LIQUIDUS SURFACE AND SOLIDIFICATION SCHEME FOR ALLOYS OF THE SYSTEM Ti–Ni–Zr CONTAINING UP TO 50% Ni

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UDC 669.295.5'296'24

Interest in alloys of the system Ti–Ni–Zr is due to the fact that by varying the composition of alloys based on titanium nickelide it is possible to change the critical points of thermoelastic martensitic transformation giving rise to the 'shape memory' effect and thus expand the field of application for these materials. Alloys of titanium with zirconium and nickel are also of interest in view of the search for new materials which absorb hydrogen and exhibit a high capacity at suitable temperatures at which hydrogen absorption and desorption occur at a sufficient rate.

By using the results of studies carried out previously on the structure of the constitution diagram for the quasibinary system TiNi–ZrNi [1] and also the structure and phase equilibrium in alloys of the ternary system Ti–Ni–Zr containing up to 50% Ni* at 700°C [2] and close to the solidus surface [3], the authors of the present communication by carrying out additional studies of the phase composition and microstructure of alloys in the cast condition suggest the structure of the liquidus surface and the solidification scheme for alloys of the ternary system Ti–Ni–Zr in the region of compositions Ti–TiNi–ZrNi–Zr. The preparation procedure (from iodide titanium and zirconium, and nickel grade N-1) and the procedure for studying alloys have been described in [1-3].

Since the TiNi–ZrNi section of the ternary system Ti–Ni–Zr is quasibinary [1] equilibrium in the region Ti–TiNi–ZrNi–Zr may be considered as independent from the rest of the system (TiNi–Ni–ZrNi). Interaction of titanium nickelide with zirconium nickelide leads to formation of a solid solution based in TiNi (δ_1-phase) with a CsCl type structure. The homogeneity region for the δ_1-phase extends up to a content of Zr ~ 46% at 1160°C and it is sharply reduced (approximately to 30% Zr) with a reduction in temperature to 700°C. With a content of about 25% Zr in the δ_1-phase there is a minimum for the fusion temperature (1100°C).

There is a narrow region of solid solution of δ_2-phase of the CrB based on the compound ZrNi. At 1160°C there is equilibrium: L (~45% Zr) + δ_2 (~48% Zr) $\rightleftarrows$ δ_1 (~46% Zr).

In the Ti–Ni–Zr system there is a ternary λ_1-phase with an $MgZn_2$ type structure based on an equiatomic compound TiZrNi. Depending on alloy composition Laves-phase may be found in equilibrium with any other phase which exists in the region Ti–TiNi–ZrNi–Zr studied in the Ti–Ni–Zr system at solidus temperatures. The region of homogeneity for λ_1-phase is considerable and close to the solidus it is 22-32% Zr and 28-38% Ni.

Phases based on the compounds Ti_2Ni (η-phase with a natural type of fcc structure) and Zr_2Ni (θ-phase with tetragonal lattice of the $CuAl_2$ type) have small regions of homogeneity. Titanium forms with zirconium at sub-solidus temperatures a continuous series of solid solutions (β-phase). The solubility of nickel in solid solutions of β-(Ti, Zr) is much less than in pure β-Zr, and much lower than in β-Ti.

The phase composition and structural components of cast alloys established from the results of x-ray and microstructural analyses are shown in Table 1. Given in Fig. 1 is a projection of the liquidus and solidus surfaces of alloys of the partial system Ti–TiNi–ZrNi–Zr. The liquidus surface consists of six fields of solidification for δ_1-, δ_2-, λ_1-, θ-, β-, and η-phases. The boundaries of these fields may be determined reliably from the posi-

*Alloy composition is given in atomic fractions expressed as a percentage.

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Translated from Poroshkovaya Metallurgiya, No. 8(344), pp. 49-54, August, 1991. Original article submitted September 11, 1989.

