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Phase Equilibria and Ternary Intermetallic Compound with $L1_2$ Structure in Co-W-Ga System

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Phase equilibria and stabilities of intermetallic phases appearing in the Co-rich portion of the Co-W-Ga ternary alloys were investigated and isothermal section diagrams at 1200, 1100, 1000, and 900 °C were determined. A fine cuboidal phase with an $L1_2$ structure was observed at 900 and 800 °C, where the composition of the new ternary compound obtained by aging at 900 °C for the Co-7.4W-12.0Ga alloy was Co-11.2W-11.4Ga (at.%). It was confirmed that this compound is metastable at 900 °C but is more stable at 800 °C. These results mean that the thermodynamic stability of the metastable Co_3W $L1_2$ phase, especially in the low temperature region, increases by the addition of Ga.

Keywords Co-W-Ga system, intermetallics, phase diagrams, phase transformation, precipitates

1. Introduction

Ni-base superalloys strengthened by γ'-Ni_3Al precipitates with an $L1_2$ structure are widely used as high-temperature materials for aircraft engines and industrial gas turbines.[1] The precipitation of the $L1_2$ compound phase in the γ (A1) disordered face-centered cubic (fcc) matrix phase is considered to be one of the key factors for alloy design because it results in superior high-temperature strength and creep properties. On the other hand, in the Co-based alloy systems the phase stability and crystal structure of geometrically close-packed (GCP) Co_3X phases[2-14] have been extensively studied, and the γ'-Co_3Ti has been reported to be the only stable $L1_2$ phase.[3-5] The melting temperature of Co_3Ti is, however, not sufficiently high to be used for the heat-resistant alloys. On the other hand, metastable $L1_2$ phases such as Co_3Al[6-8] and Co_3Ta[9-12] and a weak diffuse superlattice reflection due to $L1_2$-type short-range order in the Co-W binary system[13,14] have also been reported, but those binary ordered phases show low thermal stability and quickly change to stable phases. Thus, effective precipitate hardening due to the $L1_2$ phase has hardly been utilized in Co-base commercial alloys.

Recently, stable ternary $L1_2$-type compound phases, such as $Co_3(W, Al)$[15] and $Co_3(W, Ge)$,[16] have been found in the Co-W-Al and Co-W-Ge ternary systems, respectively. From these results, it can be said that the metastable Co_3W phase with $L1_2$ structure becomes stable due to the substitution of Al or Ge for W. This suggests the possibility that a new $L1_2$ ternary compound with high stability can be obtained in other Co-W-based systems. Ga is an element belonging to the same group as Al, and thus the Co-W-Ga system is of interest with regard to the phase stability of the $L1_2$ phase.

In the present study, the phase equilibria and the microstructure in Co-W-Ga ternary alloys were investigated, and a ternary compound phase with the $L1_2$ structure is herein reported.

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2. Experimental Procedures

Co-W-Ga alloys were prepared by arc melting under an argon atmosphere, the starting materials being Co (99.9%), W (99.9%), and Ga (99.99%), and the nominal composition range of the alloys being Co-(3-22)W-(7-30)Ga (at.%). For two ductile ingots, Co-7.4W-12.0Ga (nominally Co-8W-13Ga) and Co-9.3W-9.5Ga (nominally Co-10W-10Ga), hot-rolling was performed at 1200 °C. Small specimens cut from the hot-rolled sheets or the ingots were sealed in quartz capsules evacuated and backfilled with argon gas, and then equilibrating treatments were conducted at 900, 1000, 1100, and 1200 °C for periods between 72 and 672 h, followed by quenching in ice water. The specimens equilibrated at 900, 1000, and 1100 °C were homogenized at 1300 °C for 4 h before the equilibrating treatment.

Some specimens were solution-treated at 1300 °C for 4 h and subsequently aged at 800 °C or 900 °C for periods between 72 and 1008 h in order to investigate the phase stability, cold-rolling being performed before aging to promote atomic diffusion in some of them. Microstructural observation was carried out using a field emission scanning electron microscope (FE-SEM) and a transmission electron microscope (TEM). Thin foil specimens for the TEM observation were prepared by jet polishing in a solution of

20% perchloric acid and 80% ethanol. Compositions of the phase constituents were measured by an electron probe microanalyzer (EPMA) and a field emission electron probe microanalyzer (FE-EPMA). X-ray diffraction (XRD) analysis was carried out using Cu Kα radiation to identify the crystal structure of the bulk sample. The phase transition temperatures were determined by differential scanning calorimetry (DSC) under an argon gas atmosphere at a heating rate of 10 °C/min.

