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Ternary Hf–Co–Sn system

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Abstract

The isothermal sections of the phase diagram of the Hf–Co–Sn ternary system have been constructed at 770 and 870 K. The presence of three ternary intermetallic compounds crystallized with known structure types was confirmed and a new ternary compound was found.

Keywords: Intermetallics; Casting; X-Ray diffraction; Phase diagrams

1. Introduction

The interaction of the IVb-group elements Ti, Zr, Hf with iron group transition metals and tin within ternary systems was not sufficiently investigated before. The phase equilibria in the M–Co–Sn ternary systems (M–Ti, Zr, Hf) have already been constructed only for the Zr–Co–Sn system [1]. Other systems with Co were studied only to obtain new compounds and to investigate their physical properties [2].

In this paper we present the isothermal sections of the Hf–Co–Sn ternary system at 770 and 870 K.

The binary Hf–Co and Co–Sn systems, which bound the Hf–Co–Sn ternary system are taken from Massalski [3] and the crystal structures of the intermediate compounds are taken from Villars and Calvert [4]. The phase diagram of the binary Hf–Sn system had been partially constructed [3], including four binary compounds namely Hf_5Sn_3, Hf_5Sn_4, HfSn and $HfSn_2$.

2. Experimental

Samples were prepared by a direct arc melting of the pure metal pieces (hafnium, purity is 99.9 wt.%; cobalt, purity in 99.99 wt.%; tin, purity in 99.999 wt.%) in pure Ti-gettered argon atmosphere. Then the as-cast alloys were annealed at 870 K (up to 50 at.% Sn) and 770 K (more than 50 at.% Sn) in the evacuated (0.1 Pa) quartz tubes for 1 month and quenched in cold water.

Phase analysis was carried out using X-ray powder film data obtained with the Debye–Scherrer technique (RKD-57.3 camera, CrK radiation) and using powder patterns obtained by the DRON-2.0 diffractometer (FeK_α radiation). Calculation of the unit cell parameters and theoretical patterns were accomplished using the CSD program package.

3. Results and discussion

Phase equilibria in the Hf–Co–Sn system were studied by means of X-ray analysis of the 97 ternary alloys annealed at 770 and 870 K, respectively. The isothermal sections of the phase diagram are presented in Fig. 1. The phase analysis shows a new ~$Hf_{15}Co_{20}Sn_{65}$ ternary stannide and three previously known HfCoSn [2,5], $HfCo_2Sn$ [6] and $Hf_6Co_{1.5+x}Sn_{1.5-x}$ [7] compounds. Crystallographic characteristics of the ternary compounds are collected in Table 1. For the $HfCo_{2-x}Sn$ (type $MnCu_2Al$) compound, a homogeneity region at $x=0$–0.5 was observed. The compound of ~$Hf_{15}Co_{20}Sn_{65}$ composition is isostructural to the cubic ~$Zr_{15}Co_{20}Sn_{65}$ phase [1] with unknown crystal structure.

The X-ray analysis confirmed the existence of the solid solution formed by the insertion of cobalt into the Hf_5Sn_3 (Mn_5Si_3 type) binary compound, which can be described as $Hf_5Co_xSn_3$, where $x=0$–1.0 and lattice parameters range from $a=0.8385(5)$, $c=0.5723(3)$ to $a=0.8435(6)$, $c=0.5737(7)$ nm.

No solid solutions based on the other binary compounds in this system were observed.

The Hf–Co–Sn system is analogous to the previously investigated Zr–Co–Sn system [1] when comparing their