 0038-5735/91/3008-0664$12.50

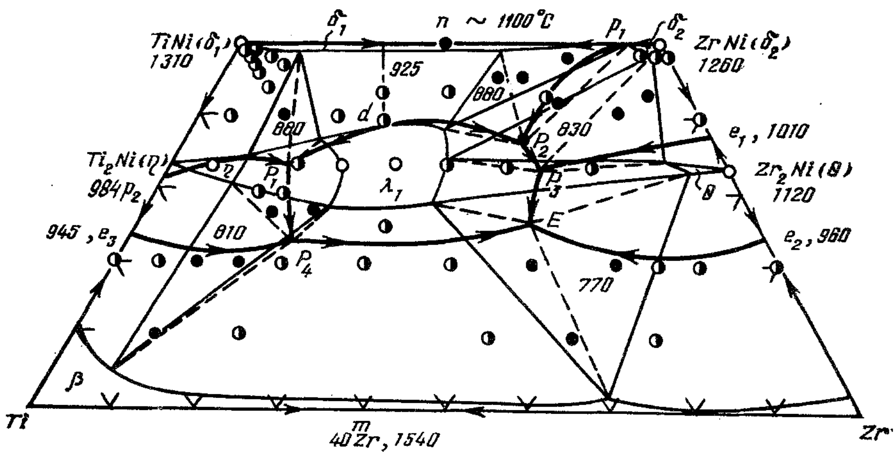

Fig. 1. Projection of the liquidus and solidus surfaces of the ternary system Ti–Ni–Zr in the region Ti–TiNi–ZrNi–Zr.

tion of crystals of the phase which precipitates first. Under rapid solidification conditions for ingots on a water-cooled hearth of an arc furnace subsequent solidification stages may not correspond to equilibrium, and therefore the structural components of cast alloys do not always reflect the equilibrium ratios of phases.

Since in the linear surface of the solidus for two-phase $(\lambda_1 + \delta_1)$-alloys [3] there is a maximum temperature at 925°C, on the boundary curve P_1dP_2 which separates the field of primary solidification for λ_1- and δ_1-phases, there is also a maximum temperature point d. Its coordinates are 925°C and 39% Ni–22% Zr.

Along the branch dP_2 of the boundary curve the temperature decreases to 880°C at point P_2. In alloys containing more than 22% Zr with displacement of a figurative point of the melt along this branch of the boundary curve a congruent process occurs for combined solidification of λ_1- and δ_1-phases, i.e., a mixture of $(\lambda_1 + \delta_1)$-phases. These formations are normally called binary eutectic. The melt of composition at point P_2 at 880°C consists of three $(\lambda_1$, δ_1, and $\delta_2)$ phases and at this temperature an invariant incongruent process $L + \delta_1 \rightleftarrows \delta_2 + \lambda_1$ occurs. The position of point P_2 is determined by the intersection of curve of the primary solidification field of δ_1- and δ_2-phases labelled p_1P_2 which originates in the quasibinary system TiNi–ZrNi at 1160°C.

With a reduction in nickel content in the melt coexisting with δ_1- and δ_2-phases the temperature along the boundary curve p_1P_2 decreases to 880°C at point P_2. Here the composition of δ_1-phase according to [1] is markedly impoverished in zirconium. The figurative point of composition of δ_1-phase coexisting with the melt moves so that along boundary curve p_1P_2 the incongruent process $L + \delta_2 \rightarrow \delta_1$ is replaced by a congruent process $L \rightarrow \delta_1 + \delta_2$. With a content of 48% Ni in the alloy the boundary curve p_1P_2 passes between 40 and 44% Zr and its further direction, and consequently the position of point P_2, is determined by the structure of cast alloys containing 43% Ni–40% Zr and 37% Ni–40% Zr (Table 1).

The third boundary curve emerging from point P_2 is the geometric position of points of melt composition from which there is combined solidification of λ_1- and θ-phases. The temperature along this boundary curve decreases from 880°C at point P_2 to 830°C at point P_3, i.e., liquid of composition P_3 is in equilibrium with λ_1-, δ_2-, and θ-phases, and consequently at this temperature the invariant incongruent process $L_{p_3} + \delta_2 \rightleftarrows \lambda_1 + \theta$ occurs. This process precedes a congruent process of combined solidification of θ- and δ_2-phases in which melt takes part whose composition changes along boundary curve e_1P_3. In the binary system Zr–Ni eutectic solidification $L_{e_1} \rightleftarrows \delta_2 + \theta$ occurs at 1010°C; consequently, the temperature along curve e_1P_3 decreases uniformly from point e_1 to P_3.