3. Results

3.1 Phase Equilibria at 900, 1000, 1100, and 1200 °C

Figure 1(a), (b), and (c) shows the back-scattering electron (BSE) images of the Co-15W-18Ga, Co-20W-30Ga, and Co-22W-7Ga alloys annealed at 1000 °C for 336 h, exhibiting typical three-phase microstructures of γ(A1) + β(B2) + μ(D8$_5$), $\beta + \mu + \alpha$(A2) and γ + χ(D0$_{19}$) + μ, respectively. It is suggested from Fig. 1(b) that the μ phase is formed by the peritectoid reaction of $\beta + \alpha \rightarrow \mu$, while the morphologies of the χ and μ phases shown in Fig. 1(c) are relatively similar to each other. The compositions of each phase determined by EPMA are listed in Table 1 and the isothermal section diagrams in the Co-rich portion of Co-W-Ga system at 900, 1000, 1100, and 1200 °C, including the phase boundary data of the Co-Ga and Co-W binary systems,[17,18] are shown in Fig. 2. The stable compound phases are the β, χ, and μ phases at 900 °C and 1000 °C, but only the β and μ phases at 1100 °C and 1200 °C. The solubilities of Ga in the χ and μ phases and of W in the β phase are limited and no ternary compound phase exists in the Co-rich region of the diagrams. Some three-phase regions such as $\gamma/\chi/\mu$, $\gamma/\beta/\mu$, and $\beta/\mu/\alpha$ occupy a wide range of the phase diagrams. It should be noted that a metastable γ' phase, which will be discussed in the following sections, was observed at 900 °C in the Co-7.4W-12.0Ga, Co-9.3W-9.5Ga, and Co-15W-18Ga alloys listed in Table 1.

3.2 Microstructural Change of Precipitates

Figure 3 represents the solubilities of the γ single-phase region at 1000, 1100, and 1200 °C shown in Fig. 2. It is seen that the solubility increases with increasing temperature. The Co-7.4W-12.0Ga and Co-9.3W-9.5Ga alloys, which are located in the γ single phase region at temperatures at least above 1200 °C, were selected to investigate the precipitation behavior of the γ' phase. Figure 4(a), (b), and (c) shows SEM images of the Co-9.3W-9.5Ga alloy annealed at 1000, 900, and 800 °C for 72 h after solution-treatment at 1300 °C, respectively, and Fig. 4(a′), (b′), and (c′) is their high-magnification micrographs. At 1000 °C, the χ and μ phases precipitate in the γ matrix and there is no other phase in this alloy. On the other hand, fine cuboidal precipitates are observed in addition to the χ phase at 900 °C and 800 °C, as shown in Fig. 4(b′) and (c′), these two-phase microstructures being similar to those of the Ni-base superalloys with the $\gamma + \gamma'$ structure. In order to identify the precipitate, TEM observation was carried out.

