PROJECTION OF THE SOLIDUS SURFACE OF THE Ti-Ni-Zr SYSTEM IN THE Ti-TiNi-ZrNi-Zr REGION

V. N. Eremenko, E. L. Semenova, and L. A. Tret'yachenko

Izvestiya Akademii Nauk SSSR. Metally,
No. 6, pp. 191-196, 1990

UDC 669.295'24'296:669.017.1

Alloys of the Ti-Ni-Zr system are studied by differential thermal, X-ray phase, local X-ray spectral, and microstructural analysis, and a solidus surface is constructed in the region of Ti-TiNi-NiZr-Zr compositions. The homogeneity region of the λ_1-Laves phase based on the compound TiNiZr is determined. This phase on the solidus surface is in equilibrium with all other phases of the system. The temperatures of the beginning of melting of the three-phase alloys are established: $\lambda_1 + \delta_1 + \eta$ at 880°C, $\lambda_1 + \delta_1 + \delta_2$ at 880°C, $\lambda_1 + \delta_1 + \theta$ at 830°C, $\lambda_1 + \beta + \eta$ at 810°C and $\lambda_1 + \beta + \theta$ at 770°C, where the phases are: δ_1 based on TiNi, δ_2 based on ZrNi, η based on Ti_2Ni, θ based on Zr_2Ni, and a β-solid solution based on β-Ti and ρ-Zr.

Alloys of the Ti-Ni-Zr system are of great scientific and practical interest, both because of the formation of a ternary Laves phase and because of the discovery of the mutual effect of the components in the ternary systems on the reversible sorption of hydrogen, the tendency of the alloys to pass into the amorphous state, and the effect of zirconium on the "form memory" effect. In order to explain the mutual effect of the components on the given properties in three-component alloys, information is required on the phase equilibria over a wide range of compositions and temperatures.

We previously studied [1] the structure of the alloys and phase equilibria in the Ti-Ni-Zr system at 700°C and at Ni contents up to 50 at.%. In this article we give some results of studying phase equilibria of alloys of the Ti-Ni-Zr system in the Ti-TiNi-ZrNi-Zr region at subsolidus temperatures.

The structure of the restricting binary systems is known [2,3]. In the regions of compositions under study (0-50 at.% Ni) in binary Ti-Ni and Zr-Ni systems phases are formed based on equi-atom TiNi(δ_1), compounds of CsCl type structure, which undergo a martensite transformation on lowering the temperature, and ZrNi(δ_2), which has a CrB rhombic structure, and also an η-phase based on Ti_2Ni with an fcc-structure of characteristic type, and a θ-phase based on Zr_2Ni, which is tetragonal, and of $CuAl_2$ type.

Solid solutions based on β-Ti and β-Zr undergo eutectoid decomposition: $<\beta\text{-Ti}> \rightarrow Ti_2Ni + <\alpha\text{-Ti}>$ at 770°C and $<\beta\text{-Zr}> \rightarrow Zr_2Ni + <\alpha\text{-Zr}>$ at 845°C.

In the Ti-Zr system the components form a continuous series of solid solutions both in the liquid and in the solid state [2].

In this work, the alloys from the original component were melted in an arc furnace with an inconsumable tungsten electrode on copper base, and were studied by microstructural analysis (MSA) differential thermal analysis (DTA), X-ray phase analysis (XRA) and local X-ray spectral analysis (LXSA). Titanium and zirconium iodides and grade N-1 nickel were used in preparation of the alloys.

From the results of these studies a projection of the solidus surface of the ternary Ti-Ni-Zr system in the region Ti-TiNi-ZrNi-Zr was constructed (Fig. 1).

The temperature at which the alloys start melting and their phase composition at the subsolidus temperature are given in Table 1, and some microstructures are given in Fig. 2.

In the Ti-Ni-Zr system a ternary Laves phase [1,4] is formed, of structural type $MgZr_2$(λ_1), of variable composition, and having a significant homogeneity region.