The lower boundary for nickel concentration of the conodal triangle $\lambda_1\theta\delta_2$, the two-phase structure of alloys containing 40 and 50% Zr through the section with 33.3% Ni at a sub-solidus temperature, and the difference in their microstructure (Fig. 2a, b) and type of invariant equilibrium with participation of melt P_3 determine the position of both point P_3 and the boundary curve for combined solidification of λ_1 and θ-phases P_3E. Along this curve the temperature from P_3 decreases to 770°C (at point E), i.e., the lowest fusion temperature

TABLE 1. Phase Composition and Structural Components of Alloys of the System Ti–Ni–Zr in the Region Ti–TiNi–ZrNi–Zr*

Alloy compo., %		Phase composition and structural components of cast alloys	Alloy compo., %		Phase composition and structural components of cast alloys
Ni	Zr		Ni	Zr	
10	10	$\beta+(\beta+\lambda_1)$**	33,3	26,7	λ_1
10	20	$\beta+(\beta+\lambda_1+\theta)$	33,3	33,3	$\lambda_1+(\lambda_1, \theta, \delta_2)$
10	50	$\beta+E$***	33,3	40	$\lambda_1+(\lambda_1+\theta)$
10	60	$\beta+E$	33,3	50	$\theta+(\lambda_1+\theta)$
10	70	$\beta+(\beta+\theta)$	33,3	62	$\theta+(\lambda_1)$
20	5	$\beta+(\beta+\eta)$	37	40	$\delta_1+(\delta_2+\lambda_1)$
20	10	$\beta+(\beta+\eta)$	39	22	$\delta_1+(\delta_1+\lambda_1)$
20	15	$\beta+(\beta+\lambda_1)$	40	4	η
20	20	$\beta+(\beta+\lambda_1)$	40	10	$\delta_1+\eta$
20	30	$\beta+(\beta+\lambda_1)$	40	16	δ_1, λ_1
20	40	$\beta+(\beta+\lambda_1)$	40	50	$\delta_2+(\delta_2+\theta)$
20	50	$\beta+E$	42	42	$\delta_2+(\lambda_1+\delta_2)$
20	60	$\beta+E$	43	20	$\delta_1+(\lambda_1+\delta_1)$
20	65	$\beta+(\beta+\theta)+E$	43	28	$\delta_1+(\lambda_1+\delta_1)$
20	70	$\beta+E$	43	40	$\delta_2+(\lambda_1+\delta_2)$
25	30	$\lambda_1+(\beta+\lambda_1)$	43	52	$\delta_2+(\delta_2+\theta)$
25	49	E	44	6	δ_1, η
27	15	$\eta+(\eta+\lambda_1)+(\lambda_1+\beta)$	45	33	$\delta_1+(\delta_1+\lambda_1)$
27	20	$\lambda_1+(\lambda_1+\beta)$	45	36	$\delta_1+(\delta_1+\lambda_1)$
30	12	$\eta+(\eta+\lambda_1)$	47	3	δ_1, η
30	15	$\eta+(\eta+\lambda_1)$	48	2	δ_1, η
33,3	5	$\eta+(\eta, \delta_1)$****	48	4	δ_1, η
33,3	10	$\eta+(\eta+\lambda_1)$	48	40	δ_1, η
33,3	15	$(\lambda_1+\eta)$	48	44	$\delta_2+(\delta_2+\lambda_1)$
30,3	20	$\lambda_1+(\eta)$	48	48	$\delta_2+(\delta_2+\lambda_1)$
			48	50	δ_2

*Detailed information about the quasibinary system TiNi–ZrNI is given in [1].
**Shown first is the phase that solidifies first, and shown in brackets is the mixture of phases which precipitate along boundary curves.
***Ternary eutectic $\beta + \theta + \lambda_1$.
****Small amount of phase.

