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Constitution of the Hf–Ni system up to 50 at.% Ni

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Abstract

The Hf–Ni system phase diagram has been reinvestigated in the hafnium-rich composition range up to 50 at.% Ni. Two intermetallic compounds Hf_2Ni and HfNi melting congruently at 1220 °C and 1505 °C, respectively, were observed. There are two eutectics: $L \rightleftharpoons \beta\text{-Hf} + Hf_2Ni$ with about 29 at.% Ni at 1145 °C and $L \rightleftarrows Hf_2Ni + HfNi$ with about 35 at.% Ni at 1175 °C. Allotropic transformation in HfNi takes place at 1150 °C. The cubic CsCl-type crystal structure of the high temperature modification of HfNi has been determined indirectly for the first time.

1. Introduction

The phase relations in the Hf–Ni system have been investigated more than once [1]. However, information on the phase diagram in the composition range 0–50 at.% Ni is less than satisfactory [2]. As the experimental thermodynamic data on intermediate phases were absent, the authors [2] carried out optimization and the calculation of the Hf–Ni phase diagram, having taken the variant as a principle [3]. Results obtained differ from initial results and, in the opinion of the authors [2], are approximate, needing experimental confirmation. According to the latest publication [4], the calculated diagram of the Hf–Ni system [2] is not acceptable on account of an unrealistic thermodynamic parameter obtained, and the Hf–Ni system diagram is subject to further study.

The doubts over the reliability of the accepted Hf–Ni variant phase diagram in the range 0–50 at.% Ni [1] was because of investigations of phase relations in the ternary Ti–Hf–Ni system. The first results obtained for alloys near the Hf–Ni side have led to the necessity of revising the phase equilibria in the binary system. Our reinvestigation of the Hf–Ni alloys with 0–50 at.% Ni was performed before the publication of ref. 2. Its results confirm [2] the method of formation of the Hf_2Ni phase and the presence of two eutectics. The temperatures of the invariant reactions and the compositions at the eutectic points differ from the calculated temperature values.

2. Experimental procedure

The Hf–Ni alloys with 12 compositions in the range 0–50 at.% Ni were prepared in an arc furnace with a non-consumable electrode in a water-cooled copper boat under an argon atmosphere. The purity of the starting metals used was as follows: Hf 99.5%; Ni 99.99%. The weight losses on melting were generally small, so nominal compositions are reported. Investigation of as-cast and annealed alloys was carried out using metallographic, differential thermal, X-ray and electron microprobe analyses [5]. The alloys were annealed at 1200 °C, 1100 °C and 1000 °C for 16 h, 55 h and 33 h respectively. The alloys containing 3 and 5 at.% Ni were annealed at 1220 and 1600 °C to confirm the metatectic nature of β-Hf solid solution transformation.

3. Results and discussion

The results of this investigation are shown in Fig. 1. The Hf_2Ni (θ) compound crystallizes from the melt at the maximum temperature of 1220 °C. Single-phase, stoichiometric composition alloys were rather difficult to obtain and no homogeneity region was determined for this phase. The tetragonal, $CuAl_2$-type structure with $a = 6.42$ Å and $c = 5.32$ Å for the Hf_2Ni compound was confirmed [1].

The phase on the base of the equiatomic compound HfNi crystallizes from the melt at 1505 °C, has no range of homogeneity and exists in two allotropic modifications. The transformation temperature of HfNi in the solid state was found to be 1150 °C; that is close

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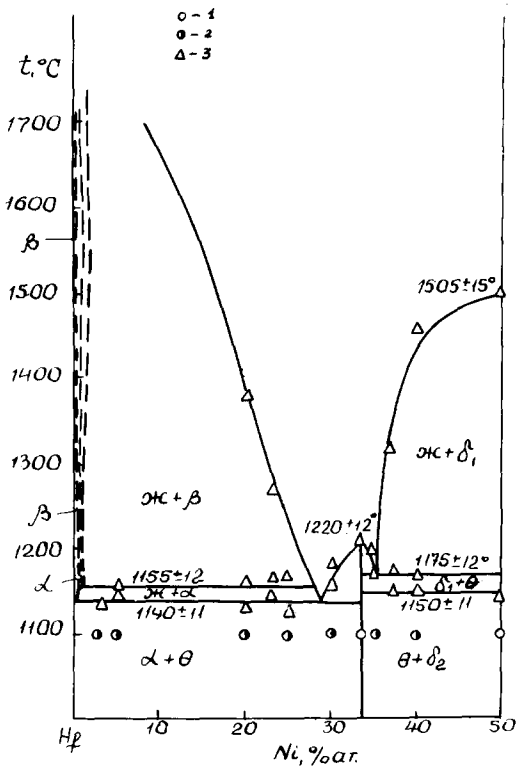

Fig. 1. Hf–Ni system state diagram in the range 0–50 at.% Ni: 1, single-phase alloys; 2, two-phase alloys; 3, DTA data.