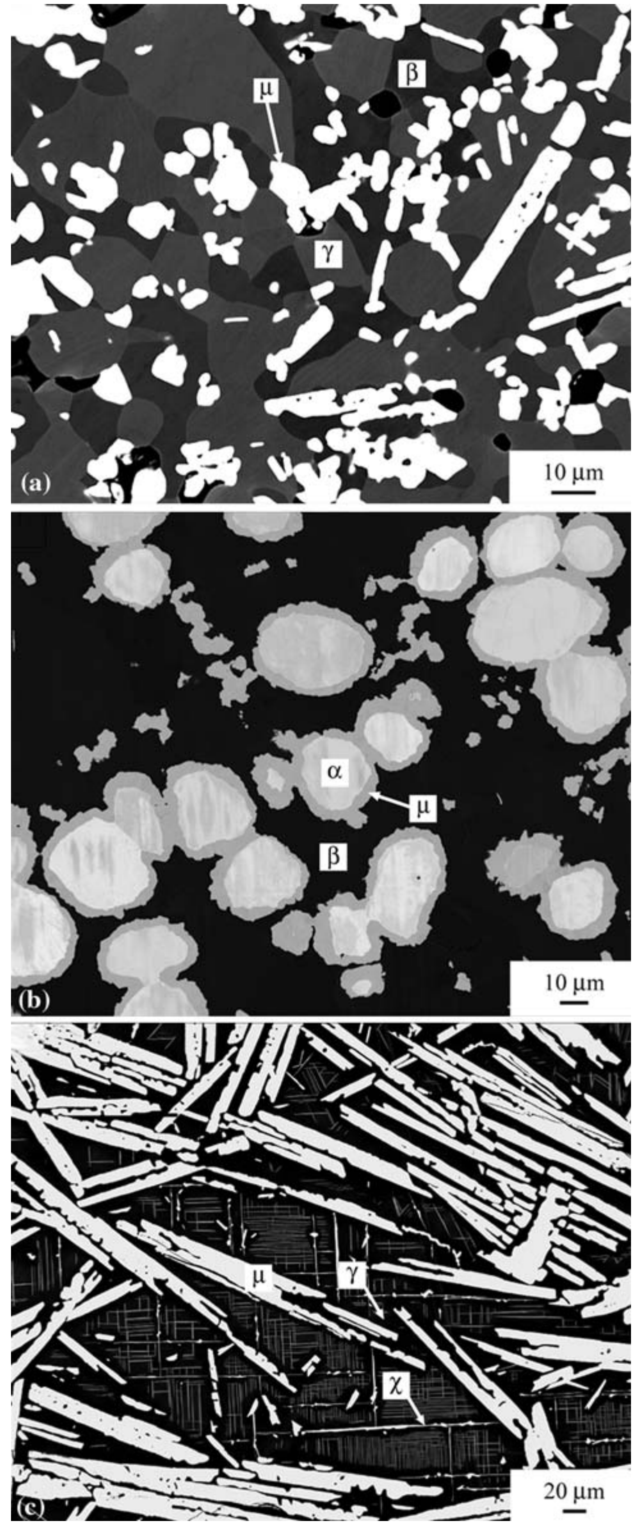

Fig. 1 Back-scattered electron images of (a) Co-15W-18Ga (at.%), (b) Co-20W-30Ga (at.%), and (c) Co-22W-7Ga (at.%) alloys annealed at 1000 °C for 336 h

Figure 5(a) and (b) shows a dark field image obtained using a superlattice reflection and a selected area diffraction pattern, respectively, taken from the Co-9.3W-9.5Ga alloy

Table 1 Equilibrium compositions of the Co-W-Ga system

		Composition, at.%													
		γ Phase		χ Phase		μ Phase		β Phase		α Phase		γ Phase*		γ′ Phase*	
Alloy composition, at.%	Treatment	W	Ga	W	Ga	W	Ga	W	Ga	W	Ga	W	Ga	W	Ga
Co-3W-25Ga	1200 °C, 72 h	3.3	18.7					2.5	26.9						
Co-15W-18Ga	1200 °C, 72 h	6.5	17.4			44.9	1.0								
Co-20W-30Ga	1200 °C, 280 h					48.6	3.4	3.9	34.4	99.0	0.0				
Co-22W-7Ga	1200 °C, 72 h	9.1	9.4			44.3	0.0								
Co-3W-25Ga	1100 °C, 168 h	3.2	17.7					2.5	27.5						
Co-15W-18Ga	1100 °C, 168 h	6.0	16.8			44.6	1.0	4.4	27.4						
Co-20W-30Ga	1100 °C, 192 h					45.2	3.3	3.8	34.7	98.9	0.0				
Co-22W-7Ga	1100 °C, 168 h	8.3	9.7			44.7	0.0								
Co-3W-25Ga	1000 °C, 336 h	3.3	16.9					2.5	28.3						
Co-15W-18Ga	1000 °C, 336 h	5.3	16.0			44.9	0.9	3.7	28.2						
Co-20W-30Ga	1000 °C, 336 h					45.5	2.8	3.4	35.9	99.3	0.0				
Co-22W-7Ga	1000 °C, 336 h	7.7	9.3	22.2	1.3	43.0	1.0								
Co-3W-25Ga	900 °C, 336 h	3.3	15.9					2.5	28.7						
Co-7.4W-12.0Ga	Cold-rolling + 900 °C, 336 h	5.2	14.0	21.6	1.8	45.4	0.7					6.5	13.0	11.2	11.4
Co-9.3W-9.5Ga	Cold-rolling + 900 °C, 672 h	5.4	12.0	21.8	0.8							**	**	**	**
Co-15W-18Ga	900 °C, 336 h	5.3	15.2			43.9	1.1	3.3	29.0			**	**	**	**
Co-20W-30Ga	900 °C, 672 h					44.6	2.9	3.1	36.3	99.0	0.0				

