Structure and functional properties of rapidly quenched TiNiCu alloys with high copper contents

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Abstract. Thin materials exhibiting the shape memory effect, with a narrow temperature hysteresis, are required to create miniature and high-speed devices. Quasi-binary intermetallic TiNi-TiCu alloys with high copper contents (more than 10 at %) demonstrate the reversible martensitic transformation with a small (4-6 K) hysteresis. Alloys of the TiNi–TiCu system with a copper content of 30–40 at.% were fabricated in an amorphous state by the planar flow casting technique at a melt cooling rate of $10^6$ K/s in the form of ribbons 30–50 μm thick. The alloy samples were subjected to dynamic crystallization using a single electric current pulse with duration of 5 ms. X-ray diffraction studies revealed almost fully martensitic state of the alloys with B19 structure at room temperature. TEM examination showed their structure to contain typical B19-martensite plates with a mean size of 20–80 nm. At the same time, the alloys exhibit a one-stage phase martensitic transformation $B2 \leftrightarrow B19$ in the temperature range of $(55÷75)°C$, as well as pronounced shape memory effect, whose properties are largely determined by the structural parameters of the alloys.

1. Introduction

Shape memory alloys (SMAs) have attracted high attention because the unique properties of the shape memory effect (SME) and superelasticity appear [1,2]. Recently, the efficiency of using SMAs alloys has been shown to create devices in various fields of technology, in particular, in micromechanics, medicine, instrument making, and power engineering [3, 4]. In order to miniaturize devices and to create micro- and, possibly, nanodevices based on the SMAs, it becomes urgent to obtain micro- and nanocrystalline thin materials. Alloys of the quasi-binary intermetallic TiNi-TiCu system, formed by sputtering and by rapid quenching from the liquid state, are attractive materials for creating microactuators due to a narrow temperature hysteresis and a relatively large recoverable strain [5, 6].

It was found that TiNiCu alloys crystallized from the amorphous state have the best SME characteristics. Amorphization can be achieved in alloys with a high copper content (25–40 at.%) upon production by the planar flow casting technique [7], which consists in melting an ingot in a quartz crucible in an atmosphere of helium and extrusion of the melt through a slot nozzle in a crucible with a width 0.4 mm on the surface of a rapidly rotating copper wheel, which provided a melt cooling rate of about $10^6$ K/s.
To use amorphous alloys as functional materials with the SME, they must be crystallized with heat treatment. Crystallization annealing plays a decisive role in the formation of the martensitic structure of amorphous TiNiCu alloys, on which the martensitic transformations (MTs) occurring in these alloys and the accompanying SME largely depend. A key role in the formation of the structural state of alloys is played by the conditions of crystallization, especially deviations from the equilibrium conditions of crystallization, where the thermally activated processes of structural and phase transformations in alloys are suppressed at the solid-phase stage. The main variable parameters of heat treatment are usually its temperature and duration.

As established in previous study [7], when alloys with 25 and 30 at.% Cu are heated in a differential scanning calorimeter with a heating rate of 10 K/min from room temperature to 500°C, one-stage polymorphic crystallization of the amorphous state occurs with the formation of the austenitic B2 phase, which upon cooling to room temperature undergoes the MT into the orthorhombic B19 phase. At the same time, in alloys with a copper content of 35 and 40 at.%, exceeding the copper solubility limit in TiNi (30 at.%), two-stage crystallization is observed with the formation of a two-phase structure with for the most part a tetragonal B11 (TiCu) phase and an insignificant fraction of B2 phase. As a result, these alloys are brittle and unable to exhibit the SME. At the same time it was shown in [8] that radical reducing the time of heat treatment by using electropulsing allows one to almost completely hinder the formation of Ti-Cu phases in the melt-spun alloys with high copper contents (up to 38 at/%) and dramatically increases the plasticity and SME value of the alloys. This work aims to study the effect of electropulse heat treatment on structural and functional properties of amorphous TiNiCu alloys with a copper content of up to 40 at.% produced by planar flow casting.

2. Experimental

2.1. Samples
TiNi-TiCu alloys with a copper content of 30–40 at.% were fabricated in the amorphous state by planar flow casting technique at a melt cooling rate of $10^6$ K/s in the form of ribbons 30–50 µm thick [7]. Dynamic (high-rate) crystallization of the alloys from the amorphous state was performed by the method of electropulsing which consists in passing an electric current pulse 5 ms in duration through the alloy sample. In accordance with the calculations using the previously obtained relationship [8], the amplitude of the pulse at its specified duration was set in such a way as to provide the release of thermal energy necessary to heat the sample to the crystallization temperature. For this purpose, we used a specially designed laboratory installation that allows one to heat treat the sample by a DC electric current pulse from a capacitor bank with a preset power and duration. In this case, the resistance value of the sample is measured in the automatic mode, the required voltage of the capacitor bank is calculated according to the selected power and the duration of the current pulse and then the sample is annealed.