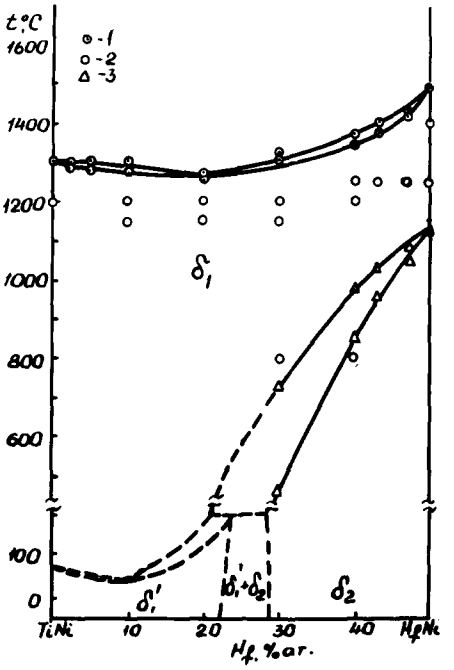

Fig. 2. Hf–Ni system state diagram: 1, DTA data on the melting of alloys; 2, single-phase alloys; 3, DTA data on the transformation in the solid state.

to previous results [3]. X-ray investigation confirms the data [1] concerning the crystal structure of the low temperature HfNi modification (δ_2) as orthorhombic, CrB-type structure with the lattice periods $a=3.21$ Å, $b=9.99$ Å and $c=4.10$ Å. The crystal structure of the high temperature modification of HfNi (δ_1) was not established earlier and according to ref. 3 it cannot be quenched.

The phase relations in the Ni–Hf–Ti system at the TiNi–HfNi section permit the assumption of the δ_1-HfNi phase crystal structure [6]; the TiNi–HfNi section is quasi-binary and its diagram of melting has continuous solidus and liquidus curves with minima at about 20 at.% Hf and 1250 °C (Fig. 2). On the micrographs of the alloys one can see grains of the primary material phase with the signs of transformation in the solid.

These data let us state that continuous solid solutions were formed during the crystallization of TiNi–HfNi alloys. As the high temperature phase of TiNi is known to have a cubic, CsCl-type crystal structure, the crystal structure of HfNi at subsolidus temperatures should be the same.

Metallographic investigation of as-cast samples showed the composition of liquid in the eutectic $L \rightleftharpoons \delta_1 + \theta$ at 1175 °C to be about 35 at.% Ni. From analysis of the peak changes in the thermal curves *vs.* the composition of the alloys containing 3–25 at.% Ni, and metallographic examination of alloys with 3 and 5 at.% Ni, the nature of the β-Hf phase transformation was established to be metatectic: an invariant process related to the reaction $\beta \rightleftharpoons \alpha + L$ occurs at a higher temperature (1155 °C) than for eutectic $L \rightleftharpoons \alpha + \theta$ (1135 °C). The eutectic composition is about 29 at.% Ni according to the electron microprobe analysis results. Thus, the Hf–Ni phase diagram in the range 0–50 at.% Ni presented in Fig. 1 differs from that accepted in ref. 3 and confirms conclusions [2] about the character of transformations in the system.

Increasing the ordinal number of group IV metals results in increases in the phase formation temperatures (984, 1120, 1220 °C) of Me_2Ni: the method of its formation changes from incongruent (Ti_2Ni) to congruent (Zr_2Ni, Hf_2Ni). This is reflected in the thermodynamic properties of these phases [7]: $\Delta H_f = -27$ (Ti_2Ni), -37 (Zr_2Ni) and -47 (Hf_2Ni) kJ mol^{-1} confirming the increase in their stabilities in this row. (The value of ΔH_f for Hf_2Ni is estimated.) Such a regularity in the change in thermodynamic character is not observed in the case of other iron group metals or copper as partners of hafnium in the compound Hf_2Me.

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