* Metastable phase

** Not determined

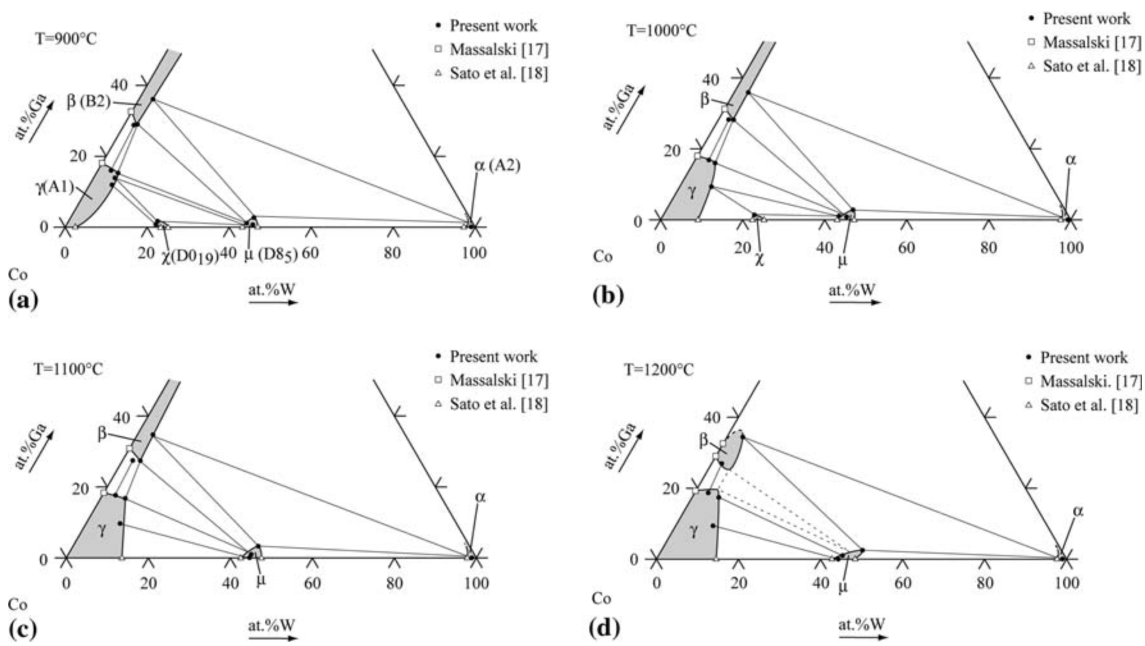

Fig. 2 Isothermal section diagrams of the Co-W-Ga ternary system in the Co-rich portion at (a) 900 °C, (b) 1000 °C, (c) 1100 °C, and (d) 1200 °C

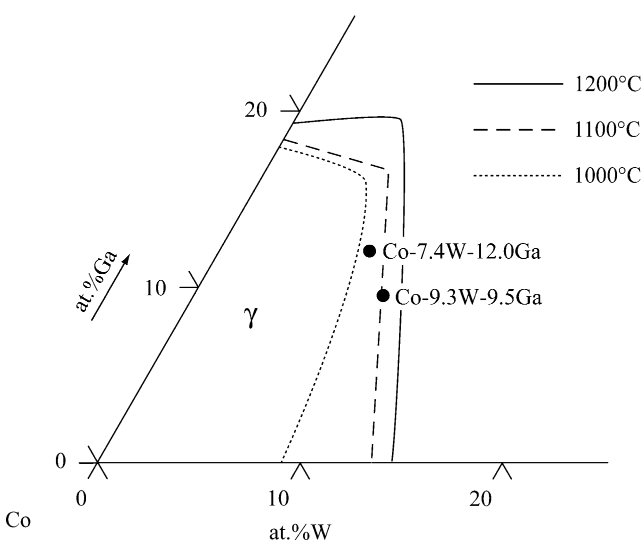

Fig. 3 Single-phase regions of the γ phase in the Co-W-Ga ternary system at 1000, 1100, and 1200 °C

annealed at 900 °C for 72 h. Fine cuboidal precipitates with a mean size of about 200 nm are observed in Fig. 5(a), and the crystal structures of the precipitate and matrix phase are identified as $L1_2$ and A1, respectively, from the diffraction pattern in Fig. 5(b).