2.2. Methods
The structure of the obtained alloys was studied by metallography, electron microscopy, and X-ray diffraction analysis. For metallographic research of ribbon samples, their cross-sections were made using Buehler equipment. The last stage of polishing was carried out using an acid-containing mixed suspension with an abrasive grain size of 50 nm. The cross-sectional microstructure of the samples was investigated using FEI Quanta 600 FEG scanning electron microscope (SEM). The fine structure of the alloys was studied using JEOL JEM 2100 high-resolution transmission electron microscope (TEM). X-ray diffraction analysis was performed by Bragg-Brentano focusing on PANalytical Empyrean diffractometer in CuK$_\alpha$ radiation.

The differential scanning calorimetry (DSC) was used to determine the characteristic temperatures and enthalpy of MTs. DSC measurements were completed on a STA 449 F1 Jupiter calorimeter in heating and cooling cycles in the temperature range from –100 to 100°C at a rate of 5°C/min. The study of the functional properties of the alloys was carried out using the bending deformation method described in [9].
3. Results and discussion

The results of X-ray diffraction studies have shown that electropulse crystallization radically changes the microstructure of the alloys in comparison with isothermal heat treatment, which leads to the formation of a two-phase structure with a growing fraction of the B11 (TiCu) phase with increasing copper content [10]. The main difference is that dynamically crystallized alloys with 35 and 40 at.% Cu at room temperature are almost completely in the martensitic state with the B19 structure, what is confirmed by the presence of reflections of the B19 phase in the X-ray diffraction patterns and by the absence of pronounced peaks of the brittle B11 phase (Figure 1). When the alloy with 40 at.% Cu is heated to a temperature of 75°C, the peaks of the B19 phase disappear, and only reflections of the B2 phase are present, that is, the alloy passes into a completely austenitic state as a result of the B19↔B2 MT. Thus, electric pulse heat treatment makes it possible to almost completely block the formation of Ti-Cu phases in alloys containing copper in an amount exceeding the limit of copper solubility in TiNi (∼30 at.%).

Figure 1. X-ray diffraction patterns of rapidly quenched alloys of the TiNi-TiCu system after 5 ms electropulse crystallization.

SEM images of the cross-section of crystallized ribbons show an inhomogeneous distribution of crystals over the ribbon thickness (Figure 2): near the ribbon surfaces, a columnar structure of crystals is formed, while the ribbon contains single or grouped coarse grains with characteristic sizes from 3 to 12 μm. The observed columnar crystals from the surface go deep into the ribbon to the crystals formed in the bulk of the ribbon. The transverse dimensions of the columnar crystals on the contact and non-contact sides are approximately the same and range from 0.5 to 2 μm, and their height is in the range from 2 to 5 μm. In this case, the sizes of grains and columnar crystals are practically independent of the copper content. It is known that annealing at an ultrahigh heating rate contributes to the reduction of crystal particle sizes while retaining the morphology and crystalline structure of the alloys. However, instead of the expected significant structural refinement in the dynamically crystallized alloys in comparison with isothermally treated alloys we observed a considerable increase in the grain sizes. It is safe to assume that the observed effect is caused, among other factors, by a dramatic reduction of the number of crystallizing nuclei in the amorphous matrix with an increase in the copper content in the TiNi-TiCu alloys or by the irregular structure of the “frozen-in” crystallizing nuclei. However, verification of this hypothesis requires further studies as far as grain growth can be caused by different processes.
Figure 2. SEM images of typical cross-sections of rapidly quenched ribbons of rapidly quenched TiNi-TiCu alloys with 30 (a), 35 (b), and 40 (c) at.% Cu after electropulse crystallization.

TEM studies of crystallized alloys revealed the presence of nanosized martensite plates (20-80 nm) inside grains of a columnar structure near the ribbon surfaces (figure 3a), the corresponding diffraction pattern refers to the structure of B19 martensite. The coarse-grained structure contains a small amount of globular precipitates of the B11 phase up to 250 nm in size (figure 3b), whose electron diffraction patterns differ from the bulk of the ribbon. In the alloy with 34 at.% Cu, a similar pattern is observed, except that the precipitates are much smaller (10-50 nm) and are fairly uniformly distributed, mainly along the grain boundaries. The martensitic B19 microstructure of the alloy with 30 at.% Cu is more homogeneous and no precipitates of other phases were found (figure 3c).

Figure 3. Bright-field TEM images with the corresponding microelectron diffraction patterns of rapidly quenched TiNi-TiCu alloys with 40 (a, b) and 30 (c) at.% Cu after electropulse crystallization.