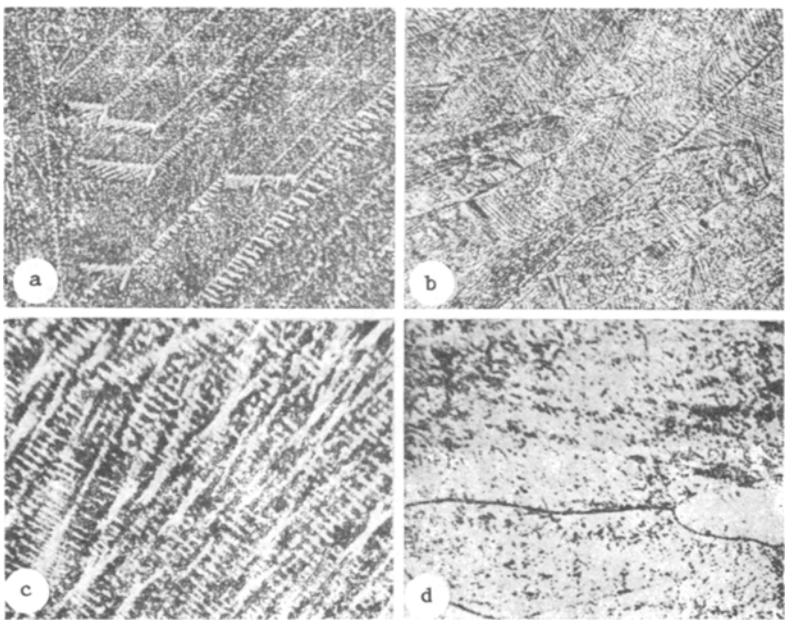

Fig. 2. Microstructure of cast alloys Ti–33.3% Ni–40% Zr (a), Ti–33.3% Ni–50% Zr (b), Ti–33.3% Ni–5% Zr (c) and alloy Ti–33.3% Ni–5% Zr annealed for 50 h at 850°C (d). Phase composition: a) $\lambda_1 + (\lambda_1 + \theta)$; b) $\theta + (\lambda_1 + \theta)$; c, d) η. Magnification: 100 (a-c), 500 (d).

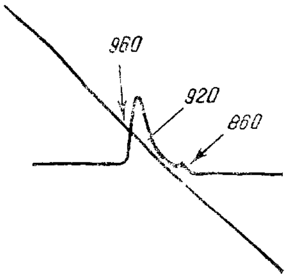

Fig. 3. Thermal solidification curve for alloy containing 5% Zr, 33.3% Ni.

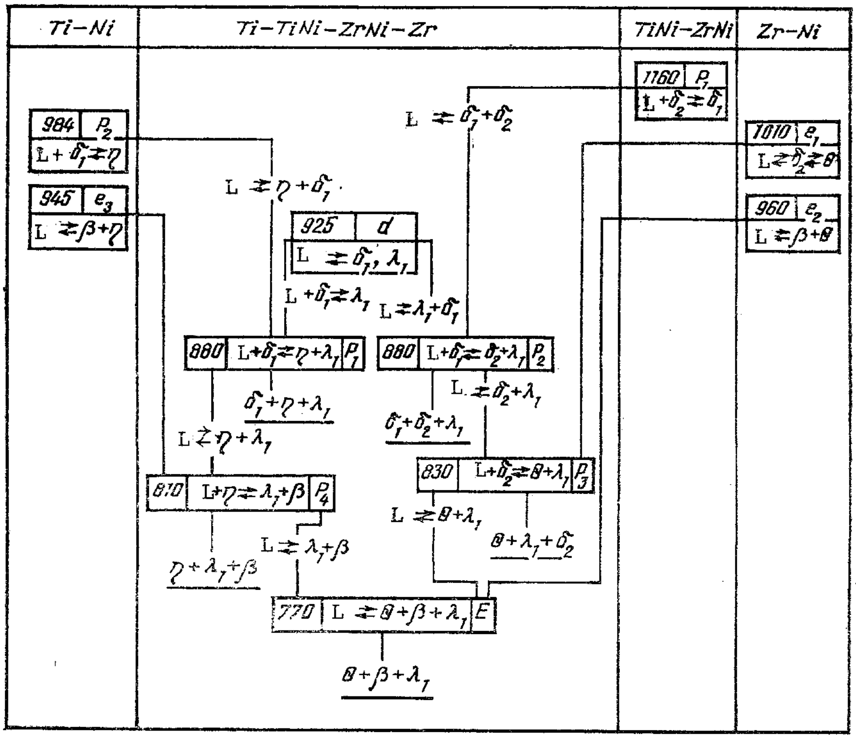

Fig. 4. Diagram of alloy solidification of the system Ti–Ni–Zr in the region Ti–TiNi–ZrNi–Zr.

in the test alloys which is the temperature for solidification of ternary eutectic $L_E \rightarrow \lambda_1 + \theta + \beta$.

