STRUCTURE AND PROPERTIES OF ALLOYS OF THE SECTION Ti_2Ni–Zr_2Ni OF Ti–Zr–Ni SYSTEMS IN AMORPHOUS AND CRYSTALLINE STATES

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A physicochemical investigation of alloys of various states, from the completely disordered (amorphous) to the crystalline, gives a more complete understanding about the mechanisms relating to changes in the structure and properties of alloys [1]. The purpose of this work was to study the phase structure and the properties of alloys in the Ti–Zr–Ni systems in either speed quenched, melted, or equilibrated states of the Ti_2Ni–Zr_2Ni section. These systems have not been considered previously.

EXPERIMENTAL METHOD

The starting materials were a 0.1 mm thick BTI-00 TI wire, Zr iodide, and a Ni electrolyte (99.90%). A 20 g solid ingot was melted by an LK-8 electrical arc oven with a permanent electrode in a water cooled copper block in a helium atmosphere at a pressure of 33 KPa. Each ingot was remelted at least 5 times. The correspondence of calculated composition was controlled by gravimetric, chemical analysis, and by the measurement of the density of the alloys (the permissible deviation is not more than 0.2%). Part of the ingot was used so as to obtain speed-quenched ribbon by the method of spinning the melt in a clean helium atmosphere. The other part was used to study the microstructure, phase structure, and the microhardness of the ingot. The cast alloys were placed in dual evacuated quartz ampoules with a Zr getter, and were annealed in a muffle furnace at 970 K for a duration of 200 h, followed by the cooling of the ampoules in water.

The microstructure was revealed by a short chemical etching (1-5 sec) in a reagent of 1 concentrated HNO_3 + 1 HF + 2 glycerin.

The x-ray analysis of the amorphous and annealed crystalline alloys were done in a DRON-2 apparatus with filtered FeK_α-radiation and in the angular range of 2θ = 30-160°. High temperature x-ray analytical studies of amorphous alloys (AA) were done in an evacuated high temperature attachment to the DRON-2 diffractometer using CuK_α-radiation. The diffraction patterns were taken at 290, 620, 670, 720, 820, 870, and 970 K after heating continuously at a rate of 50 K/min. The exposure time at each temperature was 30 min and the scanning speed was 1 deg/min.

The heating effects during melting of crystalline alloys and the temperature of the stages of crystallization of the AA were fixed by the method of differential-thermal analysis (DTA), at a heating-cooling temperature rate of 20 K/min in a clean helium atmosphere.

The specific electrical resistance (ρ) of AA was measured by the standard 4 point probe method at room temperature. In order to raise the accuracy of the measurement, a geometrical factor [2] which was calculated in terms of the mass, the density, and the length of the sample was taken into account in the determination of the absolute value of ρ. The relative measurement error did not exceed 2%.

The microhardness of the annealed, cast, and the speed-quenched alloys were measured with a PMT-3 instrument with a load of 0.98 N. Each value was found as an arithmetical average of at least 8 measurements. The relative error in the measurement of the microhardness was 8%.

RESULTS AND DISCUSSION

The bulk fraction and the morphology of the segregated phases of both the cast and the annealed alloys in the Ti_2Ni–Zr_2Ni section are found to be close by the microstructure studies

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of crystalline alloys. There is a reduction in the size of the phases for alloys containing up to 13.5 at. % Zr, as there is also a sharply defined eutectic structure for an alloy containing 13.5 at. % Zr. The structure of alloys which contain from 17.5 to 33 at. % Zr consists mainly of an easily etched single solid phase which is based on an intermetallic compound. When the Zr content is higher than 33 at. %, one notices again the appearance of eutectic composition, the volume of which increases with increasing Zr. When the Zr content is 44%, the alloy has a complete, highly-dispersed, eutectic structure. A further increase in the Zr content leads to the appearance in the eutectic background of coarse needlelike phase segregations that are based on intemetalloids of Zr_2Ni.

