The microstructure of rapidly quenched TiNiCu ribbons crystallized by isothermal and electropulse treatments

N N Sitnikov\(^{1,2,3}\), A V Shelyakov\(^{1}\), I A Khabibullina\(^{1,2}\), and E A Visotina\(^{1,2}\)

\(^{1}\)National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Moscow, 115409 Russia
\(^{2}\)Federal State Unitary Enterprise "Keldysh Research Center, Moscow, 125438 Russia

Email: sitnikov_nikolay@mail.ru

Abstract. The work is devoted to the study of the effect of isothermal and electropulse heat treatments on the structure of Ti\(_{50}\)Ni\(_{25}\)Cu\(_{25}\) (at.%) alloy with the shape-memory effect. The alloy was fabricated by rapid quenching from the liquid state (melt spinning technique) at the cooling rate of the melt of about 10\(^8\) K/s in the form of a layered amorphous-crystalline ribbon with a thickness of 28 \(\mu\)m. To obtain a completely amorphous state, the ribbon thickness was reduced to 22 \(\mu\)m by means of electrochemical polishing. The alloy samples were subjected to the electropulse treatment (dynamic crystallization) by passing a single electric current pulse with a duration of 10 ms through the sample. The electron microscopy and X-ray diffraction studies have shown that electropulse treatment leads to a significant change in the crystalline structure being formed, in comparison with that obtained by isothermal crystallization. It was revealed that after dynamic crystallization, the microstructure of alloys in cross-section has a non-uniform distribution of crystals (grains) over the ribbon thickness. A structure of columnar crystals is formed near the ribbon surfaces, while individual crystals or grouped large crystals are present in the ribbon bulk. In addition, the columnar structure is textured.

1. Introduction

Currently, one of the priority areas for the development of modern technologies is the development of new materials and the improvement of the properties of those already known. In accordance with modern trends in the development of science and technology, promising industries urgently require «smart» multifunctional materials, combining high-performance characteristics in addition to unique properties. Alloys with a shape memory effect (SME) represent a vivid example of such material, and various high-tech applications of these alloys stimulate their development [1-5]. Several studies have shown that excellent prospects for materials with the SME can be in micromechanics as thermal actuators. The unique simplicity and flexibility of the design of drive elements in the form of thin SME ribbons make them suitable for micromechanics. In the case of the use of micro-actuators with the SME in the form of thin ribbons, due to the significant value of the surface-to-mass ratio, the limitations arising during cooling for conventional SME actuators are significantly reduced.

For most applications, thin materials with the SME, which have a narrow hysteresis of the phase martensitic transformations (MTs) that gives rise to shape-memory behavior, are required at room temperature conditions [6-9]. Shape-memory materials that satisfy these requirements are alloys of the TiNi-TiCu quasi-binary intermetallic system. However, the conventional metallurgical fabrication (casting or sintering) of these alloys with a copper content of above 10 at.\% may lead to the formation of undesired Ti-Cu phases, which would embrittle alloys and hinder their MT. One of the promising
ways to produce "workable" microelements with the SME based on the quasi-binary TiNi-TiCu alloys is an ultra-rapid quenching from the liquid state [10, 11]. This method of extreme exposure allows one to produce thin ribbons in the crystalline, amorphous-crystalline, and amorphous states [12-14]. The advantage of obtaining the initial amorphous state is that, during the subsequent crystallization, it is possible to form structures with necessary characteristics that determine the parameters of MT and the accompanying SMEs. A promising method of forming a crystalline structure in an amorphous alloy is the electropulse heat treatment (EHT), which consists in passing an electric current pulse through the processed sample, resulting in the crystallization of the sample without isothermal exposure [15, 16]. Electropulse crystallization makes it possible to vary the parameters of heat treatment using additional external influences, for example, tensile mechanical stresses. The EHT, together with the application of external tensile stress, allows activation of the nucleation and crystal growth processes in an amorphous alloy, as a result of which structures with unique properties can be formed.

The aim of this work was the formation and study of new structural states in TiNiCu alloys with a high copper content as a result of extreme impacts.