The alloy containing 33.3% Ni and 33.3% Zr (here and in the remainder of this article the compositions of the alloys are given in at.%) at the subsolidus temperature contains a small quantity of a second phase (Fig. 2a) as well as λ_1, which is the reason for its position close to the boundary of the λ_1-phase homogeneity region. The extent of this region on the solidus surface is 22 and 32% Zr and 28 to 38% Ni. The temperature at which the λ_1-

Table 1

Chemical and Phase Composition of Ti-Ni-Zr Alloys on the Solidus Surface and Temperature at Which They Start Melting

Alloy number	Composition, at.%		t_{sol}, °C	Phase composition under solidus	Lattice periods of phases, nm								
	Ni	Zr			η	λ_1		θ		δ_1	δ_2		
					a	*a*	*c*	*a*	*c*	*a*	*a*	*b*	*c*
1	10	10	810	$\beta+\lambda_1+\eta$	—	—	—	—	—	—	—	—	—
2	10	20	800	$\beta+\lambda_1$	—	0,519	0,896	—	—	—	—	—	—
3	10	50	780	$\beta+\lambda_1$	—	0,527	0,852	—	—	—	—	—	—
4	10	60	770	$\beta+\lambda_1+\theta$	—	0,523	0,857	—	—	—	—	—	—
5	10	70	—	$\beta+\theta$	—	—	—	—	—	—	—	—	—
6	20	5	—	$\beta+\eta$	1,139	—	—	—	—	—	—	—	—
7	20	10	810	$\beta+\eta+\lambda_1$	1,148	0,515	0,854	—	—	—	—	—	—
8	20	15	810	$\beta+\eta+\lambda_1$	—	0,516	0,841	—	—	—	—	—	—
9	20	20	810	$\beta+\lambda_1$	—	0,518	0,849	—	—	—	—	—	—
10	20	30	785	$\beta+\lambda_1$	—	0,523	0,846	—	—	—	—	—	—
11	20	40	780	$\beta+\lambda_1$	—	0,524	0,854	—	—	—	—	—	—
12	20	50	770	$\beta+\lambda_1+\theta$	—	0,524	0,856	—	—	—	—	—	—
13	20	60	780	$\beta+\lambda_1+\theta$	—	—	—	—	—	—	—	—	—
14	20	65	790	$\beta+\theta$	—	—	—	0,648	0,525	—	—	—	—
15	20	70	810	$\beta+\theta$	—	—	—	—	—	—	—	—	—
16	20	80	—	$\beta+\theta$	—	—	—	—	—	—	—	—	—
17	25	30	—	$\beta+\lambda_1$	—	—	—	—	—	—	—	—	—
18	25	49	770	$\beta+\theta+\lambda_1$	—	0,526	0,855	0,643	0,526	—	—	—	—
19	27	15	—	$\lambda_1+\eta+\beta$	—	0,510	0,845	—	—	—	—	—	—
20	27	20	—	$\lambda_1+\eta+\beta$	—	0,516	0,845	—	—	—	—	—	—
21	30	12	830	$\eta+\lambda_1$	1,141	0,515	0,842	—	—	—	—	—	—
21	30	15	800	$\eta+\lambda_1$	1,146	0,517	0,849	—	—	—	—	—	—
22	33,3	5	915	η	1,137	—	—	—	—	—	—	—	—
23	33,3	10	870	$\eta+\lambda_1$	1,142	—	—	—	—	—	—	—	—
24	33,3	15	865	$\eta+\lambda_1$	1,143	0,514	0,837	—	—	—	—	—	—
25	33,3	20	865	$\eta+\lambda_1$	1,143	0,515	0,841	—	—	—	—	—	—
26	33,3	26,7	870	λ_1	—	0,517	0,844	—	—	—	—	—	—
27	33,3	33,3	870	λ_1	—	0,519	0,850	—	—	—	—	—	—
28	33,3	40	810	$\lambda_1+\theta$	—	0,520	0,851	0,645	0,525	—	—	—	—
29	33,3	50	790	$\lambda_1+\theta$	—	0,519	0,852	0,645	0,525	—	—	—	—
30	33,3	62,5	850	θ	—	—	—	0,648	0,524	—	—	—	—
31	33,3	66,7	1000	θ	—	—	—	0,649	0,527	—	—	—	—

Table 1 (continued)