3.3 Phase Stability of γ′ Phase at 800 and 900 °C

In order to investigate the phase stability of the γ′ phase, microstructural observation was carried out for the Co-9.3W-9.5Ga alloy subjected to various annealing conditions after solution treatment at 1300 °C. The phase constituents for those treatments are summarized in Table 2. Figure 6(a) shows a BSE image of the Co-9.3W-9.5Ga alloy annealed at 900 °C for 672 h. A three-phase microstructure consisting of the γ, γ′, and χ phases was observed in the same alloy annealed at 900 °C for 72 h, as shown in Fig. 4(b), while an additional phase μ appears due to the longer aging, as shown in Fig. 6(a).

Figure 6(b) and (c) shows BSE images of the Co-9.3W-9.5Ga alloy annealed at 900 °C for 96 and 672 h after cold-rolling with 50% reduction, respectively. Here, it is seen that only the γ and χ phases appear and neither γ′ nor μ phases exist. This confirms that the γ′ phase is metastable at 900 °C in this specimen. On the other hand, the γ′ phase appeared in Co-9.3W-9.5Ga alloy annealed at 800 °C for 1008 h after cold-rolling with 50% reduction, as exhibited in Fig. 6(d). Judging from these results, it can be said that the microstructural stability of the γ′ phase at 800 °C is higher than that at 900 °C in this sample, but it is not clear if the γ′ is a stable phase at 800 °C.

Figure 7(a) and (b) shows the microstructure of Co-7.4W-12.0Ga alloy annealed at 900 °C for 336 h after cold-rolling to 50% reduction. Three phases, i.e., γ′, μ, and χ, precipitated in the γ matrix in this ternary alloy. It is seen that the metastable γ′ phase did not precipitate in the vicinity of the χ and μ phases. As the size of the precipitate was sufficiently large, chemical composition analysis of this sample was carried out, the black ring in the γ′ precipitate particle in Fig. 7(b) being the contamination trace by FE-EPMA. The metastable equilibrium compositions of the γ and γ′ phases at 900 °C in Co-7.4W-12.0Ga are Co-6.5W-13.0Ga and Co-11.2W-11.4Ga, respectively,