Following annealing at 970 K for 200 h, the x-ray structure study of the crystalline alloys of the section showed the presence of the following phases in the alloys: δ-Ti_2Ni, face centered cubic (Fd3m), stable at up to 20% Zr content; an ℓ-Zr_2Ni, a body centerd tetragonal like $CuAl_2$ (I4/mcm), is present in the alloys containing 33-66.6 at. % Zr; and λ_I-ZrTiNi, a Laves phase of the $MgZn_2$ ($P6_3/mmc$). The parameters of the primitive cell of the Laves ternary phase of ZrTiNi with Zr content of 30 at. % were determined to be a = 5.191 Å, c = 8.520 Å, and c/a = 1.64. By changing the parameters of the λ_I phase primitive cell, it was determined that, at 970 K, the region of homogeneity of the Laves phase lies in the interval of 21-30 at. % Zr, for which case the parameters of the primitive cell are reduced from a = 5.142 Å, c = 8.433 Å to a = 5.191 Å and c = 8.520 Å. The region of homogenenous phase expands from that at stoichiometric composition to that corresponding to Ti enrichment. The values obtained for primitive cell parameter of the Laves phase differ from those given in [3] (a = 5.23 Å, c = 8.53 Å, c/a = 1.63). The difference may be related to the inequilibrium state of the alloy investigated in the cited work.

According to the results of DTA of an alloy having a Ti_2Ni stoichiometry, two effects are stable in the melting region of 1253 and 1273 K. Replacing Ti with Zr up to 13.5 at. % leads to a lowering of the liquidus temperature to 1173 K. The thermogram of the indicated alloys shows two endoeffects, and the temperature of the first effect T = 1173 K does not change while its intensity rises with increasing Zr. For 13.5 at. % Zr, there is one narrow endoeffect which indicates that the alloys are eutectic. In the Zr concentration interval from 17 to 30 at. %, the thermograms contain one endothermic peak which corresponds to the Laves phase λ_I, whose melting temperature changes from 1183 to 1193 K. A further increase in Zr content up to 44 at. % causes the reduction of the liquidus temperature to 1123 K, in which case, once again, two endoeffects, one of which is eutectic with T = 1123 K, are present in the thermograms. An alloy with 44 at. % Zr is eutectic (there is only one narrow endothermic peak). In the Zr concentration region from 44 to 66.6 at. % the liquidus temperature rises sharply, and for Zr_2Ni compounds, reaches (1313 ± 5) K.

The microhardness of the section changes from the value of 6000 MPa for the Ti_2Ni to 5000 MPa for that of Zr_2Ni when Ti is replaced by Zr (Fig. 1). In the Laves phase existence region, the value of the microhardness increases up to 7000-7300 MPa. In the main, the regularity in the change of the microhardness of both the cast and the annealed alloys of the section are maintained, except that, for the annealed alloys, it is expressed more sharply and obeys the Kurnakov law.

On the basis of the results of the physicochemical studies carried out on both the cast and the annealed alloys of Ti–Zr–Ni systems, a polythermic section of Ti_2Ni–Zr_2Ni (Fig. 2) is constructed. The special features of the structure of the given section is determined by the interaction of three intermetallic compounds of Ti_2Ni, Zr_2Ni, and ZrTiNi. The data of the eutectic type section consists of two low temperature eutectics that crystallize according to the reaction: $L \xrightarrow{1173K} \delta + \lambda_I$ and $L \xrightarrow{1123K} \lambda_I + l$. To the right and to the left of the centrally placed Laves phase, occur the dual phase regions. Although there is no Laves phase [4], in the binary systems of Ti–Ni, Ti–Zr, and Zr–Ni, a ternary Laves phase ZrTiNi with a broad region of homogeneity is formed in the Ti–Zr–Ni systems. Within the investigated section, the λ_I phase is congruently formed at a temperature of 1193 K, with the maximum occurring at 30 at. % Zr. The deviation of the position of the maximum from stoichiometry is apparently due to the incomplete dimensional correspondence. The Laves phase ZrTiNi has a large hardness H = 7000-7300 mPa and is very brittle, which is connected with the covalent components in the chemical binding energies [5]. The region of homogeneity of the phase narrows with decreasing temperature, and at 970 K it lies between 21 and 30 at. % Zr.

