REACTION OF EQUIATOMIC BINARY COMPOUNDS IN TERNARY SYSTEMS
FORMED BY GROUP-IV TRANSITION METALS WITH NICKEL

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In previous work on ternary systems M^{IV}–M^{IV}–Ni we studied the reaction of equiatomic intermetallic compounds of binary systems formed by group-IV transition metals with a common component, nickel. The data are of interest since they can be used to track changes in the structure of phase diagrams when one of the components is replaced by an analog with a different atomic number. These diagrams reflect the difference in the metal-chemical properties of the intermetallic compounds.

According to the phase diagrams of the binary systems Ti–Ni, Zr–Ni, and Hf–Ni (Fig. 1), the phases based on the equiatomic compounds TiNi, ZrNi, and HfNi crystallize from the melt with a maximum on the liquidus curves at 1300, 1260, and 1530°C, respectively [1]. Phases based on ZrNi and HfNi do not have an appreciable homogeneity region while TiNi dissolves about 5 at. % Ni at 1000°C. At room temperature the homogeneity region of the TiNi-based phase narrows down to 1 at. %.

Compounds formed by metal-analogs with a common component have a different crystal structure: the high-temperature TiNi modification has the CsCl structure from the melting point to the martensite transformation point ~80°C while the low-temperature modification has the AuCd orthorhombic structure with a monoclinic distortion; as shown elsewhere [2], ZrNi has the orthorhombic CrB structure over the entire temperature range.

The phase based on HfNi has a CrB base-centered orthorhombic structure, as ZrNi does, at room temperature.

According to the results of [3], a thermal effect is observed at 1170°C in alloys containing HfNi. It has been suggested that two modifications of this compound exist. The high-temperature phase could not be preserved by quenching and its crystal structure has not been determined.

The experimental and calculated heats of formation of titanium, zirconium, and hafnium mononickelides indicate that these compounds have considerable thermodynamic stability, which increases with the atomic number of the group-IV metal:

Compound	TiNi	ZrNi		HfNi	
ΔfH, kJ/mole	−33.9	−73.4	−52	−118.5	−64.9
Source	[4]	[5]	[6]	[7]	[8]

The discussion above gives reason to suppose that the systems TiNi–ZrNi, ZrNi–HfNi, and TiNi–HfNi formed by equiatomic compounds will be quasibinary.

The literature give data about the effect of small additives of zirconium and hafnium, on the martensite transformation temperature (M_n) [9-11]. They are contradictory and agree only in that 1 at. % additions of these metals have little effect on M_n.

We studied the systems TiNi–ZrNi, TiNi–HfNi, and ZrNi–HfNi by microstructural, x-ray, and differential-thermal analysis (DTA) (transformation data were obtained from annealed samples during heating) as well as local x-ray spectral analysis (LXSA) of cast and annealed alloys, prepared in an arc furnace by melting components together (titanium, zirconium, and hafnium iodides; grade N–0 nickel).

Difficulties were encountered in the study since the nickelides TiNi, ZrNi, and HfNi are plastic materials; cold working and deformation during the preparation of thin sections of alloys based on these materials changed the crystal structure and microstructure. The plasticity of the phases based on these compounds decreased with growing atomic number of the group-IV metals.
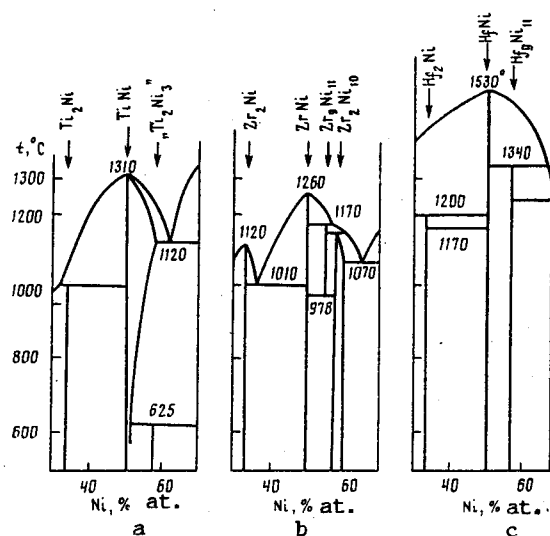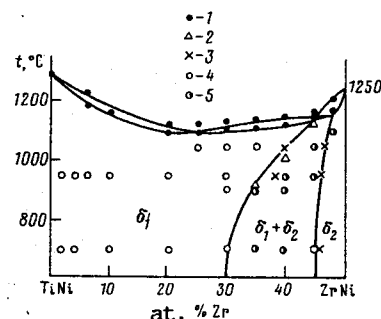
Fig. 1. Phase diagrams of the Ti—Ni (a), Zr—Ni (b), and Hf—Ni (c) systems in the domain of equiatomic phases.