Alloy number	Composition, at.%		t_{sol}, °C	Phase composition under solidus	Lattice periods of phases, nm								
					η	λ_1		θ		δ_1	δ_2		
	Ni	Zr			a	a	c	a	c	a	a	b	c
32	37	40	890	$\lambda_1+\theta+\delta_2$	—	—	—	—	—	—	—	—	—
33	39	22	925	$\delta_1+\lambda_1$	—	0,511	0,831	—	—	—	—	—	—
34	40	4	930	$\delta_1+\eta$	1,136	—	—	—	—	—	—	—	—
35	40	10	880	$\delta_1+\lambda_1+\eta$	1,138	0,511	0,813	—	—	0,304	—	—	—
36	40	16	900	$\delta_1+\lambda_1$	—	0,511	0,817	—	—	—	—	—	—
37	40	50	830	$\delta_2+\lambda_1+\theta$	—	0,515	0,845	0,647	0,522	—	0,326	0,999	0,409
38	40	60	—	$\delta_2+\theta$	—	—	—	0,648	0,527	—	0,327	9,995	0,410
39	42	42	850	$\lambda_1+\delta_2+\theta$	—	—	—	—	—	—	—	—	—
40	43	20	925	$\lambda_1+\delta_1$	—	0,512	0,834	—	—	—	—	—	—
41	43	28	910	$\lambda_1+\delta_1$	—	0,514	0,834	—	—	—	—	—	—
42	43	40	870	$\lambda_1+\delta_2$	—	0,517	0,845	—	—	—	0,325	0,988	0,409
43	43	52	850	$\lambda_1+\delta_2+\theta$	—	—	—	0,641	0,527	—	0,326	0,995	0,410
44	44	6	—	$\eta+\delta_1$	1,136	—	—	—	—	—	—	—	—
45	45	33	880	$\delta_1+\delta_2+\lambda_1$	—	0,515	0,832	—	—	—	0,326	0,988	0,408
46	45	36	885	$\delta_1+\delta_2+\lambda_1$	—	0,515	0,824	—	—	—	—	—	—
47	46	4	930	$\eta+\delta_1$	1,135	—	—	—	—	—	—	—	—
48	47	6	—	$\eta+\delta_1$	1,137	—	—	—	—	—	—	—	—
49	48	2	—	δ_1^*	—	—	—	—	—	—	—	—	—
50	48	40	880	$\delta_2+\lambda_1+\delta_1$	—	0,513	0,834	—	—	—	0,324	0,991	0,409
51	48	44	870	$\delta_2+\lambda_1+\delta_1$	—	—	—	—	—	—	0,327	1,000	0,406
52	48	48	—	$\delta_2+\lambda_1$	—	—	—	—	—	—	—	—	—
58	48	50	890	δ_2	—	—	—	—	—	—	0,326	0,993	0,408
54	48	52	—	$\delta_2+\theta$	—	—	—	—	—	—	—	—	—
55	50	2	—	δ_1'	—	—	—	—	—	—	—	—	—
56	50	4	—	δ_1'	—	—	—	—	—	—	—	—	—
57	50	6	1190	δ_1'	—	—	—	—	—	0,304	—	—	—
58	50	10	—	δ_1	—	—	—	—	—	0,305	—	—	—
59	50	20	1090	δ_1	—	—	—	—	—	0,308	—	—	—
60	50	25	1100	δ_1	—	—	—	—	—	—	—	—	—
61	50	30	1120	δ_1	—	—	—	—	—	—	—	—	—
62	50	35	1110	δ_1	—	—	—	—	—	—	—	—	—
63	50	40	1130	δ_1	—	—	—	—	—	—	—	—	—
64	50	45	1160	δ_1	—	—	—	—	—	—	—	—	—
65	50	48	1180	δ_2	—	—	—	—	—	0,318	0,323	0,991	0,412
66	50	50	1290	δ_2	—	—	—	—	—	—	—	—	—

*These alloys experienced a martensite transformation.

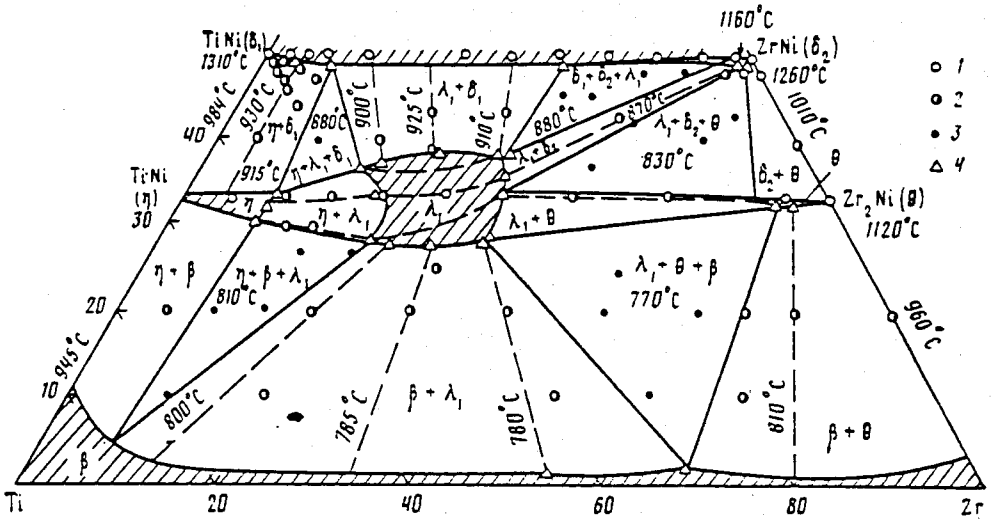

Fig. 1. Projection of the solidus surface of the Ti-Ni-Zr system: 1) single-phase; 2) two-phase; 3) three-phase alloys; 4) LXSA data.