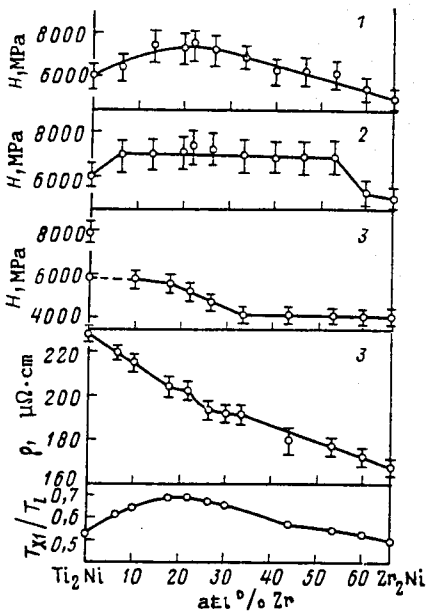

Fig. 1

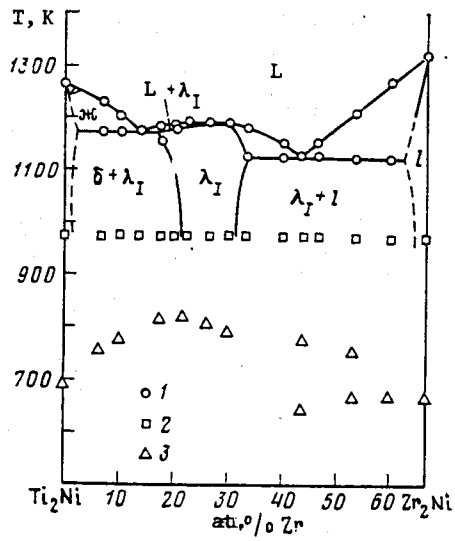

Fig. 2

Fig. 1. Composition diagram – properties of amorphous and crystalline alloys of a section of Ti_2Ni–Zr_2Ni in Ti–Zr–Ni systems [1 – crystalline (annealing 970 K, 200 h), 2 – crystalline cast, 3 – amorphous alloys].

Fig. 2. State diagram of polythermic section of Ti_2Ni–Zr_2Ni of Ti–Zr–Ni systems (1 – data of DTA, 2 – composition of crystalline alloys, 3 – crystallization temperature of amorphous alloys).

The alloys in the section were obtained in a speed-quenched state by the method of spinning the melt. It was determined by x-ray structure analysis of the speed-quenched ribbon that, in the angular region of 2θ = 40-60, there is a wide halo for all the investigated alloys, which indicates an amorphous state, with the exclusion of the Ti_2Ni alloy that has an amorphous structure. During heating, exothermic effects are present also on the amorphous structure of the speed-quenched ribbon. The temperatures of crystallization stages of the AA, as determined by the exoeffect, are given in Fig. 2. The thermal stability, AT, evaluated at the beginning of the crystallization peak T_{x1}, increases by increasing the Zr content in the alloys and reaches a maximum at 815 K at a composition with a 20-22 at. % Zr (Fig. 2). A further increase of the Zr content leads to a smooth diminution of T_{x1}. With Zr content more than 40 at. %, crystallization of AA proceeds in two stages. For example, an alloy with 53 at. % Zr crystallizes at temperatures of (T_{x1} = 663 K and T_{x2} = 753 K), and both stages have nearly the same value of exoeffects. Amorphous alloys corresponding to intermetallic compounds Ti_2Ni, ZrTiNi, and Zr_2Ni crystallize in one stage, accompanied by a strong and narrow exopeak.

By high-temperature x-ray investigation, it was determined that AA with Zr content less than 18 at. % crystallize in one stage with the formation of a face centered cubic phase of Ti_2Ni. At a Zr concentration from 18 to 40 at. %, the crystallization of AA proceeds also in one stage, but by already forming the Laves phase λ_I. In the Zr concentration region from 40 to 55 at. %, the AA crystallize in two stages: in the first, Zr_2Ni phase segregates, and in the second, the Laves phase λ_I. For alloys containing more than 55 at. % of Zr, only Zr_2Ni phase crystallizes.

When Ti is replaced by Zr the specific electrical resistance of AA changes from 222 to 168 μΩ·cm (Fig. 1), such that in the Zr concentration region of 22-33 at. % the course of the change in ρ deviates from linearity, and goes over a minimum at 30 at. % Zr.

The microhardness of the AA ribbon is higher by 3-5% on the contact side than on the free side. When Ti is replaced by Zr the microhardness decreases from 6200 to 4200 MPa (Fig. 1). According to the data of [6], the microhardness of AA Ti_2Ni is 5700 MPa, which is substantially lower than the 7800 MPa which is the value obtained. This discrepancy of the re-

sults is explained by the fact that the quenching speed was not enough in order to obtain the Ti_2Ni in a completely amorphous state. Therefore, the literature values are considered more reliable. A substantial change, approximately 25%, in the microhardness of AA is observed in the Zr concentration region from 20 to 33 at. %.

