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Review article

Experimental investigation and thermodynamic calculation of Ti-Co-Hf system

X.M. Huang[a], W.J. Zeng[a], J.L. Liu[a], G.M. Cai[a,*], S.H. Liu[b], H.S. Liu[a,*], Z.P. Jin[a]

[a] School of Materials Science and Engineering, Central South University, Changsha, Hunan 410083, PR China
[b] State Key Laboratory of Powder Metallurgy, Central South University, Changsha, Hunan 410083, PR China

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ABSTRACT

Phase relationship of Ti-Co-Hf ternary system, which may contribute to the development of both new Ti-based biomaterials and $Co_{11}Hf_2$ based rare-earth-free magnetic materials, have been studied by using Ti-Co-Hf diffusion triple and selected equilibrated alloys. Isothermal sections of the Ti-Co-Hf ternary system at both 1173 and 1073 K were experimentally determined by means of electron probe microanalysis (EPMA), scanning electron microscope (SEM) and X-ray diffraction (XRD). Meanwhile, structure refinements of three continuous solid solutions, i.e. Co(Ti, Hf)$_2$, Co_2(Ti, Hf) and BCC_B2 which were formed between $CoTi_2$ and $CoHf_2$, Co_2Ti(c) and Co_2Hf as well as CoTi and CoHf, respectively, were performed by Rietveld method. The stable temperature range of $Co_{11}Hf_2$ was revised to be from 1310 ± 12.5–1516 K. And Ti (about 3.7 at%) partly dissolves in $Co_{23}Hf_6$ at 1173 K while the solubility of Hf in Co_3Ti at both 1173 and 1073 K is relatively limited. Based on the available data of binary system, thermodynamic modeling of Ti-Co-Hf ternary system was carried out, with Co(Ti, Hf)$_2$, Co_2(Ti, Hf) and BCC_B2 being respectively described with models, (Co, Hf)$_1$(Co, Ti, Hf)$_2$, (Co, Ti, Hf)$_2$(Co, Ti, Hf)$_1$ and (Co, Ti, Hf, VA)$_{0.5}$(Co, Ti, Hf, VA)$_{0.5}$. A set of self-consistent thermodynamic parameters, which can reasonably reproduce the measured results, has been obtained.

1. Introduction

Titanium and its alloys have been increasingly applied in orthopedic and dental implants due to their excellent corrosion resistance, specific strength and outstanding biocompatibility [1,2]. However, high melting temperature, high elastic modulus, and high affinity for oxygen has limited their application as biomaterials [1,3]. Disadvantages of titanium and its alloys can be improved by the addition of alloying elements, such as Nb, Zr, Hf, Mo, Co and Cr [3,4]. For instance, Co and Hf have been used in implant alloys in dentistry and medicine for many years, e.g. the TiNiCo and Tiadyne 1610 ($Ti_{51.4}Hf_{9–10}Nb_{15.5–16.5}$) (in wt %) alloys [2,5]. Ti-based alloys with Co addition show higher strength [6,7] and have lower melting temperature which can alleviate many casting problems, especially at the eutectic composition. Since hafnium (Hf) belongs to the same group as titanium in the element periodic table and there is no any intermetallic compounds formed in Ti-Hf alloy system [8], Ti-Hf alloys can be expected to have better corrosion resistance characteristics [9,10]. Moreover, the addition of Hf can not only gently reduce the Young's modulus but also strongly enhance the strength of Ti-Hf alloys [11,12]. Meanwhile, $Co_{11}Hf_2$ based alloys, with the minor addition of Ti, Zr and B, are reported with high T_c (Curie temperature) and energy product value [13], and have been extensively studied recently as promising rare-earth-free magnetic materials [14–17].

In order to better understand the effects of Co and Hf addition in Titanium alloys for biomedical application and to acquire the phase-forming regulation of $Co_{11}Hf_2$-based magnetic materials, knowledge concerning phase equilibria and related thermodynamics of Ti-Co-Hf system is of fundamental importance.

