Influence of copper content and thermal treatment on shape memory effect in rapidly quenched TiNiCu alloys

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Abstract. Amorphous alloys of the TiNi - TiCu system with a copper content of 25 to 40 at.\% were prepared by planar flow casting at a melt cooling rate of 10^6 K/s. Crystallization of the alloys was carried out by isothermal annealing and by action of single electric pulse with a duration of 5 ms. Shape memory behavior and structure of the alloys was investigated by means of bending tests and X-ray phase analysis. It was found that increasing the copper content to above 30 at.\% considerably reduces the plasticity and shape memory effect of the alloys. However, abrupt decreasing the annealing duration significantly improves the shape memory performance due to prevention of the formation of brittle Ti-Cu phases in the alloys structure.

1. Introduction
Shape memory alloys (SMA) are a prime example of the so-called intelligent functional material [1,2]. The ability of the SMAs to retain their unique characteristics at the microscale level makes it possible to create on their basis effective devices for micro-electromechanical systems (MEMS) [3-5], which are currently one of the most innovative and fastest growing technologies. Alloys of the TiNi-TiCu quasi-binary intermetallic system, produced by rapid quenching from the liquid state in the form of thin ribbons about 40 μm thick, are an attractive material for creating microactuators due to the narrow temperature hysteresis of the martensitic transformation (MT) and the shape memory effect (SME) and the relatively large recoverable strain [6-10]. Recently, we have developed a number of micro-tweezers, which are a micromechanical instrument that provides gripping and holding micro- and nano-objects for spatial manipulation [11-13]. The possibility of manufacturing composite amorphous-crystalline microgrippers with SME using pulsed laser action is shown, the operation of the devices and their compatibility with most of the known micro- and nano-positioning systems are demonstrated experimentally.

It was found that the best characteristics are possessed by TiNiCu alloys crystallized from the amorphous state. Amorphization is achieved in alloys with a high copper content (more than 20 at.\%) at a melt cooling rate of about 10^6 K/s [6,9,14-17]. Recently, it was shown that an increase in the copper content up to 38 at.\% significantly affects both their structural and functional properties [18-20]. In this work, we investigated the shape memory behavior in rapidly quenched TiNiCu alloys depending on the copper content, as well as the method and duration of crystallization from the amorphous state.
2. Experimental

2.1. Samples
To obtain test samples, we have used the planar flow casting method [21], by means of which alloys of the TiNi–TiCu quasi-binary system with a copper content of 25, 30, 35, and 40 at.% (denoted below 25Cu, 30Cu, 35Cu, and 40Cu, respectively) were manufactured by rapid quenching from the liquid state at a melt cooling rate of 10^6 K/s in the amorphous state in the form of 30–50 µm thick ribbons.

2.2. Techniques
Thermal treatment of the alloys was carried out in two ways: by isothermal annealing in a muffle furnace in air at 500°C for 100–300 s and by passing a short (5 ms duration) electric current pulse through the sample. The annealing temperature was selected on the basis of the data [18], and the current amplitude and duration of the electric pulse heat treatment in accordance with the procedure presented in [22].

X-ray phase analysis was performed on a PANalytical Empyrean diffractometer in Cu-Kα radiation using Bragg-Brentano focusing with a hybrid monochromator.

The study of thermomechanical properties and parameters of the SME in alloys was carried out using the bending test method [23]. A ribbon sample of thickness d, to which a rectilinear shape memory was given, was bent through 180 degrees in the martensitic state and placed between the fixed and movable pressure plates. The distance D between the plates was set so that the sample acquired a given initial deformation ξ = d/D, which corresponds to the maximum deformation on the sample surface. After removing the load and subsequent heating above the temperature A measuring the the reverse MT, as a result of the SME implementation, the sample restored the specified rectilinear shape completely or partially, returning part of the accumulated strain ξsme, which characterizes the SME value. Observation and measurement of the shape change of the sample were implemented using a special video recording system and a data processing program.

3. Results and Discussion
For each alloy, we studied the thermomechanical characteristics of four samples, subjected to isothermal crystallization for 100 s, 200 s, 300 s, as well as dynamic crystallization by a single electric current pulse with duration of 5 ms.

Measurements of the value of the maximum deformation ξ, at which the fracture of the ribbon occurs, showed that an increase in the copper content leads to a sharp embrittlement of the alloys after isothermal treatment. If in alloys 25Cu and 30Cu the value of strain ξ reaches 8-11% depending on the duration of thermal treatment, then in alloy 35Cu it decreases to 1.5-3%. At the same time, the alloy 40Cu, regardless of the duration of isothermal treatment, is destroyed at ξ < 0.2% and, as a consequence, is unable to exhibit the SME. In this case, an increase in the time of isothermal treatment from 100 s to 300 s causes a decrease in ξ by several percent. The use of high-rate electro-pulse crystallization increases the plasticity of all alloys, especially sharply increasing the value of ξ for alloys 35Cu (up to 6%) and 40Cu (up to 4%).

