{16}Ta_{11}$ alloy

3.2 Equilibrium phase compositions

Based on the microstructure observation and XRD analysis above, the phase constituents of the treated alloys can be decided. The phase compositions are further determined by SEM-EDS. It should be mentioned that all these results show that the treated alloys have come to a good equilibrium, so the measured phase compositions can be regarded as the equilibrium phase compositions as listed in Table 1.

3.3 Isothermal sections

According to the microstructure analysis performed to the equilibrium Co−Ti−Ta alloys, the isothermal sections in the Co-rich region of the Co−Ti−Ta system at 1 000, 1 100 and 1 200 °C can be established, as shown in Fig. 3. The tie lines and tie triangles corresponding to the two-phase and three-phase equilibrium compositions are from the data listed in Table 1. It can be seen that the solubilities of Ti and Ta in the α-Co phase have been well determined. The Co_3Ta phase is detected to have a very high solubility of Ti at these temperatures. In fact, the Co_3Ta phase is reported to form a continuous ternary solid solution extending from the Laves_C36_Co_3Ta to the Laves_C36_Co_2Ti phase [13]. The Co_3Ti phase also has a certain solubility of Ta. At 1 000 °C, it can dissolve more than 10% Ta, while at 950 °C, the solubility of Ta is reported to be slightly higher than 10%, which is in a good agreement with this work. It is obvious that Ta can stabilize the γ'-Co_3Ti phase, and the composition range of the Co_3Ti phase presents like a narrow strip pointing to the $Co_{75}Ta_{25}$ composition, with Co content remaining

Table 1 Equilibrium phase constituents and compositions in Co-rich Co-Ti-Ta system

Temperature/°C	Alloy	Equilibrium phase constituent	Equilibrium phase composition (molar fraction, %)		
			Co	Ti	Ta
1000	$Co_{85}Ti_3Ta_{12}$	α-Co	95.2	2.1	2.7
		Co_3Ta	75.0	4.1	20.9
	$Co_{85}Ti_8Ta_7$	α-Co	91.5	6.5	2.00
		Co_3Ta	75.5	9.3	15.2
		Co_3Ti	75.7	12.0	12.3
	$Co_{76}Ti_5Ta_{19}$	α-Co	93.3	4.0	2.7
		Co_3Ta	74.4	5.3	20.3
	$Co_{76}Ti_{12}Ta_{12}$	Co_3Ta	74.7	11.2	14.1
		Co_3Ti	75.7	13.0	11.3
	$Co_{73}Ti_{16}Ta_{11}$	Co_3Ta	70.7	20.9	8.4
		Co_3Ti	75.0	17.9	7.1
	$Co_{73}Ti_{20}Ta_7$	Co_3Ta	74.3	11.9	13.8
		Co_3Ti	75.1	14.6	10.3
1100	$Co_{85}Ti_3Ta_{12}$	α-Co	93.16	2.64	4.20
		Co_3Ta	72.70	3.37	23.93
	$Co_{85}Ti_8Ta_7$	α-Co	89.62	7.45	2.93
		Co_3Ta	73.44	10.38	16.18
		Co_3Ti	76.95	11.21	11.84
	$Co_{76}Ti_5Ta_{19}$	α-Co	91.15	4.95	3.90
		Co_3Ta	74.21	5.05	20.74
	$Co_{76}Ti_{12}Ta_{12}$	α-Co	88.38	9.04	2.58
		Co_3Ta	72.77	11.54	15.69
		Co_3Ti	77.02	12.44	10.54
	$Co_{73}Ti_{16}Ta_{11}$	Co_3Ta	71.60	20.16	8.24
		Co_3Ti	75.74	18.23	6.03
	$Co_{73}Ti_{20}Ta_7$	Co_3Ta	73.42	14.63	11.95
		Co_3Ti	76.95	14.15	8.90
1200	$Co_{85}Ti_3Ta_{12}$	α-Co	92.13	2.87	5.00
		Co_3Ta	74.80	2.67	22.51
	$Co_{85}Ti_8Ta_7$	α-Co	87.61	8.56	3.83
		Co_3Ta	73.58	10.75	15.67
	$Co_{76}Ti_5Ta_{19}$	α-Co	90.61	4.93	4.47
		Co_3Ta	72.86	5.91	21.33
	$Co_{76}Ti_{12}Ta_{12}$	α-Co	87.17	9.66	3.17
		Co_3Ta	73.02	12.68	14.30
	$Co_{73}Ti_{16}Ta_{11}$	α-Co	85.12	12.49	2.39
		Co_3Ta	72.21	15.80	11.99
	$Co_{73}Ti_{20}Ta_7$	α-Co	83.50	15.13	1.36
		Co_3Ta	72.00	19.64	8.36
		L	77.45	19.66	2.89