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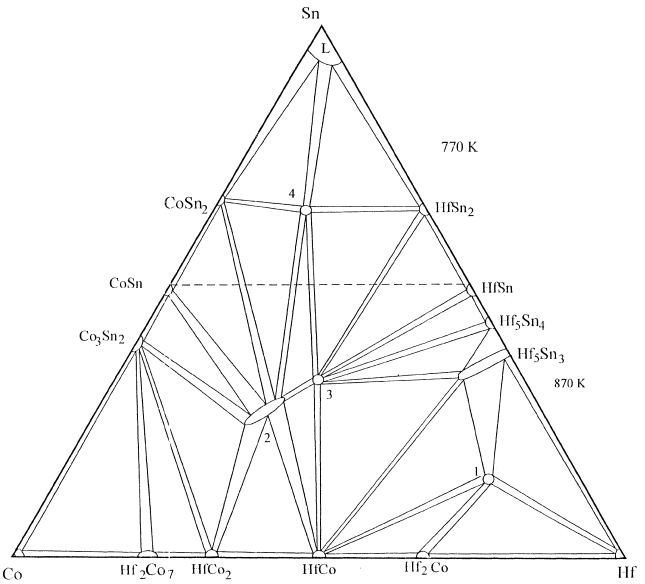

Fig. 1. Isothermal sections for the Hf–Co–Sn system at 870 K (0–50 at.% Sn) and at 770 K (50–100 at.% Sn).

phase equilibria, the number of the present ternary compounds and the structure types of these appropriate compounds. It is remarkable that in the Zr–Co–Sn and Hf–Co–Sn systems the equiatomic compounds have a ZrNiAl structure type that is a superstructure to Fe_2P. $Zr_6Co_{1.5+x}Sn_{1.5-x}$ and $Hf_6Co_{1.5+x}Sn_{1.5-x}$ stannides are crystallized with their own structure type also being the superstructure to Fe_2P. But the way of generation of these phases is somewhat different. In the equiatomic ZrCoSn and HfCoSn compounds the Fe atom positions in Fe_2P are occupied by Hf(Zr) and Sn atoms, while Co and statistical mixture of (Co,Sn) atoms occupy the P atoms positions. Characteristic of the ZrCoSn and HfCoSn compounds is the appearance of nets of trigonal prisms occupied by Co atoms that is in accordance with atomic radius of this component. But in another crystal structure the Zr(Hf) atoms are situated on the prism vertices but Co and Sn atoms take the place of the atoms with the lesser dimensions, respectively.

It is interesting that in the investigated Hf–Co–Sn and Zr–Co–Sn systems the equiatomic compounds crystallize with ZrNiAl type structure whereas TiNiSn, ZrNiSn and HfNiSn with their respective ternary nickel systems have the cubic MgAgAs structure type. These compounds with cubic *F43m* space group structures may be generated at a certain valence electron number per formula unit namely equal to 8. The increase of the valence electron number in the HfCoSn and ZrCoSn compounds results in the formation of a more close-packed structure (for example ZrNiAl type). In contrast to the MNiSn semiconducting stannides [8] the HfCoSn and ZrCoSn compounds are characterized by a metallic type of electrical conductivity [2].

It is possible that the atomic dimension factor is of importance in the generation of the MCoSn compounds. To make a comparison we note that Ti with a smaller atomic radius than Zr or Hf atoms forms a ternary compound with an MgAgAs structure [2].

4. Conclusions

The isothermal sections of the phase diagram of the ternary Hf–Co–Sn system at 870 K (0–50 at.% of tin) and 770 K (more than 50 at.% of tin) were constructed by means of X-ray analysis.

The presence of three early known ternary compounds was confirmed and a new unresolved intermetallic compound with the approximate $Hf_{15}Co_{20}Sn_{65}$ composition was found.

The existence of the $Hf_5Co_xSn_3$ solid solution based on Hf_5Sn_3 binary compound was confirmed.

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Table 1
Crystallographic data for the ternary Hf–Co–Sn system

No.	Compound	Structure type	Space group	Unit cell parameters, nm		Ref.
				a	*c*	
1	$Hf_6Co_{1.65}Sn_{1.35}$	$Zr_6Co_{1.65}Sn_{1.35}$	*P62m*	0.7906(3)	0.3415(1)	[1]
2	$HfCo_{2-x}Sn$	$MnCu_2Al$	*Fm3m*	0.6125–0.6185		[2]
3	HfCoSn	ZrNiAl	*P62m*	0.7140	0.3527	[2]
4	~$Hf_{15}Co_{20}Sn_{65}$	Unresolved structure				

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