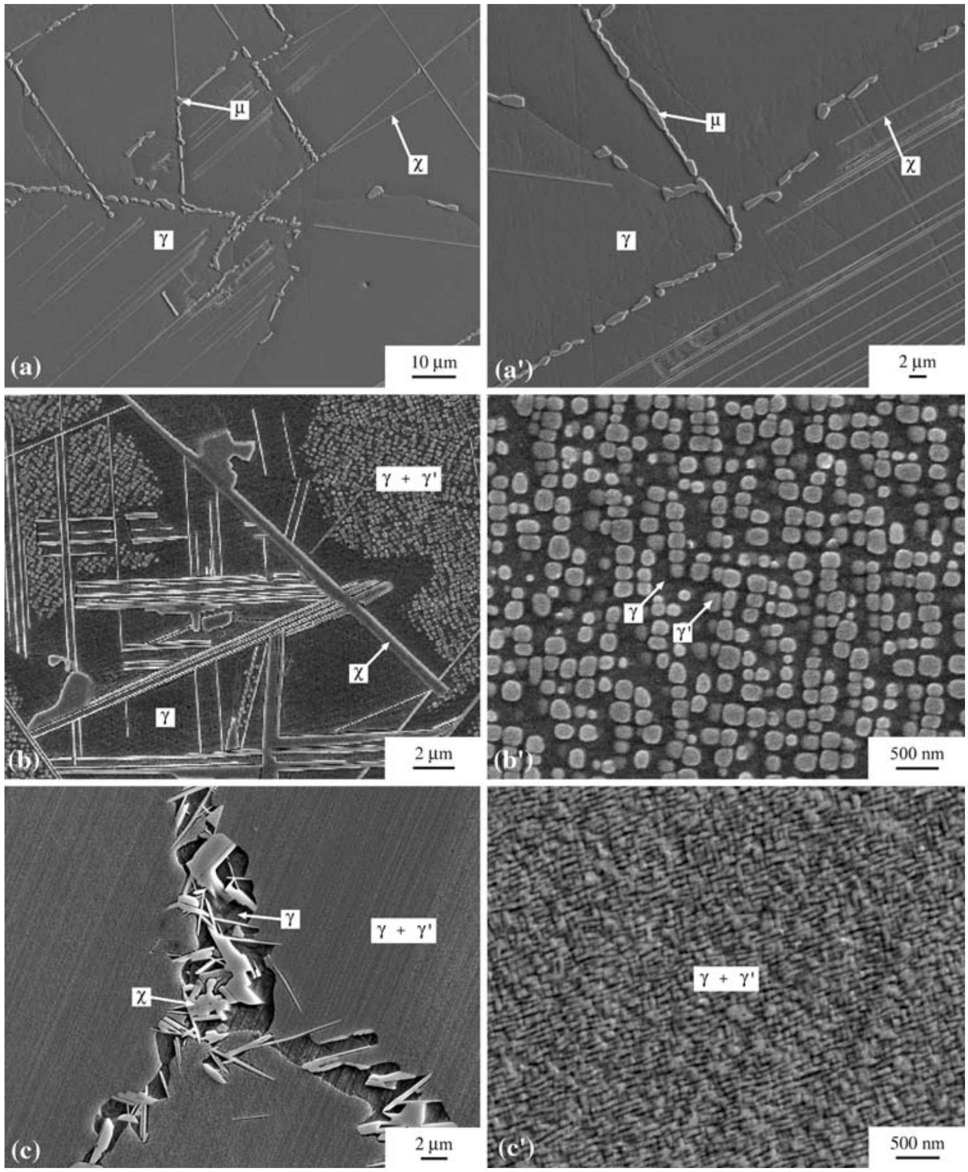

Fig. 4 Secondary electron images of the Co-9.3W-9.5Ga (at.%) alloy annealed at (a) and (a′) 1000 °C, (b) and (b′) 900 °C, and (c) and (c′) 800 °C for 72 h

as shown in Table 1 and are plotted in the isothermal section diagram at 900 °C in Fig. 8. In the γ′ phase, the composition of W is almost equal to that of Ga and the total composition of W and Ga is about 23%, which is comparable to that of W and Al in the γ′ phase in the Co-W-Al system[15] and that of W and Ge in the Co-W-Ge system.[16] It was also found that Ga has a tendency to partition to the γ phase rather than the γ′ phase, while W is a strong γ′ former.

Figure 9 shows the DSC heating curves obtained from the Co-7.4W-12.0Ga and the Co-9.3W-9.5Ga alloys solution-treated at 1300 °C for 4 h. There are peaks corresponding to a dissolution reaction of the γ′ phase, and the end temperatures defined as the metastable γ′ phase solvus in Co-7.4W-12.0Ga and Co-9.3W-9.5Ga alloys were determined to be 926 °C and 939 °C, respectively. The solvus temperature of the Co-9.3W-9.5Ga alloy was found to be slightly higher than that of the Co-7.4W-12.0Ga alloy.

Table 2 Phase constituents in the Co-9.3W-9.5Ga alloy under each condition

Treatment	Phase constituent
900 °C, 72 h	γ + γ′ + χ
900 °C, 672 h	γ + γ′ + χ + μ
Cold-rolling + 900 °C, 96 h	γ + χ
Cold-rolling + 900 °C, 672 h	γ + χ
Cold-rolling + 800 °C, 1008 h	γ + γ′ + χ

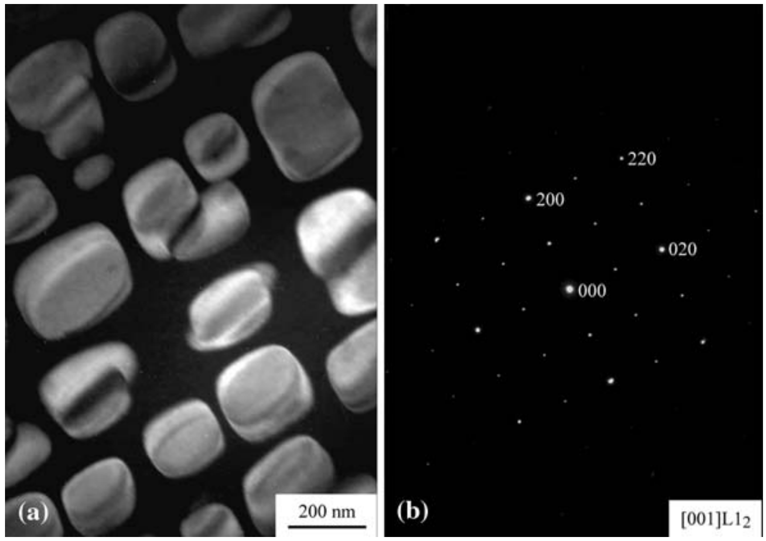

Fig. 5 Transmission electron micrograph of a Co-9.3W-9.5Ga (at.%) alloy annealed at 900 °C for 72 h. (a) Dark field image and (b) selected area diffraction pattern