Fig. 2. Phase diagrams of the TiNi—ZrNi system: 1) solidus and liquidus temperature of the alloys from DTA data; 2) solid-state transformation according to DTA data; 3) LXSA data; 4) one-phase alloys; 5) two-phase alloys.

The fusibility diagram of the TiNi—ZrNi system is characterized by a very flat minimum on the solidus and liquidus at 1100°C and ~25 at. % (Fig. 2, Table 1). A solid solution based on the cubic CsCl-type modification of TiNi (δ_1) crystallizes from the melt over a wide range of compositions (0-46 at. % Zr). The solid solution based on ZrNi (δ_2) with the CrB structure crystallizes from melts containing 48-50 at. % Zr. The peritectic transformation δ_2 + liq. $\rightleftarrows$ δ_1 occurs in a narrow range of compositions at 1160°C.

This interpretation of the data on the solidus and liquidus temperatures of TiNi—ZrNi alloys [with allowance for the fact that up to the melting point ZrNi preserves the same modification as at room temperature (CrB type)] is the only possible one, even though we did not observe the microstructure, characteristic of the peritectic transformation, in cast alloys containing 45 and 48 at. % Zr. The two-phase region δ_1 + δ_2, which is very narrow near the solidus, expands to 15 at. % as the temperature is lowered to 700°C.

The data on the effect of zirconium on the martensite transformation in TiNi are ambiguous. Thermochemical methods did not reveal a transformation in alloys with 2-6% at. % Zr and the results of microstructural and x-ray analyses indicate that these alloys undergo transformation above room temperature.

In the ZrNi—HfNi system the low-temperature modification of the compound of HfNi with ZrNi forms a continuous series of solid solutions (δ_2) (Fig. 3, Table 1) with the CrB structure. The unit-cell parameters of this phase, measured at room temperature, virtually do not change as the zirconium (or hafnium) content varies in the solid solution because zirconium and hafnium are so close in atomic size.

A continuous series of solid solutions based on the high-temperature HfNi modification (δ) with unknown type of crystal lattice crystallizes from melts of the ZrNi—HfNi system (judging by the microstructure of cast alloys) over a wide range of compositions (10-50 at. % Hg).

The microstructure of these alloys is represented by inherited polyhedra, inside which characteristic features of solid-state transformations are visible.

DTA data on alloys of this system show that when their zirconium content increases the solidus temperature of the alloys decreases continuously from the HfNi melting point (1505°C) and the temperature of the transition from the phase with the CrB structure (δ_2) to the high-temperature phase rises to 1265°C, which is the solidus temperature of the alloy containing about 47 at. % Zr.