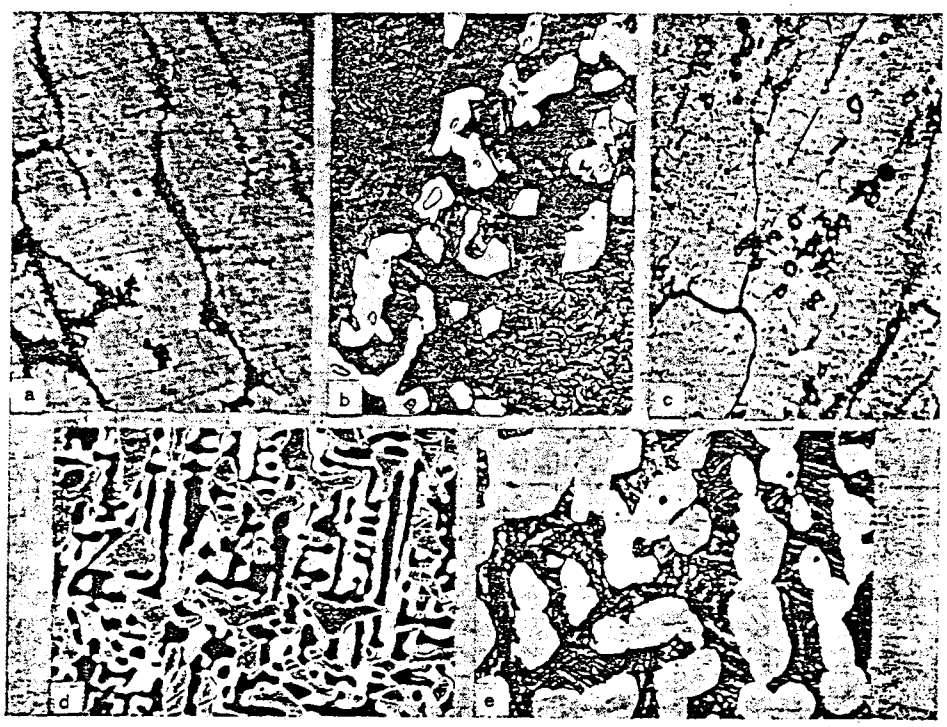

Fig. 2. Microstructures of alloys of the Ti-Ni-Zr system at the subsolidus temperature: a) alloy 27 (Table 1), ×100; b) alloy 1, ×500; c) alloy 20, ×500; d) alloy 35, ×1000; e) alloy 6, ×500.

phase starts melting depends only to a slight extent on the ratio of Ti and Zr in it, and is increased from 800 to 925°C when the Ni content is increased. Its lattice periods (a and c) show important changes with composition: alloys rich in titanium, lying on the upper boundary of the homogeneity region with respect to nickel show the minimum values, and alloys with a minimum content of nickel and titanium the maximum values (Table 1).

The solubility of nickel at the subsolidus temperature in the β-phase of the ternary system is less than in the bounding binary systems and amounts to around 1% at. Ni at the $\beta/\beta + \lambda_1$ boundary over a wide range of Ti-Zr ratios (Fig. 1). Over this small range of nickel contents the temperature on the β-phase solidus surface is sharply decreased by 800-1000°C.

Table 2

Compositions of Coexisting Solid Phases at Invariant Equilibrium Temperatures on the Solidus Surface*

t, °C	Coexisting phases	Composition of phases, at.%					
		δ_1	δ_2	η	λ_1	θ	β
880	$\delta_1+\eta+\lambda_1$	49 Ni; 7 Zr	—	34 Ni; 8 Zr	37 Ni; 16 Zr	—	—
880	$\delta_1+\delta_2+\lambda_1$	49 Ni; 31 Zr	49 Ni; 47 Zr	—	38 Ni; 30 Zr	—	—
830	$\lambda_1+\theta+\delta_2$	—	49 Ni; 49 Zr	—	33 Ni; 33 Zr	33 Ni; 60 Zr	—
770	$\lambda_1+\theta+\beta$	—	—	—	29 Ni; 33 Zr	32 Ni; 62 Zr	1,5 Ni; 69 Zr
810	$\lambda_1+\eta+\beta$	—	—	31 Ni; 9 Zr	28 Ni; 22 Zr	—	4,5 Ni—7,6 Zr

*LXSA data for the two-phase regions given in Fig. 1.

