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High-strength and ductile (Ti–Ni)-(Cu–Zr) crystalline/amorphous composite materials with superelasticity and TRIP effect

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ABSTRACT

Composition modification of (Ti–Ni)-(Cu–Zr) alloys with addition of Y, Co, Nb, Al and B was performed with the purpose of production of high-strength crystal-glassy phase composites. The structure of these samples with an amorphous phase was examined by X-ray diffraction, scanning and transmission electron microscopy. It was found that the addition of Y does not lead to increase in the glass forming ability of the Ni–Ti–Cu–Zr system alloys. Dual-phase structure allows developing the composite materials, which combine high strength of glassy alloys and good plasticity of crystalline alloys. Sixteen different alloy compositions were prepared and investigated. Mechanical characteristics of the alloys were determined using universal testing machines. For example, $Ti_{40}Ni_{39.5}Cu_8Zr_{10}Co_2Y_{0.5}$ alloy showed the compressive strength about 2600 MPa and total strain about 25%. Transformation-induced plasticity and superelasticity effects were found to exist. Large amount of Y (more than 0.5 at%) induces precipitation of the $NiTi_2$ phase which is harmful for mechanical properties. The addition of Nb, Al and B leads to increase in yield strength, but Al and B suspend martensitic transformation and as a result these alloys have lower overall plasticity. The specimens demonstrate a good combination of strength and plasticity owing to both the composite effect of a dual-phase structure and the dynamic martensitic transformation that develops during deformation.

1. Introduction

Bulk metallic glassy alloys exhibit a significantly higher level of mechanical properties than their crystalline equivalents [1–12]. However, these materials have one serious drawback, namely poor ductility in general. Developing a composite material consisting of amorphous and crystalline phases can allow solving this problem.

An effective method of increasing the plasticity of amorphous alloys can become a phenomenon of TRIP effect (Transformation Induced Plasticity) [3,13]. This effect is observed in the iron-, titanium- and nickel-based alloys. Deformation-induced martensitic transformations in which the austenite phase tends to transform into martensite during plastic deformation can enhance significantly the ductility and the fracture toughness of crystalline alloys [14–16]. This leads to the redistribution of stresses giving rise to a composite effect, which is associated with the observed large uniform elongation. TRIP effect takes place when the austenitic-type phase with cP2 type lattice, is transforming into mP4 phase (or rhombohedral one) during deformation [13,17,18].

It has been shown that the alloys of the (Ti–Zr)-(Cu–Ni)–Co system demonstrate a good combination of strength (1800 MPa) and ductility (5%) [19–21]. Also, for the $Ni_{40}Cu_{10}Ti_{33}Zr_{17}$ alloy the authors obtained ductility in compression up to 15% at maximum strength of about 2000 MPa [22].

The main idea of this research is to develop new dual-phase materials with good combination of strength and ductility. High strength comes from the amorphous phase. On the other hand, because of large fraction of a crystal structure, resulting material also has higher ductility (compared to fully amorphous materials). In this work, we analyze the structure and properties of Ni–Cu–Ti–Zr dual-phase materials additionally alloyed with Y, Co, Nb, Al and B that contain an amorphous phase, in which a martensitic transformation occurs during plastic deformation, which results in a substantial increase in their plasticity. Due to the

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presence of the amorphous phase these materials exhibit high strength. On the other hand, the presence cP2 NiTi phase leads to an increase in ductility in comparison with the completely amorphous alloys. In some series of these alloys Y was added as well in order to increase the glass forming ability (GFA) of the alloys, according to Ref. [23], and boron to obtain finer cP2 grain size [19,24].

2. Materials and methods

The raw materials for these metallic glasses films are elemental pieces with the purity higher than 99.9%. Alloys were firstly prepared by arc-melting under argon atmosphere with Ti-getter. Cylindrical specimens 3 mm in diameter and 50 mm long were fabricated from these ingots by melting and solidification using a moderate pressure die casting into a copper mold. The alloys compositions which were investigated in the present work are listed in Table 1. Base system (Ti–Ni–Cu–Zr) was chosen from the previous works [12,13,21,22]. The alloying elements were added keeping nearly equal content of nickel and titanium.

The structure of the specimens was studied by X-ray diffraction in monochromatic Cu-Kα radiation using a Bruker D8 diffractometer. The specimens for X-ray diffraction examination were shaped as disks 3 mm in diameter and 1 mm thick that were cut out from the original ingot using a Struers Accutom-2 bar-cutting machine with an accuracy of 0.03 mm. The examination of samples of this composition was carried out in a range of diffraction angles 2θ of 30°–80° with a step of 0.02° and an exposure time of 10 s. The structure of the samples and fracture surfaces after failure were observed using scanning electron microscopy (SEM).

The fine structure of the specimens was examined by transmission electron microscopy (TEM) at a voltage of 200 kV using a JEOL JEM 2010 microscope. High-resolution transmission electron microscopy (HRTEM) imaging was also performed. The specimens for TEM were produced initially by mechanical and finally by ion polishing.