The amorphization tendency AT of the alloys in the section was evaluated by the well-known empirical criterion T_xT_ℓ [7]. As can be seen from Fig. 1, the AT of the alloys has a clearly expressed maximum at 22 at. % Zr, where for all the alloys in the section, the given criterion has a very high value from 0.50 to 0.69, when for most of the AA T_x/T_ℓ is 0.45-0.66 [7]. The lowest values of 0.53 and 0.50 are noted for AA having stoichiometric Ti_2Ni and Zr_2Ni, and the highest values of 0.66-0.69 for AA corresponding to the Laves phase λ_I.

A simultaneous examination of the results of the investigation of alloys that have been speed-quenched, cast, or in an equilibrium crystalline state shows that there is a relationship between the structure of the equilibrium state diagram and the character of the change of the properties in the amorphous and crystalline states. The thermal stability and the AT increase with increasing Zr content, and reaches a maximum at T_x = 790-815 K and T_x/T_ℓ = 0.66-0.69 for alloys in the stable Laves phase region. Then, the highest crystallization temperature and AT occur for a composition corresponding to the maximum solubility Ti in the ternary Laves phase, ZrTiNi. The same is observed when Ti is replaced by Zr in Ti_2Ni phase (very high quenching speed significantly expands the region of phase homogeneity). Apparently, the high AT and the thermal stability is connected with the existence in the given system of ternary Laves phase ZrTiNi that is characterized by the presence of icosahedral coordination, while such coordination practically does not exist for other phases [8]. The behavior of the change of the graph of composition vs property points to the special role of the Laves phase. In the concentration region corresponding to the existence of the Laves phase, kinks are seen in the curves for the dependence of ρ and H on the components of AA, with the reversal point at 30 at. % Zr. A similar change of property is characteristic of a phase with well expressed glass forming efficiency [9].

CONCLUSIONS

The structure and properties of alloys in the system Ti–Zr–Ni in the section of Ti_2Ni–Zr_2Ni, in speed-quenched, cast, and equilibrium crystalline states, were studied using methods of analysis for microstructure, x-ray structure, DTA, and resistance measurement, and by measuring the microhardness.

It was determined that the highest stability temperature, the tendency of alloys for amorphization as well as the kinks in the microhardness curves, and the electrical resistance of amorphous alloys are due to the existence in the given system of ternary Laves phase ZrTiNi of the $MgZn_2$ type, having a high glass-forming efficiency.

LITERATURE CITED

1. Yu. K. Kovneristyi, E'. K. Osinov, and E. A. Trofimova, Physicochemical Basis for the Creation of Amorphous, Metallic Alloys, Nauka, Moscow (1983).
2. E. Babich, Z. Maronich, D. Pavuna, et al., Analysis of Electrical Resistance of Amorphous Alloys of $Fe_{40}Ni_{40}B_{20}$ during Phase Transformations, Speed-Quenched Metals, Metallurgiya, Moscow (1983), p. 196.
3. M. Yu. Teslyuk, Metallic Compounds with Laves Phase Structure, Nauka, Moscow (1969), p. 127.
4. M. Hansen and K. Anderko, Constitution of Binary Alloys, Metallurgiya, Moscow (1962), p. 1111, 1125, 1316.
5. V. K. Grigorovich, Chemical Binding of Metalloids, Structure, Properties and Application of Metalloids, Nauka, Moscow (1974), p. 26.
6. D. E. Folk, A. Calka, and B. C. Giessen, The preparation and thermal and mechanical properties of new titanium rich metallic glasses, Acta Metall., No. 26, 1097 (1978).
7. G. A. Davis, Methods of Speed-Quenching and the Formation of Amorphous, Metallic Alloys, Speed Quenching of Metals, Metallurgiya, Moscow (1983), p. 11.
8. J. H. Guntherodt and H. Beck (editors). Glassy Metals II, Springer-Verlag, Berlin (1983).
9 A. Felt, Amorphous and Glassy Inorganic Solids, Mir, Moscow (1986).