The established structural features in crystallized alloy samples significantly affect the character of the DSC curves (Figure 4). The main result is that in the alloys with copper content more than 30 at.%, after electropulse crystallization, pronounced peaks of heat release and absorption accompanying MTs are observed, while after isothermal heat treatment they were very weak and diffuse, or completely absent [10]. Obviously, this is due to the fact that, according to the X-ray structural analysis data, these alloys at room temperature are completely in the martensitic state with the B19 structure, which upon heating transforms into the austenitic B2 phase. The splitting of the DSC peaks, observed in the alloy with 30 at.% Cu, is obviously associated with the bimodality of the alloy structure, which consists of a grain structure in the bulk of ribbons and columnar crystals at the surface of the ribbons (Figure 2). Such structures can have different MT temperatures, what leads to superposition of peaks from each structure and bifurcation of the common peak. It should be noted that high-rate electropulse heat treatment of the alloys with 35 and 40 at.% leads to a significant increase in the MT enthalpy, as well as to a noticeable shift in the MT intervals to higher temperatures. The observed phenomena are
associated with an increase in the fraction of the B2 phase during electropulse crystallization by preventing the formation of the B11 phase.

Figure 4. DSC curves measured heating and cooling of rapidly quenched TiNi-TiCu alloys after electropulse crystallization.

Previously obtained results of bending tests of rapidly quenched TiNiCu alloys after isothermal treatment showed that with an increase in the copper content, ribbon samples become noticeably embrittled [9]. So, the alloy with 30 at. % Cu fail at the bending strain of 8-11%, the alloy with 35 at. % Cu - at the strain of 2-3%, and the alloy with 40 at. % Cu at the strains less than 0.2% and, as a consequence, is not able to exhibit the SME. As noted, this is due to the formation of the brittle TiCu phase. High-rate electropulse crystallization largely prevents the formation of this phase, which contributes to a noticeable increase in the plasticity of alloys with a copper content of more than 30 at.%, in particular, the alloy with 40 at.% Cu is able to withstand strains to fracture of about 4%. This ensures the manifestation of a significant SME characterized by a relatively large recovery strain up to 6.4, 4.1 and 2.5% in the alloys with 30, 35, and 40 at.% Cu, respectively.

4. Conclusions
The quasi-binary TiNi–TiCu alloys with high copper contents (30, 35 and 40 at.%) were produced by the planar flow casting technique in the form of thin amorphous ribbons and crystallized by high-rate electropulse heat treatment with duration of 5 ms.

The analysis of the X-ray diffraction and electron microscopy data shows that at room temperature the alloys are in almost fully martensitic state with B19 structure. Columnar structure of crystals is formed near the ribbon surfaces, while the bulk ribbon contains coarse grains with characteristic sizes from 3 to 12 μm. Nanosized B19-martensite plates (20-80 nm) and small amount of globular precipitates (10-250 nm) of the В11 phase are observed inside the grains. DSC study reveals the one-stage martensitic transformation B2↔B19 in the alloys; however certain splitting of the DSC peaks is observed because of the bimodality of the alloy structure. Results of bending tests demonstrate that the high-rate electropulse treatment ensures advanced plasticity and generates pronounced shape memory effect of the alloys.

Acknowledgments
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References
[1] Otsuka K and Ren X 2005 Prog. Mater. Sci. 50 511
[2] Sun L, Huang W M, Ding Z, Zhao Y, Wang C C, Purnawali H and Tang C 2012 Mater. Design 33 577
[3] Kohl M, Ossmer H, Gueltig M and Megnin C 2018 Shape Mem. Superelasticity 4 127
[4] Jani J M, Leary M, Subic A and Gibson M A 2014 Mater. Design 56 1078
[5] Shelyakov A V, Sitnikov N N, Menushenkov A P, Korneev A A, Rizakhanov R N and Sokolova N A 2013 J. Alloys Compd. 577 S251
[6] Ishida A, Sato M and Gao Z Y 2013 J. Alloys Compd. 577 S184
[7] Shelyakov A V, Sitnikov N N, Khabibullina I A, Sundeev R V and Sevryukov O N 2020 Phys. Solid State 62(6) 937
[8] Shelyakov A V, Sitnikov N N, Menushenkov A P, Koledov V V and Irjak A I 2011 Thin Solid Films 519 5314
[9] Shelyakov A V, Sitnikov N N, Borodako K A and Sevryukov O N 2020 Russ. Metall. 2020(4) 345
[10] Sitnikov N, Shelyakov A, Rizakhanov R, Mitina N and Khabibullina I 2017 Mater. Today: Proc. 4 4680