Investigation of thermal-structural characteristics at two-way shape memory effect of rapid quenched laminated amorphous-crystalline ribbons of Ti$_{50}$Ni$_{25}$Cu$_{25}$ alloy

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Abstract. The work is devoted to the study of processes of structural changes leading to the realization of the two-way shape memory effect (TWSME) in the rapid quenched amorphous-crystalline alloy Ti$_{50}$Ni$_{25}$Cu$_{25}$. The object of the study was a rapid quenched laminated amorphous-crystalline Ti$_{50}$Ni$_{25}$Cu$_{25}$ alloy ribbon with a thickness of about 39 $\mu$m and with a thickness of surface crystal layer about 10 $\mu$m present on the non-contact side relative to the quenching wheel. In the ribbon under study, without any additional heat treatments the TWSME with bending deformation from a rectilinear shape during heating and cooling in the range of martensitic transformation is manifested. The samples were characterized by means: scanning and transmission electron microscopy; X-ray diffraction analysis; differential scanning calorimetry; measuring the characteristics of the crystalline layer during the implementation of TWSME and the temperature dependence of the form change. It was shown that the formation of a laminated amorphous-crystalline composite occurs due to the martensitic transformation of B2$\leftrightarrow$B19 in the crystal layer and the accompanying TWSME as a result of which the crystal layer is reduced.

1. Introduction

Recently, the efficiency of using alloys with the shape memory effect (SME) to create microdevices in various fields of technology, in particular, in instrumentation, medicine, energy, space technology, and robotics, has been shown [1-3]. The ever-increasing demand for ultra-portable and highly efficient equipment is stimulating the development of small-sized, cheap and high-speed devices based on such alloys. To miniaturize devices, create micro- and, possibly, nanodevices, it becomes relevant to obtain fine-sized materials with the two-way shape memory effect (TWSME). In works [4-7] it was shown that laminated structures in which one of the layers is made of a material with SME are promising micro-sized drives.

A feature of TiNi-TiCu alloys with a high copper content is that when quenched by melt spinning methods, these alloys can be obtained in an amorphous state, and after crystallization by heat treatment they exhibit a pronounced SME [8, 9]. With partial crystallization of amorphous alloys, it is possible to obtain an amorphous-crystalline state, which is characterized by significant distinctive features. The laminated amorphous-crystalline state can be obtained by rapid quenching methods, for
example, by planar flow casting. A laminated amorphous-crystalline composite can be obtained directly during solidification of the melt due to the difference in the cooling rate of the melt on the contact (from the side of the cooling wheel) and non-contact (free) surface of the ribbon [10-12]. A remarkable feature of the manufactured amorphous-crystalline ribbons is that they exhibit the TWSME by bending without additional thermomechanical processing.

The aim of this work is to study the processes of structural changes that lead to the implementation of the TWSME in rapid quenched laminated amorphous-crystalline ribbons of Ti$_{50}$Ni$_{25}$Cu$_{25}$ alloy during thermal cycling in the range of martensitic transformations.

2. Experimental

As an object of study, an alloy of the quasi-binary system TiNi-TiCu with 25 at. % Cu obtained by rapid quenching (planar flow casting technique). Preliminarily, alloy ingots were prepared from ultrapure metals with sixfold remelting in an arc furnace in an argon atmosphere. The obtained preforms were melted in a quartz crucible in a helium atmosphere and extruded through a narrow nozzle in a crucible onto the surface of a rotating copper wheel. As a result of this process, occurring at a melt cooling rate of $10^5$ to $10^6$ C/s, rapid quenched laminated amorphous-crystalline Ti$_{50}$Ni$_{25}$Cu$_{25}$ alloy ribbons 30–50 μm thick and 1 to 2 mm wide in amorphous-crystalline states were obtained.

To determine the structure of the obtained samples of amorphous-crystalline ribbons, their transverse sections were made using Buehler metallographic research equipment. The last stage of polishing thin sections and the non-contact surface of the ribbon was carried out using a diamond suspension with a grain size of 1 μm. For additional clarification of the samples structures, their polished surfaces were etched with a HF(5%)+H$_2$NO$_3$(25%)+H$_2$O(70%) solution. The cross-sectional microstructure of the samples was studied using «Carl Zeiss Axiovert 40 MAT» inverted reflected light metallographic microscope and a «FEI Quanta 600 FEG» scanning electron microscope (SEM). The study of the microstructure of the free surface of the ribbon during heating and cooling was carried out in a SEM in the low vacuum mode on a specially made thermostat table with an integrated Peltier element at temperatures of 10 and 70 °C. X-ray phase analysis was carried out by Bragg-Brentano focusing using a hybrid monochromator on a «PANalytical Empyrean» diffractometer in Cu-Kα radiation, and heating and cooling studies were performed using a specialized thermostat. The investigation of the occurrence of martensitic transformations and concomitant electron-phase transition was carried out by differential scanning calorimetry (DSC) using a «STA 449 F1 Jupiter» calorimeter and methods of measuring the temperature dependence of the shape change.