The compressive mechanical tests were carried out in the Instron 5581 universal testing machine. The specimens 3 mm in diameter and 6 mm in height were subjected to compressive deformation at a rate of 5×10^{-4} s^{-1}.

3. Results and discussion

3.1. Structure

The XRD patterns of as-cast samples are shown in Figs. 1a, 2a and 3a. The XRD pattern indicates that the structure of samples contains a certain amount of the glassy phase (a broad peak is observed in the 2θ range 37°–46°) and the cP2 NiTi crystalline phase. A few samples contain the $NiTi_2$ crystalline phase in the structure. $NiTi_2$ phase precipitates in samples containing 1 at% Y (Fig. 2a). The difference in Ti and Ni content of more than 3 at% (alloys 1–4) also leads to precipitation of $NiTi_2$ phase. When the content of Ni and Ti is roughly equal (the difference is lower than 1 at%), $NiTi_2$ phase precipitations are not observed.

Table 1
Chemical composition of the studied alloys (in atomic percentage).

№	Ti	Ni	Cu	Zr	Co	Y	B/Nb/Al
1	42.0	39.0	9	10			–
2	42.0	39.0	7	10	2		–
3	42.0	38.5	7	10	2	0.5	–
4	42.0	38.0	7	10	2	0.5	B 0.5
5	40.0	39.5	8	10	2	0.5	–
6	40.0	39.0	8	10	2	1.0	–
7	40.0	39.4	8	10	2	0.5	B 0.1
8	40.0	39.0	8	10	2	0.5	B 0.5
9	40.0	38.9	8	10	2	1.0	B 0.1
10	39.5	39.0	8	10	2	0.5	B 1
11	41.0	40.5	8	8	2	0.5	–
12	40.5	40.0	8	8	2	0.5	Nb 1
13	40.0	39.5	8	8	2	0.5	Nb 2
14	39.5	39.0	8	8	2	0.5	Nb 3
15	40.5	40.0	8	8	2	0.5	B 1
16	40.0	39.5	8	8.5	2	0.5	Al 1.5

The results of structure investigation by using SEM and HRTEM are shown in Fig. 4 and Fig. 5, respectively. According to SEM image (Fig. 4) it can be found that the structure consists of a large amount of the crystalline phase (dark areas) and small amount of the amorphous phases (white areas at the grain boundaries). The average volume fraction of amorphous phase was about 20–25%. Energy dispersive X-ray spectroscopy (EDX) method was used to determine the chemical composition of the phases. As it was established by using the EDX spectroscopy method the crystalline phase is a highly alloyed cP2 NiTi phase while the amorphous phase is somewhat enriched in Zr and Cu. Both phases composition is close to the composition of the alloy. The Fig. 5 clearly shows the boundary between crystalline and amorphous phases (see red dashed line). Also Fig. 5 presents a selected-area electron diffraction pattern with the zone axis of [111]. The electron diffraction pattern shows the presence of a halo ring from the amorphous phase. The lattice parameter of the cP2 NiTi phase calculated, using the X-ray diffraction patterns was 0.312 nm, somewhat increased owing to dissolution of Zr. For comparison the lattice parameter of the equiatomic NiTi phase without other alloying elements is 0.3 nm [14].

According to our expectation [19] the addition of boron to (Ti–Ni)-(Cu–Zr) alloy improved morphology of the crystalline phase (Fig. 7). The structure of alloys 10 and 15 is shown in Figs. 6 and 7, respectively. It can be found that boron addition makes dramatic effect on the structure of the alloys. Grain size in Alloy 15 is much smaller than that in Alloy 10, about 0.5–1 micron for Alloy 15 and about 5–15 micron for Alloy 10. Also precipitation of $NiTi_2$ phase on the boundaries of the matrix phase (dark inclusions in bright phase) is no longer observed. It can be concluded that higher zirconium content promotes precipitation of the $NiTi_2$ phase. Presence of a large amount of $NiTi_2$ phase in the structure has negative effect on the mechanical properties.

3.2. Mechanical behavior

Three stages can be distinguished in the compression test curve (Fig. 8): A - elastic deformation, B - superelasticity caused by the martensitic transformation and C – plastic deformation. Strain hardening can be seen in the second stage (region B in Fig. 8); while region C is characterized by the intensive formation of shear (in the glassy phase) and slip bands (in the crystalline phase) on the surface of the sample. The values of ultimate stress (σ_b), stress of onset plastic deformation (σ_R), stress that induces martensitic transformation (σ_M) and total strain (ε) are presented in Table 2.

According to Figs. 1b, 2b and 3b it can be found that in most of the samples superelastic behavior takes place by using a reversible stress-induced martensitic transformation which greatly increases plasticity of these dual-phase samples. Mechanical engineering strength of the most samples, exhibiting martensitic transformation, exceeds 2000 MPa. One can also assume that the crystalline particles of the austenitic phase cP2 also act as barriers, which spread the shear deformation in the glassy phase that allows to activate multiple shear deformation channels and prevent brittle fracture of the sample. The diffusionless shear martensitic transformation takes place by the mechanism of the nucleation and rapid growth of crystals [25–27]. Usually, the martensitic phase