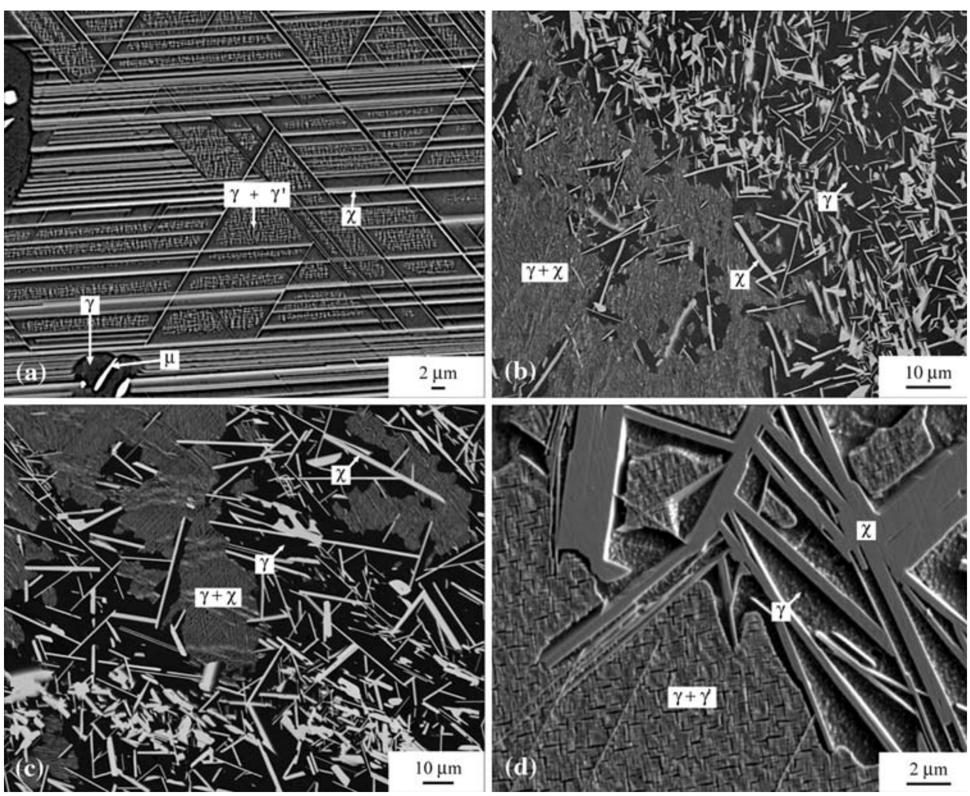

Fig. 6 Back-scattered electron images of the Co-9.3W-9.5Ga (at.%) alloy annealed at 900 °C for (a) 672 h, and 900 °C for (b) 96 h and (c) 672 h after cold-rolling with 50% reduction. (d) Secondary electron image of the Co-9.3W-9.5Ga (at.%) alloy annealed at 800 °C for 1008 h after cold-rolling to 50% reduction

In the Co-W binary system, the only data suggesting the precipitation of the γ' phase are limited to the presence of the weak diffuse superlattice reflection indicating the L1$_2$-type short-range order in the Co-5.2W (at.%) alloy,[13,14] and no $\gamma + \gamma'$ two-phase microstructure has been reported. In the Co-Ga binary systems there is no report on the