Phase diagrams of Ti-Hf [8] and Ti-Co [18] binary systems have been well investigated and thermodynamically assessed, as shown in Fig. 1. There are three equilibrium phases existing in the Ti-Hf system, i.e. Liquid, BCC (β) and HCP (α). The latest version of Ti-Co binary phase diagram was reassessed and constructed by Davydov et al. [18], based on the evaluation reported by Murray [19]. According to the work of Davydov et al. [18], the Ti-Co system contains Liquid, A3 (Co- and Ti-rich hcp), αCo, βTi (BCC_A2), and five intermediate phases, i.e. Co_3Ti, Co_2Ti(h), Co_2Ti(c), CoTi and $CoTi_2$. The congruent melting temperature of CoTi was determined to be 1776 ± 5 K [18].

Differing from Ti-Hf and Ti-Co systems, some controversies exist in Co-Hf system. The early Co-Hf binary phase diagram reviewed by Ishida et al. [20] consists of five intermetallic phases, i.e. Co_7Hf, $Co_{23}Hf_6$,

* Corresponding authors.
E-mail addresses: caigemei@csu.edu.cn (G.M. Cai), hsliu@csu.edu.cn (H.S. Liu).

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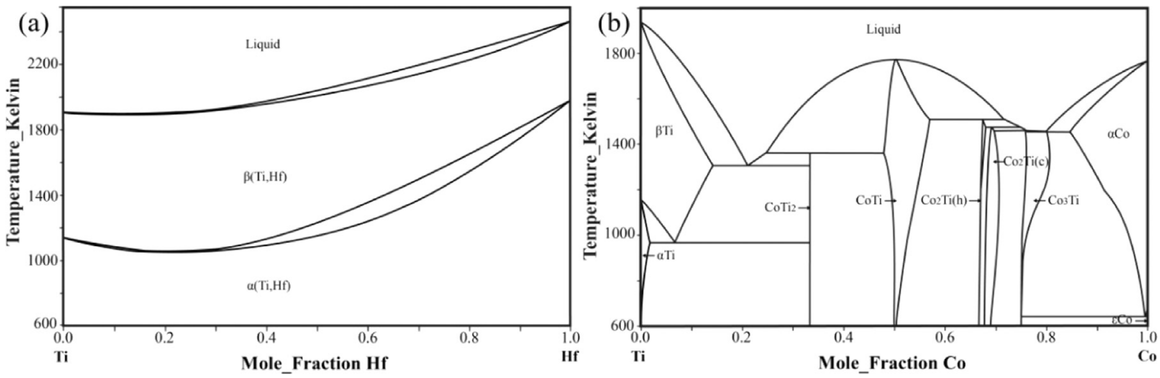

Fig. 1. The phase diagram of (a) Ti-Hf [8] and (b)Ti-Co [18] binary system.

Table 1
Stable solid phases in the Ti-Co-Hf system.

Phase	Stability range (K)	Person symbol	Prototype	Space group	Reference
εCo	< 640	hP2	Mg	*P6*$P6_3/mmc$	Cacciamani et al. [24]
αCo	640 < T < 1768	cF4	Cu	*Fm3m*	Cacciamani et al. [24]
Co_3Ti	< 1455	cP4	$AuCu_3$	*Pm3m*	Cacciamani et al. [24]
Co_2Ti(c)	< 1475	cF24	$MgCu_2$	*Fd3m*	Cacciamani et al. [24]
Co_2Ti(h)	< 1515	hP24	$MgNi_2$	$P6_3/mmc$	Cacciamani et al. [24]
CoTi	< 1723	cP2	CsCl	*Pm3m*	Cacciamani et al. [24]
$CoTi_2$	< 1333	cF96	$NiTi_2$	*Fd3m*	Cacciamani et al. [24]
αTi	< 1764	hP2	Mg	$P6_3/mmc$	Cacciamani et al. [24]
βTi	1155 < T < 1963	cI2	W	$Im\bar{3}m$	Cacciamani et al. [24]
$Co_{11}Hf_2$	923 < T < 1546	–	Orthorhombic	*B-centered*	Li et al. [23]
$Co_{23}Hf_6$	< 1599.5	cF116	Th_6Mn_{23}	*Fm3m*	Lu et al. [21]
Co_2Hf	< 1943	cF24	$MgCu_2$	*Fd3m*	Lu et al. [21]
CoHf	< 1913	cP2	CsCl	*Pm3m*	Lu et al. [21]
$CoHf_2$	< 1588	cF96	$NiTi_2$	*Fd3m*	Lu et al. [21]
βHf	1963 < T < 2016	cI2	W	$Im\bar{3}m$	Lu et al. [21]
αHf	< 1963	hP2	Mg	$P6_3/mm$	Lu et al. [21]