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TABLE 1. Data from Differential Thermal Analysis of Alloys of the Systems TiNi–ZrNi, ZrNi–HfNi, and TiNi–HfNi

Composition of alloy, at. %	t_{sol}, °C	t_{liq}, °C	t_{trans}, °C	
			onset	end
TiNi – ZrNi				
Zr				
0	–	1300	--	–
6	1190	1230	–	–
10	1160	–	–	--
20	1100	1130	–	–
25	1100	1140	–	–
30	1120	1140	–	–
35	1110	1145	910	–
40	1130	1160	1050	–
45	1150	1165	1145	–
48	1180	1225	–	–
50	–	1250	–	–
ZrNi – HfNi				
Hf				
1	1245	1270	–	–
3	1265	1280	1235	1265
5	1250	1275	1220	1245
10	1265	1300	1200	1240
20	1310	1350	1180	1210
30	1335	1400	1180	1210
40	1420	1460	1150	1190
45	1440	1480	1180	1195
50	–	1505	1140	–
TiNi – HfNi				
Hf				
2	1295	1300	–	–
4	1295	1300	–	–
10	1290	1300	–	–
20	1260	1270	–	–
30	1310	1330	460	730
40	1345	1375	850	980
43	1380	1420	960	1040
47	1420	1430	1050	1080

Notes. t_{sol} and t_{liq} are the solidus and liquidus temperatures; t_{trans} is the solid-state transformation temperature of the alloys.

This position of the $\delta_1/(\delta_1 + liq)$ and $\delta_1/(\delta_1 + \delta_2)$ phase boundaries in the phase diagram suggests a three-phase equilibrium with the participation of the liquid phase and two solid phases $(\delta_1 + \delta_2)$. This equilibrium is of the peritectic type liq + $\delta_1 \rightleftarrows \delta_2$, where the coexisting phases are of similar composition (differing by only 2-3 at. %). The temperature of this equilibrium (1265 + 12)°C is close to the melting point of zirconium nickelide of equiatomic composition (1250 + 12)°C. The phase δ_1 based on the high-temperature modification of HfNi is not quenched and so its crystal structure in these alloys was not determined.

The fusibility diagram of the TiNi–HfNi system, drawn from DTA data, is represented by continuous liquidus and solidus curves with a shallow minimum at ~20 at. % Hf and ~1250°C (Fig. 4, Table 1). The crystallization interval of the alloys is small, especially for titanium-rich alloys (up to 15 at. % Hf); hence the alloys crystallize without appreciable liquation.

The microstructure of all the alloys of this system, annealed at a subsolidus temperature, is represented by inherited polyhedra. Signs of a solid-state transformation are observed in hafnium-rich alloys (more than 25 at. % Hf).

The DTA data and the microstructure of alloys annealed at subsolidus temperatures warrant the conclusion that a continuous series of solid solutions is formed during the crystallization of alloys of the TiNi–HfNi system. This suggests that the high-temperature modifications of titanium and hafnium nickelides have the same CsCl-type crystal structure.
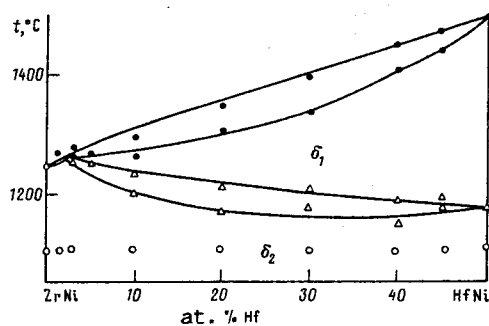
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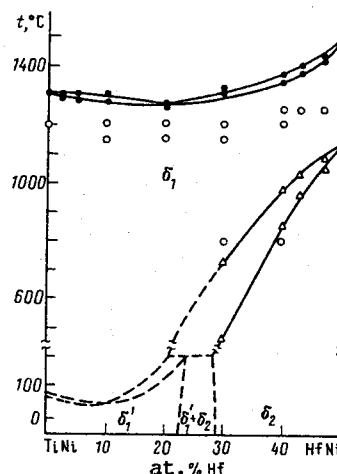Fig. 3. Phase diagram of the ZrNi–HfNi system (notation as in Fig. 2).

Fig. 4. Phase diagram of the TiNi–HfNi system (notation as in Fig. 2).