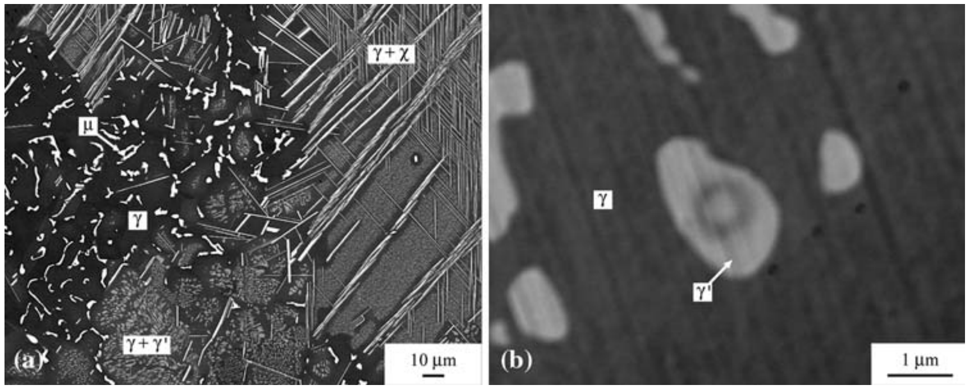

Fig. 7 (a, b) Back-scattered electron images of the Co-7.4W-12.0Ga (at.%) alloy annealed at 900 °C for 336 h after cold-rolling to 50% reduction

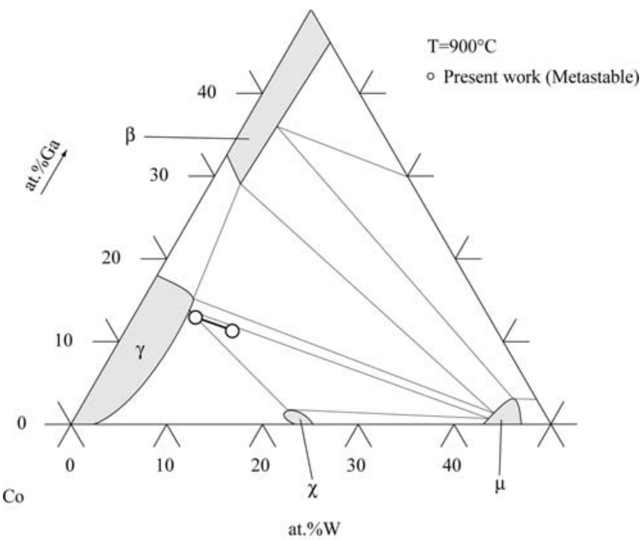

Fig. 8 Isothermal section diagram of Co-W-Ga ternary system in the Co-rich portion at 900 °C with the metastable phase boundary of γ and γ' phase

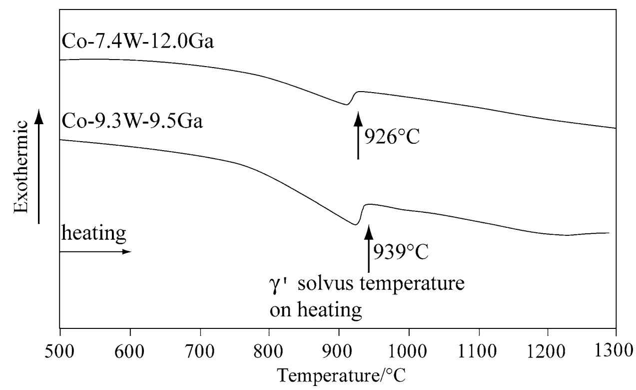

Fig. 9 DSC heating curves of Co-7.4W-12.0Ga and Co-9.3W-9.5Ga (at.%) alloys solution-treated at 1300 °C for 4 h

precipitation of the γ' phase. These facts suggest that the phase stability of the γ' phase increases due to the combination of W and Ga.

4. Conclusions

(1) Isothermal section phase diagrams of the Co-W-Ga ternary system in the Co-rich portion were determined at 1200, 1100, 1000 °C and 900 °C.

(2) The γ' phase with the $L1_2$ structure was found in Co-W-Ga alloys aged at 900 °C and 800 °C, and the $\gamma + \gamma'$ two-phase microstructure was observed to have cuboidal morphology.

(3) Microstructural observation revealed that the γ' phase obtained in Co-W-Ga alloys is a metastable phase at 900 °C and that the microstructural stability of the γ' phase is higher at 800 °C than that at 900 °C. The composition of the metastable γ' phase at 900 °C was determined to be Co-11.2W-11.4Ga (at.%).

(4) The solvus temperatures of the metastable γ' phase in the Co-7.4W-12.0Ga and the Co-9.3W-9.5Ga alloys were determined to be 926 °C and 939 °C, respectively.

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