3. Results and discussion

Depending on the melt cooling rate determined by the technological parameters of the quenching process, an amorphous, crystalline, or amorphous-crystalline state is formed in the ribbons [15-18]. At melt cooling rates of $10^6$ C/s and higher, the entire volume of the Ti$_{50}$Ni$_{25}$Cu$_{25}$ alloy ribbons is in an amorphous state, and at melt cooling speeds of $10^5$ C/s and below, the ribbon has a crystalline structure. At intermediate values of the melt cooling rate ($10^5$–$10^6$ C/s), crystallization can occur in the volume of the amorphous matrix, and as a result, an amorphous-crystalline ribbon forms with a crystalline phase unevenly distributed over the volume [11]. With uniform heat removal and observing the optimal technological parameters of spinning, a thin layer of the crystalline phase forms on the non-contact surface of the ribbon and an amorphous-crystalline ribbon forms with a sharp boundary separating the amorphous and crystalline states into layers. Such a ribbon is a laminated bimorph composite (Fig. 1).

In the work, from a series of obtained samples of rapid quenched ribbons for research, we selected a ribbon obtained at an alloy cooling rate of about $4 \cdot 10^5$ °C/s. For thermo-structural investigations the amorphous-crystalline ribbon of the total thickness about 39 μm and the crystalline layer thickness as 10 μm (Fig. 1) was chosen. Electron microscopic studies in cross-sectional SEM revealed a sharp boundary between the amorphous and crystalline layers, and also showed that the crystalline layer has
a columnar structure. The surface layer of columnar crystals is characterized by micron transverse dimensions of the crystals and has a pronounced texture.

Figure 1. SEM images of the characteristic cross-section of the laminated amorphous-crystalline ribbons of the Ti<sub>50</sub>Ni<sub>25</sub>Cu<sub>25</sub> alloy after etching (a), surface crystalline layer (b).

In the test sample of a rapid quenched amorphous-crystalline ribbon without any additional thermomechanical treatment, the effect of a TWSME with bending deformation is realized (Fig. 2). This effect is realized as follows, in the initial state at room temperature the ribbon has a straight shape, when heated, it begins to bend and takes a shape close to the ring (provided that the ribbon is of sufficient length). Cooling the amorphous-crystalline ribbon to room temperature leads to its return to its initial rectilinear state. Subsequently, when the temperature changes, this effect is cyclically repeated. The typical temperature dependence of the radius of the bending of the amorphous-crystalline ribbon is given in Fig. 2. For the test ribbon sample, the minimum ring diameter is approximately 15 mm. The measured values of the critical temperatures of shape change amount to: start (H<sub>s</sub> = 33 °C) and finish (H<sub>f</sub> = 43 °C) of forming during heating and start (C<sub>s</sub> = 41 °C) and finish (C<sub>f</sub> = 30 °C) of forming during cooling.

Figure 2. The variation in the shape of the amorphous-crystalline composite as a function of temperature (implementation of TWSME).

For the investigated object the heating and cooling cycles at an interval from 20 to 80 °C at the rate of 5°C/minute were conducted at the differential scanning calorimeter (DSC). As is seen from the DSC curves (Fig. 3a), in the original sample the characteristic peaks of heat absorption and release, attending martensitic transformations (MTs), and are evident in heating and cooling in the temperature region 28÷44 °C. The temperatures of start and finish of forward (martensitic) and reverse (austenitic) MTs have the following values: M<sub>s</sub> = 42; M<sub>f</sub> = 28; A<sub>s</sub> = 31; A<sub>f</sub> = 44 °C. The transformation energies comprise 2.3 and 2.1 J/g at the forward and reverse MT, respectively.

The comparison of the shape-recovery temperatures with the MT critical temperatures, obtained with the DSC, verify, that the ribbon shape changes due to SME realization as a result of MT occurring in the crystalline layer.
Figure 3. The DSC curves (a) and the XRD patterns at various temperatures (b) of the laminated amorphous-crystalline ribbon of the Ti₅₀Ni₅₀Cu₂₅ alloy.

Data from x-ray diffraction studies (Fig. 3b) obtained from the contact and free surfaces of the studied amorphous-crystalline ribbon showed that the free surface of the ribbon together with the martensitic phase B19 (the type orthorhombic martensite) has a residual austenitic phase B2 (the CsCl type of austenite). Phase B2 when cooled to room temperature does not completely pass into phase B19. This may be due to mechanical stresses in the surface crystal layer. It is noted that the most intense reflexes of the B19 phase are observed in the region of 58-65 degrees 2θ, and not in the region near 42 degrees, which is usually characteristic of the Ti₅₀Ni₂₅Cu₂₅ alloy [8]. There are also duplicate peaks in the area of 28 degrees. This arrangement of the main peaks indicates the texture of the surface crystal layer. From the contact surface of the ribbon peaks from the crystal phases are not observed, the layer is amorphous.