The extents of the homogeneity regions of the phases based on TiNi and ZrNi on the solidus surface differ significantly. At the subsolidus temperature along the 50% Ni section the cubic phase extends to ~46% Zr, and a total of 2% Ti is dissolved in the rhombic δ_2 phase. Along this section the solidus of the alloys is gently sloping, and the curve for the δ_1-phase solidus at the 25% Zr has a minimum (1000°C).

According to the LXSA data (Fig. 1) the lower bound of the δ_1- and δ_2-phase homogeneity regions with respect to nickel deviate from the 50% Ni section by not more than 1% Ni. Moreover, the temperature on the solidus surface of the δ_1 and δ_2-phases is lowered by 200-300°C.

On dissolution of zirconium and titanium in the γ- and θ-phases up to 8% of their regions of homogeneity with respect to nickel are somewhat widened, this being greater with the η-phase; the lattice periods are also increased (Table 1).

The temperature on the solidus surface of both phases is inversely related to the content of the third component.

The ternary Laves phase (λ_1) as indicated above, on the solidus surface coexists with all the phases formed on the basis of binary compounds and a β(Ti, Zr) solid solution solid solution in the ternary system in the Ti-TiNi-ZrNi-Zr region, which results in five invariant equilibria of the melts with solid phases; $\delta_1 + \eta + \lambda_1$ at 880°C; $\delta_1 + \delta_2 + \lambda_1$ at 880°C; $\eta + \lambda_1 + \beta$ at 810°C; $\lambda_1 + \theta + \delta_2$ at 830°C; and $\lambda_1 + \beta + \theta$ at 770°C. The compositions of the coexisting solid phases in these equilibria are given in Table 2. These values of the compositions are obtained by the LXSA method and are confirmed by data from other methods, or at least are not contradicted by them, with the exception of the composition of the λ_1-phase from the $\lambda_1 + \eta + \beta$ region. The latter has been fairly accurately established by microstructural analysis (Fig. 2b, c); the three phase alloys containing 27% Ni + 20% Zr and 10% Ni + 10% Zr unambiguously determine the position of the limiting tie line bounding the conoid triangle for coexistence of the $\lambda_1 + \eta + \beta$ system at solidus temperatures.

On the ruled surfaces of the ($\eta + \lambda_1$)- and ($\lambda_1 + \theta$)-phases in equilibrium with the melt, a decrease in temperature and in the content of nickel in the alloys is observed in the ternary system.

On the ruled surfaces (assuming the start on the horizontal belonging to the binary systems Ti-Ni and Zr-Ni) of the phases: $\delta_1 + \eta$ (984°C), $\eta + \beta$ (945°C), $\delta_2 + \theta$ (1010°C), $\theta + \beta$ (960°C) a lowering in temperature was observed to the three-phase conoid triangles $\delta_1 + \eta + \lambda_1$, $\eta + \beta + \lambda_1$, $\lambda_1 + \delta_2 + \theta$ and $\theta + \beta + \lambda_1$ on the solidus surface.

A sharp fall in the solidus temperature over a very restricted concentration range (~1 at.%) is characteristic of the two-phase region $\delta_1 + \delta_2$: from the corresponding tie line along the section through the equi-atom system TiNi-ZrNi at 1160°C to the tie line restricting the plane of the three-phase equilibrium $\delta_2 + \eta + \lambda_1$ at 880°C. It should be noted also that the extent of the $\delta_1 + \delta_2$ region on the solidus surfaces is considerably dependent on the temperature.

The ruled surface of the ($\lambda_1 + \delta_1$)-phases coexisting with the melt has a gently sloping maximum at 925°C, from which the equilibrium temperature of these phases is decreased.

The solidus surface of the ($\lambda_1 + \delta_1$)-phases is also very gently sloping, and the temperature on it is lowered from 810 to 770°C on increasing the Zr:Ti ratio.

REFERENCES

1. V. N. Eremenko, E. L. Semenova, and L. A. Tret'yachenko, "Structure of Ni-Zr-Ti alloys in the region of 0-50% (at.) Ni at 700°C," Dokl. Akad. Nauk UkSSR. Ser. A, no. 2, p. 79, 1988.

2. O. Kubaschevski and O. Von Goldbeck, "II phase diagrams," Atomic Energy Rev., Spec. Issue, no. 9, p. 75, 1983.

3. P. Nash and C. S. Jaganth, "The Ni-Zr system," Bull. Alloy Phase Diagrams, vol. 5, no. 2, p. 144, 1984.

4. M. Yu. Teslyuk, Metallic Compounds with a Laves Phase Structure [in Russian], Nauka, Moscow, 1969.

19 June 1989 Kiev