2. Experimental
For the study was chosen the Ti50Ni25Cu25 (at.%) alloy, which has a high tendency to amorphization. The ingots of the alloy were prepared from pure metals with a sixfold remelting in an arc furnace in an argon atmosphere. The obtained ingots were melted in a quartz crucible in a helium atmosphere and extruded through a narrow nozzle in a crucible onto the surface of a rapidly rotating copper wheel. The cooling rate of the melt was about 10^6 K/s. Thus, the rapidly quenched Ti50Ni25Cu25 alloy was obtained in the form of continuous ribbons with a thickness of 28–30 μm.

In order to thin and remove crystalline phases from the surface, the obtained rapidly quenched ribbons were additionally subjected to electrochemical polishing using a PLS-3 electrolyte on the base of thiourea and sulfuric acid with complexing agents produced by the Technocom AS company. The applied voltage and current density were 5 V and 30–50 mA/cm², respectively, at the operation temperature of 20-25°C.

The alloy samples were subjected to EHT (dynamic crystallization) by passing a single electric current pulse with a duration of 10 ms through the sample. The pulse amplitude was set in such a way as to ensure the release of thermal energy necessary for heating the sample to the crystallization temperature [15]. For comparison, samples of the alloy were also crystallized by standard isothermal heat treatment in a furnace at 500°C with a holding time of 300 s.

The metallographic cross-sections of the rapidly quenched ribbons were made using «Buehler» equipment: an Isomet 1000 precision cutting machine, a Simplimet 1000 automatic hot-pressing hydraulic press machine, and an EcoMet 250+AutoMet 250 grinding and polishing machine. For additional revealing the structure, we used etching of the polished surface with a solution of HF(5%)+H₂O₃(25%)+H₂O(70%), followed by wiping with a 9% solution of H₂O₂.

The microstructure of the samples was studied «FEI Quanta 600 FEG» scanning electron microscope (SEM). The phase structure of the alloys was studied at room temperature via a PANalytical Empyrean X-ray diffractometer using Cu-Kα radiation, the Bragg–Brentano focusing scheme, and a hybrid monochromator.

3. Results and Discussion
For performing EHT of the ribbon, the uniformity of its geometric characteristics is very critical. The obtained rapidly quenched ribbon of Ti50Ni25Cu25 alloy (at.%) had a fairly uniform width, even edge, and uniform thickness. However, a crystalline layer forms on the free surface of the ribbon that is noncontact with the quenching wheel (Figure 1a), i.e., the ribbon is a layered amorphous-crystalline composite [12, 14]. Full amorphization of the ribbon can be achieved by increasing the melt cooling rate above 10^6 K/s, which is usually reached by increasing the wheel rotation speed. However, this degrades the stability of the geometric parameters of the resulting ribbon (uneven edges and holes are formed, and heterogeneity is observed in the thickness). Therefore, in this work, an amorphous ribbon
was obtained by removing the crystalline layer. For this, the method of electrochemical polishing was used. Its advantage is that the thinning is accompanied by the alignment of the surface of the ribbon due to the preferential removal of the protruding parts of the ribbon, thereby improving the geometric uniformity. The thinning rate can be controlled by the applied voltage. Under the condition of 5 V at 25 °C, the polishing rate was about 0.5 µm/min. The amorphous Ti₅₀Ni₂₅Cu₂₅ alloy ribbon of 50 mm long was polished in 12 min, providing ribbon thickness of about 22 µm. Typical SEM micrographs of the cross-section of a thinned (after electrochemical polishing) ribbon are shown in figure 1b. It is seen that, during the electrochemical processing, both thinning and polishing of samples occur. In particular, some irregularities disappear, and the surface becomes smoother.

![SEM micrographs of a typical cross-section of Ti₅₀Ni₂₅Cu₂₅ rapidly quenched ribbon in the initial (a) and thinned (after electrochemical polishing) (b) states.](image)

X-ray diffraction analysis confirmed (figure 2) that a crystalline layer is present on the free (noncontact) surface of the ribbon in the initial state, which at room temperature has a mixed structure of the martensitic phase B19 (orthorhombic martensite) and the austenitic phase B2 (austenite of CsCl type). Non-standard for Ti₅₀Ni₂₅Cu₂₅ alloys location of the most intense reflections in the range of 58-66 degrees on the diffractogram is explained by the textured crystalline layer, which is consistent with previous studies of rapidly quenched layered amorphous-crystalline ribbons [12-14]. On the diffractogram of the contact side of the ribbon, a wide diffuse maximum (“halo”) is observed in the absence of any structural peaks, which makes it possible to characterize it as amorphous.