When hafnium atoms in the nickelide are substituted by titanium atoms the temperature of the HfNi polymorphous transformation is lowered, while the temperature range of the transformation expands. The introduction of titanium, therefore, stabilizes the high-temperature modification of hafnium mononickelide.

The stabilizing effect of titanium is insufficient for the high-temperature phase based on HfNi to be preserved completely during cooling. At room temperature, however, in addition to the δ_2 phase with the CrB structure, we detected an amount of phase with the CsCl structure (δ_1 phase) in alloys containing 20–50 at. % Hf. The lattice constant of the δ_1 solid solution $Hf_{1-x}Ti_xNi$ with the CsCl structure varies from 0.302 nm at x = 0.3 to 0.313 nm at x = 0.

CONCLUSIONS

We have determined that systems formed by titanium, zirconium, and hafnium mononickelides (TiNi–ZrNi, TiNi–HfNi, and ZrNi–HfNi) are quasibinary. The systems TiNi–ZrNi and ZrNi–HfNi are of the peritectic type. The peritectic transformations liq + $\delta_2(Zr_{1-x}Ti_xNi)$ $\rightleftarrows$ $\delta_1(Ti_{1-y}Zr_yNi)$ at 1160°C and liq + $\delta_1(Hf_{1-x}Zr_xNi)$ $\rightleftarrows$ $\delta_2(Zr_{1-y}Hf_yNi)$ at 1265 ± 12°C occur in zirconium-rich alloys (45–48 at. % Zr). The high-temperature modification of hafnium mononickelide (δ_1) has the CsCl structure and forms a continuous series of solid solutions with titanium nickelide during crystallization from a melt. The low-temperature modification of hafnium nickelide with the CrB structure forms a continuous series of solid solutions with zirconium nickelide of analogous structure.

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GROWTH OF SINGLE CRYSTALS IN THE Bi—Sr—Ca—Cu—O SYSTEM

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Both ceramic stoichiometric samples and single crystals must be considered in the study of high-temperature (high-T_c) superconductors. The incongruent melting of phases, the high volatility of some components, and deviations in the composition of the anion sublattice (oxygen defectiveness) complicate the growth of high-quality high-T_c semiconductor single crystals under controlled conditions. Moreover, the heat-treatment conditions have a large effect on the properties of the single crystals grown [1-4].

Various methods have been developed for obtaining high-T_c semiconductor single crystals from stoichiometric melts [3, 5-9]. Possible ways of growing single crystals under a flux have been noted [10, 11].

Our aim was to study the conditions for obtaining single crystals from melts in the Bi—Sr—Ca—Cu—O system under various fluxes, with the molecular stoichiometric melts corresponding to Bi:Sr:Ca:Cu ratios of 1—1—1—2, 2—2—1—2, and 2—2—2—3.

We assumed that the flux would not be mixed in with the bulk of the starting material but would be poured on top of the material in the crucible, acting as a "plug" to contain volatile components of the molten stock. The physicochemical properties of the fluxes chosen, therefore, should meet the following requirements: a) the melting point of the flux should be lower, and its melting point much higher, than the temperature of the molten stock; b) the flux should be a rather simple salt, which does not form when by-products melt; c) in the molten state the flux should not react with the stock and the crucible material; d) the flux should be less dense than the stock.

On the basis of these requirements, we chose three salts: NaCl, KCl, and $CaCl_2$ (in the particular case we used PbO and CuO). The necessary properties of these salts are shown in Table 1.

We used stock synthesized by solid-phase reactions with bismuth oxide introduced in the final stage of the treatment as well as 2—2—1—2 stock prepared by the Khimkor branch of SP Ural. The stock was used as powder and as pellets (diameter 6 mm and height 2-3 mm) pressed at 4 MPa.

EXPERIMENTAL

The samples were melted in round-bottomed alundum crucibles with length 150 mm and inside diameter 8 mm. The crucibles were placed on an aluminum oxide cushion so that the lower part was in the zone of maximum temperature to within ±2 deg. This zone was chosen

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