Co_7Hf_2, CoHf and $CoHf_2$, and four terminal solid solutions. Among these intermetallic phases, the $Co_{23}Hf_6$ phase is reported stable at the temperature range of 1223–1548 K. Subsequently, phase diagram of the Co-Hf system was experimentally reconstructed and thermodynamically reassessed by Lu et al. [21,22]. The early reported phases Co_7Hf_2 and Co_7Hf [20] were not confirmed by Lu et al. [21]. Nevertheless, the orthorhombic phase $Co_{11}Hf_2$ which exists stably from 923 to 1546 K was found for the first time in Lu's work [21]. Additionally, $Co_{23}Hf_6$ was found to be stable down to room temperature instead of 1223–1548 K in Ref. [20]. Recently, phase relations in the composition ranging from Co_4Hf to Co_8Hf in the Co-Hf system were reinvestigated by Li et al. [23]. In the work of Li et al., the Co_7Hf and $Co_{11}Hf_2$ phases were regarded to be one common phase.

Crystal structure data for solid phases in the constituent binary systems, Ti-Hf, Ti-Co and Co-Hf, are summarized in Table 1.

So far, phase diagrams or phase relationships in the Ti-Co-Hf ternary system have been scarcely studied. The present work intends to measure phase relations of the Ti-Co-Hf ternary system at 1073 and 1173 K using diffusion triples and equilibrated alloys, and then thermodynamically assess the Ti-Co-Hf ternary system in virtue of CALPHAD method.

2. Experimental details

Diffusion-triple approach [25,26] and equilibrated-alloys method were employed to determine the phase equilibrium of Ti-Co-Hf system. Pure titanium (99.99% Ti), cobalt (99.99% Co), and hafnium (99.95% Hf) were used as starting materials for diffusion triples and alloying samples.

The fabrication procedure of the diffusion triple is shown schematically in Fig. 2. The dimensions of Ti and Hf pieces in the diffusion triple are all 3 × 4 × 5 mm, while that of Co is 6 × 4 × 5 mm. All the pure metal pieces were cut into shapes using electrical discharge machining (EDM), and the re-cast layer on the EDM's surfaces was removed by SiC paper. It's worth noting that all of the blocks were ultrasonically cleaned in alcohol before being placed together. The Ti-Hf couple was first heated at 1173 K kept 8 h for diffusion-bonding in vacuum furnace. Then, the diffusion triple was assembled from the Ti-Hf couple and the pure Co block at 1173 K for 8 h. Subsequently, the prepared triples were sealed in evacuated quartz capsules and annealed at 1073 and 1173 K for 1440 and 960 h, respectively. After annealing, the tubes with samples were taken out and broken to make the samples quickly quench into ice water. It is worth mentioning here that all the samples were wrapped by Ta sheet during the heat treatment processes in order to minimize the oxidation of the diffusion triples.

To confirm the phase relations determined from diffusion triple, a set of button alloys (5 g) in different compositions were prepared by arc-melting on a water-cooled copper plate under purified argon atmosphere with titanium as getter material placed in the arc chamber. Each ingot was melted 3 times to ensure homogeneity. Afterwards, the ingots were generally cut into three pieces by EDM. One piece of each alloy was used for analysis of as-cast microstructure, and the others