Since invariant processes in which melts of composition P_2 and P_3 participate occur at similar temperatures (880 and 830°C respectively), under solidification conditions with rapid cooling certain transformations in alloys of this composition region do not occur. For example, in alloy 37% Ni–40% Zr after primary solidification of δ_1-phase there is solidification of binary eutectic ($\lambda_1 + \delta_2$) by-passing the process $L_{P_1} + \delta_1 \rightleftarrows \lambda_1 + \delta_2$.

The temperature along boundary curve e_2E of congruent solidification of θ- and β-phases in the binary system Zr–Ni decreases from 960 to 770°C. The third boundary curve P_4E of combined solidification of β- and λ_1-phases directed at the point of ternary eutectic E originates at point P_4 of the liquid composition which takes part in four-phase equilibrium $L_{P_4} + \eta \rightleftarrows \beta + \lambda_1$ at 810°C. In two-phase alloys as the zirconium content increases, as was shown in [3], the solidus temperature decreases. The position of the point of ternary eutectic E is determined by local x-ray microanalysis of eutectic colonies ($\beta + \lambda_1 + \theta$) and it corresponds to the composition 25% Ni–49% Zr. The microstructure of cast alloy of this composition is almost pure eutectic.

The process of combined solidification of η- and β-phases which precedes invariant equilibrium with participation of liquid phase of composition P_4 occurs from melts whose composition changes along boundary line e_3P_4. In the binary system eutectic solidification

$L_{e_4} \to \beta + \eta$ occurs at 945°C. In three-component alloys as zirconium content increases in the melt the temperature for combined solidification of β- and η-phases decreases uniformly to 810°C at point P_4.

As indicated above, on boundary curve P_1dP_2 there is a temperature maximum at point d at 925°C. Here the congruent process of combined solidification of δ_1- and λ_1-phases along branch dP_2 changes to an incongruent process $L + \delta_1 \to \lambda_1$ in section dP_1; the temperature decreases uniformly from 925°C to 880°C at point P_1. Melt of composition P_1 is in equilibrium with λ_1-, δ_1-, and η-phases: $L_{p_1} + \delta_1 \rightleftarrows \lambda_1 + \eta$. The second monovariant process which precedes this invariant process occurs with participation of melts whose composition changes along boundary curve p_2P_1. In it apart from melt there is participation of η- and δ_1-phases. The η-phase in binary system Ti—Ni forms at 984°C by a peritectic reaction $L_{p_2} + \delta_1 \rightleftarrows \eta$. Here melt composition and η-phase formed differ little (by about 1 at. %).

In three-component alloys with dissolution of zirconium in Ti_2Ni the temperature for formation of the η-phase decreases and there is a change in the process to congruent: $L \to \eta + \delta_1$. Cast alloy along section 33.3% Ni containing 5% Zr is a strongly liquated solution of zirconium in Ti_2Ni (Fig. 2c). On annealing the alloy composition levels out and the structure becomes polyhedral (Fig. 2d).

On the thermal solidification curve for this alloy (Fig. 3) apart from the powerful effect of primary precipitation of η-phase (temperature for the start of solidification 960°C with a cooling rate of about 30 deg/min) a very small thermal effect is observed relating to the invariant process $L_{p_1} + \delta_1 \rightleftarrows \lambda_1 + \eta$. Thus, substitution of the process $L + \delta_1 \rightleftarrows \eta$ by $L \rightleftarrows \delta_1 + \eta$ occurs close to the alloy composition 5% Zr—33.3% Ni. Combined solidification of η- and λ_1-phases occurs in the temperature range 880-810°C; the melt composition which takes part in the process $L \to \eta + \lambda_1$, changes along boundary curve P_1P_4. A diagram of the solidification for alloys of the Ti—Ni—Zr system in the region of compositions Ti—TiNi—ZrNi—Zr is presented in Fig. 4.

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