After electrochemical polishing, the ribbon structure became amorphous as revealed by X-ray analysis (figure 2) The study of the surface and cross-section of the ribbon after electrochemical polishing confirmed the absence of a crystalline layer and made it possible to measure the average thickness of the obtained thinned ribbon, which is about 22 µm (figure 1b).

To compare the microstructures and the properties obtained, we studied the samples of the ribbons in both thinned (amorphous) and amorphous-crystalline (initial) states. The resulting ribbons were subjected to dynamic crystallization using a single pulse of electric current with a duration of 10 ms. For comparison, some alloy samples were crystallized by standard isothermal heat treatment in a furnace at a temperature of 500 °C for 300 s. As stated earlier [17], such annealing makes it possible to form a homogeneous crystal structure in amorphous TiNi-TiCu alloys with a copper content of 25 at.% and to obtain optimal characteristics of the SME.
As a result of the heat treatments, in all samples, a crystal structure was formed, which was characterized by X-ray diffraction studies (figure 3). On the diffractogram from the noncontact surface of the amorphous-crystalline ribbon after isothermal crystallization, as in the initial state, there is a non-standard arrangement of the primary reflections of the B19 phase (most intensive reflections in the region of 58-65 degrees). In the region of 42-43 degrees there are small peaks from the B19 phase. Reflexes from phase B2, observed in the initial state, are very weak. The data obtained may indicate a relaxation recrystallization of the crystalline layer with retention of texture. The contact side of this ribbon showed the presence of the main reflections of the B19 phase, located about 42 degree, that was typical for this alloy. The intensity of peaks from the contact surface is significantly less than those from the noncontact surface.

After EHT of the amorphous-crystalline ribbon, crystallographic reflections from the noncontact surface have a similar character as after isothermal treatment, the non-standard arrangement of the main reflexes of the B19 structure repeats. Still, the intensity of the peaks is almost two times less. Crystallographic reflexes from the contact surface differ somewhat from a similar curve obtained after isothermal treatment. There are observed reflexes of phase B19, located both in the region of 40-46 degrees (basic) and more pronounced reflexes in the region of 58-65 degrees, which was not observed after isothermal treatment. The data obtained indicate that, after isothermal crystallization, the surface of the crystalline layer remains textured from the noncontact side, which decreases somewhat after the

Figure 2. X-ray diffraction patterns of the contact (II, IV) and noncontact (I, III) surface of the Ti50Ni25Cu25 rapidly quenched ribbons in the initial (I, II) and thinned (III, IV) (after electrochemical polishing) states.

Figure 3. X-ray diffraction patterns of the contact (a) and noncontact (b) surface of the Ti50Ni25Cu25 rapidly quenched ribbons in the initial (I, III) and thinned (II, IV) states after isothermal crystallization (I, IV) and 10 ms dynamic crystallization (II, III).
EHT. On the contact side of the ribbon after EHT, some texture of the formed structure is also observed.

In the thinned ribbon (with the crystal layer removed) after isothermal crystallization from the noncontact side of the ribbon, peaks from the B19 martensite phase are observed, and the observed peaks, as well as in the initial state, are characterized by a non-standard intensity distribution. The peaks with the greatest intensity and area are located in the region of 58-65 degrees, and the peaks with lesser intensity are located around 42 degree. Peaks located in the region of 28-32 degrees are present, but are characterized by lower intensity. The main crystallographic reflexes from the contact surface are located in the region of 40-46 degrees, which corresponds to their typical location obtained on amorphous Ti50Ni25Cu25 alloys after isothermal treatment. X-ray diffraction studies of the thinned ribbon after EHT showed the different character of the main reflexes from the previously obtained data. The main intensity and area of crystallographic reflexes from the noncontact surface are located in the region of 58-65 degrees. Additionally, there are intense peaks in the region of 28-32 degrees, dual peaks in the region of 40-44 degrees, which may indicate the formation of a bimorph structure. The main peaks and area of crystallographic reflections from the contact surface repeat the data obtained from the contact surface of the initial ribbon after EHT, the intensity of the peaks is somewhat less. According to the data obtained, it can be assumed that during EHT with a duration of 10 ms, a heteromorphic structure is formed in the amorphous ribbon, part of which has some preferential orientation.