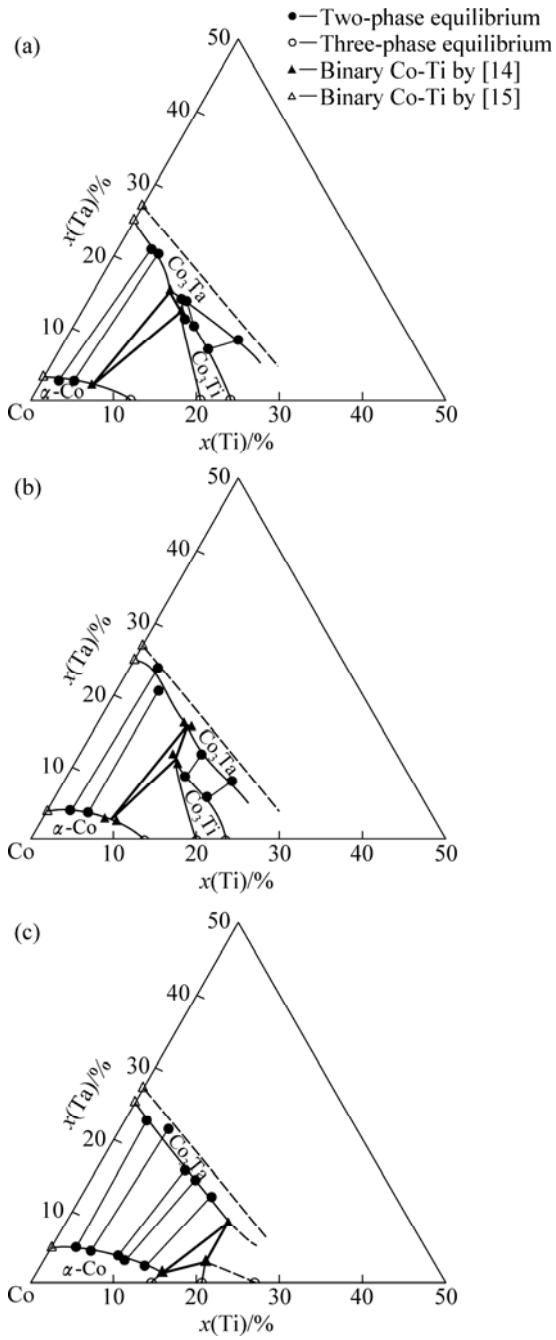

Fig. 3 Isothermal sections in Co-rich region of Co−Ti−Ta system: (a) 1 000 °C; (b) 1 100 °C; (c) 1 200 °C

at about 75%. Then it is deduced that Ta mainly substitutes Ti in the γ'-Co_3Ti phase.

The fact that Ta can substitute Ti in γ'-Co_3Ti phase more than 10% at 1000 °C means there should exist a metastable γ'-Co_3Ta phase in the Co−Ta binary system. From the view point of thermodynamics, due to the metastable γ'-Co_3Ta phase as well as the entropy increased from the mixing of Ti and Ta in the same atomic lattice of Ti, Ta exhibits a stabilizing effect on the γ'-Co_3Ti phase. With the reliable phase relationship in the Co−Ti−Ta system discussed above, a thermodynamic description of the metastable γ'-Co_3Ta phase can be estimated, which will be done in further work.

4 Conclusions

1) In the Co-rich region of the Co−Ti−Ta system, the $L1_2$ type Co_3Ti phase and the Laves_C36_Co_3Ta phase get equilibrium with the α-Co phase from 1 000 to 1 200 °C.

2) The Co_3Ti phase is detected to possess a solubility of Ta higher than 10%. The addition of Ta makes the Co_3Ti phase more stable, and Ta mainly substitutes Ti in the $L1_2$ type Co_3Ti phase.

3) Isothermal sections in the Co-rich region of the Co−Ti−Ta system at 1 000, 1 100 and 1 200 °C are constructed based on the measurements in this work. The determined solid solubilities of the α-Co phase, $L1_2$ type Co_3Ti phase and the Laves_C36_Co_3Ta phase are in good agreement with the previous determination.

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Co−Ti−Ta 三元系富 Co 区的相平衡

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摘　要：研究 Co−Ti−Ta 三元系富 Co 区的相平衡。显微组织和 XRD 分析以及 EDS 检测结果表明，在 1 000~1 200 °C 温度范围内，$L1_2$ 结构 Co_3Ti 相和 Laves_36_Co_3Ta 相与 α-Co 构成相平衡。Co_3Ti 相中 Ta 的固溶度超过 10%，Ta 的加入使 Co_3Ti 相更稳定。根据实验结果构建 Co−Ti−Ta 三元系富 Co 区在 1 000、1 100 和 1 200 °C 等温截面图。

关键词：$L1_2$ 型金属间化合物；相平衡；Co−Ti−Ta；钴基高温合金

(Edited by FANG Jing-hua)