To determine the structural and phase characteristics of the surface crystalline layer at various temperatures known to be higher than Aᵣ and lower than Mᵣ, a specialized thermostat was used. Fig. 3b shows the resulting diffractograms. When heated to a temperature of +80 °C, the observed diffraction peaks of phase B19 almost completely pass into phase B2. Further cooling to room temperature returns the structure to its original state. When cooled to a temperature of -40 °C, the diffraction peaks of the residual phase B2 completely pass into the structure of type B19. Subsequent heating to room temperature returns the structure to its original state. Thus, it was shown that phase transformations of B₂↔B₁₉ occur in an amorphous-crystalline ribbon in a crystal layer on a free surface of the ribbon during heating and cooling.

To study the changes of geometrical parameters of structural elements of the crystal layer on the free surface of the amorphous-crystalline ribbon at transformation B₁₉↔B₂ and implement TWSME was held in the chamber of the SEM on specially made thermostat table. Previously, the surface of the ribbons was cleaned and polished with a diamond abrasive with a grain of 1 microns. To display the structural elements, the prepared surface was etched. The prepared samples were fixed on a thermostat table in the REM working chamber. Preliminary experiments with heating and cooling of the studied sample of an amorphous-crystalline ribbon on a thermostat table, performed at room temperature in the atmosphere, allowed us to visually observe a reversible shape change.

During the experiment, SEM obtained images of the free surface of the ribbon in the following temperature states: initial state (Tᵣᵣᵣᵣ); heated state (about +70 °C); cooled state (about +10 °C). Realized temperature states in accordance with the data of X-ray diffraction analysis and DSC correspond to martensitic and austenitic structural states. The obtained SEM images are shown in Fig. 4.
Figure 4. Schematic representation of temperature studies of the free surface of an amorphous crystalline ribbon (a) and SEM images in the initial state ($T_{\text{room}}$) (b), in the heated state (about +70 °C) (c), and in the cooled state (about +10 °C) (d).

At the images, it can be seen that in the heated state, the structural elements of the crystalline layer of the free surface of the ribbon change their size (compress) in the longitudinal direction of the ribbon (Fig. 4c), and no noticeable changes in the sizes of structural elements are observed in the transverse direction. According to the results of the measurements, upon transition to the austenitic state, the size of some structural elements in comparison with the initial state is reduced by up to 5%. Upon subsequent cooling of the ribbon of the amorphous-crystalline composite to a low-temperature state (10 °C), the structural elements return to sizes close to the original ones (Fig. 4d).

The obtained experimental data confirm the structural model of the formation of a rapid quenched layered amorphous-crystalline composite ribbon and the TWSME implementation scheme proposed in [10]. In accordance with this model, the formation of an amorphous-crystalline structure of an alloy and the appearance of a TESME are described in stages as follows:

1. In the process of manufacturing the ribbon, part of the melt, when it enters the quenching copper wheel, solidifies with the formation of an amorphous phase, while the other part of the melt does not solidify on the surface of the quenching wheel, but on the already formed amorphous alloy layer. In this case, the cooling rate of the external (non-contact) layer decreases, which upon solidification leads to the formation of a crystalline structure in this layer.

2. Further cooling of the crystalline layer should lead to its reduction due to the thermal compression process, however, an amorphous layer having a lower coefficient of thermal linear expansion, higher strength and greater thickness prevents this process.

3. As a result, upon cooling to room temperature, the crystalline layer is stretched and pseudoplastic deformed.

4. If this composite would be heated up to the temperature in the crystalline layer material, higher than $A_s$, then, at the expense of SME realization the crystalline layer will be aiming for compression (Fig. 4c), which gives rise to the bending of the composite much like the bimetallic plate (Fig.2). By the cooling, due to elasticity of the amorphous layer the composite comes back to the initial state.
4. Conclusions
The study of structural changes in the surface crystalline layer of a rapidly quenched layered amorphous-crystalline ribbon of the Ti_{50}Ni_{25}Cu_{25} alloy leading to the realization of the two-way shape memory effect (TWSME) is carried out.

It is shown that the shape change of the amorphous-crystalline ribbon composite occurs due to the occurrence of martensitic transformation in the crystalline layer and the accompanying shape memory effect. The data obtained confirm the structural model of the formation of a rapid quenched laminated amorphous-crystalline composite and the TWSME realization scheme, according to which, after the quenching process, the crystalline layer is stretched. When such a composite is heated above the temperature austenitic start, the crystalline layer will tend to compress due to the implementation of the electron-phase transition, which will lead to bending of the composite like a bimetallic plate. After cooling, the composite returns to its original state due to the elasticity of the amorphous layer.

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