![Figure 4. SEM images of the cross-sectional structure of Ti50Ni25Cu25 alloy ribbons after isothermal treatment at 500°µ for 300 s in the initial (a) and thinned (b) states and after 10 ms EHT (dynamic crystallization) in the initial (c) and thinned (d) states.](Image)

Electron-microscopy studies of cross-sections of heat-treated ribbons have confirmed that the isothermal crystallization of the amorphous state leads to the formation of a crystalline structure in the entire ribbon volume (figure 4). It has been established that the isothermal treatment of the initial amorphous-crystalline ribbon leads to the formation in the ribbon of a bimorph crystalline structure.
consisting of a recrystallized crystalline layer (from the noncontact side) and a crystalline layer formed from the amorphous state (a part of the ribbon from the contact side). Formed structures have a clearly defined interface (Figure 4a). The recrystallized crystalline layer from the noncontact side has an average thickness of about 5 µm. The initial thickness of the crystalline layer before heat treatment was 2.5–3.0 µm, which indicates its growth during isothermal processing. The crystalline layer formed from the amorphous part on the contact side is characterized by a predominant submicrocrystalline structure with an average grain size of 0.6-1.1 µm.

In the thinned ribbon after isothermal treatment, a predominantly homogeneous crystal structure was formed with an average crystal size of 0.8-1.4 µm (Figure 4b). On the noncontact side of the ribbon, regions of columnar crystals up to 2 µm in height are locally observed. Such areas on the side of the polished noncontact surface of the ribbon could have been formed from the initial crystal layer that was not completely removed or that the surface had some defects after electrochemical polishing.

The EHT (dynamic crystallization), compared with isothermal heat treatment, fundamentally changes the microstructure of rapidly quenched Ti<sub>50</sub>Ni<sub>25</sub>Cu<sub>25</sub> alloy ribbons (Figure 4c, d). In dynamically crystallized alloys, there is a non-uniform distribution of crystals across the thickness of the ribbon: near the surfaces of the ribbon, there is a columnar structure of crystals, while in the volume of the ribbon, there are single or grouped larger grains with characteristic sizes from 5 to 15 µm. In the cross-sectional view of the amorphous-crystalline ribbon after the dynamic crystallization from the noncontact surface, the boundary of the initial crystalline layer is not revealed. Observed columnar crystals from the surface go deep into the ribbon to the crystals formed in the ribbon volume, some columnar crystals growth until they touch in the center of the ribbon. The dimensions of the columnar crystals with contact and noncontact sides in the diameter are approximately the same and on average, have sizes from 2 to 5 µm. A similar structure was formed in the thinned ribbon, with the exception of the transverse dimensions of the columnar crystals. The crystals located from the noncontact surface of the ribbon, are characterized as in the above case, the average transverse dimensions from 2 to 5 µm. The crystals located from the contact surface of the ribbon have smaller transverse sizes from 0.5 µm to 3 µm. Besides, in the thinned ribbon, there are more areas in which the columnar crystals adjoin in the center of the ribbon (figure 4d).

4. Conclusion
The EHT (dynamic crystallization) of the amorphous-crystalline and amorphous rapidly quenched Ti<sub>50</sub>Ni<sub>25</sub>Cu<sub>25</sub> alloy led to the formation of new structural states. It has been established that in contrast to isothermal treatment, the microstructure of alloys in cross-section has a non-uniform distribution of crystals (grains) over the ribbon thickness: a structure of columnar crystals has formed near the surfaces of the ribbon, and individual crystals or grouped large crystals are present in the ribbon volume. Columnar crystals from the surface were found to go deep into the ribbon to the crystals formed in the bulk. In some parts, the columnar crystals adjoin each other in the ribbon bulk, thus creating a uniform border. The resulting column structure is textured.

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