The results of studying the SME parameters showed that for isothermally crystallized alloys 25Cu and 30Cu, the strain ξsme increases almost linearly with an increase in the initial strain ξ (Fig. 1). However, at ξ more than 3-5%, this increase noticeably slows down, which is probably because of an excess of the characteristic value of pseudoplastic strain in alloys of the TiNi-TiCu system [23] and with the occurrence of noticeable plastic strain. It is important to note that with a decrease in the duration of isothermal treatment from 300 s to 100 s, the ξsme value increases at the same ξ. The increase in the maximum value of ξsme is especially noticeable, which, for example, in the 30Cu alloy increases from 4.4 to 5.5%. In this case, an increase in the copper content noticeably decreases the maximum value of ξsme, and the 40Cu alloy is so brittle that any shape memory behavior is not observed in it.
Figure 1. Dependence of strain $\xi_{sme}$, recovered due to SME, on initial strain $\xi_i$ for alloys 25Cu (a), 30Cu (b) and 35Cu (c) after isothermal treatment with different durations (100 s, 200 s and 300 s).

The dependences of $\xi_{sme}$ on $\xi_i$ for alloys 25Cu and 30Cu, exposed to dynamic electro-pulse crystallization with a duration of 5 ms, have a similar character, however, the maximum strain $\xi_{sme}$ increases significantly (from 5.2% to 6.5% for the 25Cu alloy and from 4.6% to 7.1% for 30Cu alloy). At the same time, dynamic crystallization of samples with higher copper content (35Cu and 40Cu) dramatically changes their thermomechanical properties (Fig. 2). In the 35Cu alloy, a sharp increase in plasticity and the maximum value of $\xi_{sme}$ is observed, and in the 40Cu alloy, a significant SME appears after electro-pulse crystallization. In this case, the strain $\xi_{sme}$, restored due to the SME, continuously increases up to the fracture itself, and the alloy is able to withstand high strains until fracture.

Figure 2. Dependence of strain $\xi_{sme}$, recovered due to SME, on initial strain $\xi_i$ for TiNiCu alloys with different copper contents after isothermal crystallization for 100 s (a) and dynamic crystallization for 5 ms (b).

To clarify the reasons for the observed shape memory behavior, X-ray diffraction studies of crystallized alloys were carried out. It is known that the SME in alloys of the TiNi-TiCu system originates from thermoelastic martensitic transformation B2 $\leftrightarrow$ B19 [9,10]. The high-temperature austenitic B2-phase has a bcc lattice of the CsCl type, which upon cooling transforms into the martensite B19-phase (orthorhombic lattice). It has been established in this work that in alloys 25Cu and 30Cu after isothermal heat treatment for 300 s, a martensitic state with the B19 structure is formed, which is illustrated by characteristic diffraction patterns in Fig. 3a. A decrease in the time of isothermal crystallization from 300 s to 100 s does not lead to noticeable changes in the diffractograms. It is obvious that these structural features explain the large value of the SME in these alloys.
Figure 3. X-ray diffraction patterns of TiNiCu alloys after isothermal crystallization: 25Cu and 30Cu for 300 s (a), 35Cu (b) and 40Cu (c) with different durations (100 s, 200 s and 300 s)

The isothermal treatment of the 35Cu alloy for 300 s predominantly forms a B11-type structure (Ti-Cu phase) (Fig. 3b), which embrittles the alloy and prevents the appearance of SME. A decrease in the duration of crystallization to 100 s causes a noticeable decrease in the intensity of the peaks of the B11-phase and the appearance of reflections of the B19 phase, as a result of which a two-phase structure (B19+B11) is formed. As a result, the alloy exhibits the SME, but its value is rather small (Fig. 3c). In the 40Cu alloy, after holding for 300 s, only reflections from the B11-phase are visible in the diffractogram (Fig. 3c). With a decrease in the processing time to 100 s, the shape of the diffraction patterns slightly changes, but, in contrast to the 35Cu alloy, the peaks of the B11-phase are completely retained and peaks of reflections from the planes of the B19-phase do not appear. Thus, the structural state of the 40Cu alloy after isothermal treatment with any duration is determined by the brittle B11-phase, which explains its extremely low plasticity and the inability to exhibit SME.

The microstructure of 35Cu and 40Cu alloys radically changes after high-rate electro-pulse crystallization in comparison with isothermal heat treatment. The main difference is that at room temperature these alloys are almost completely in the martensitic state with the B19 structure, which is confirmed by the presence of reflections of the B19 phase in the X-ray diffraction patterns and the absence of pronounced peaks of the brittle B11-phase (Fig. 4). When the 40Cu alloy is heated to a temperature of 75°C (above $A_f$), 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$\leftrightarrow$B2 MT, which ensures the appearance of the SME.

Figure 4. X-ray diffraction patterns of the alloys 35Cu and 40Cu after electro-pulse crystallization for 5 ms
structural analysis were used to determine the SME parameters in alloys and their relationship with the crystal structure formed during thermal treatment.

It was found that an increase in the copper content of more than 30 at.% leads to a sharp decrease in the plasticity of isothermally crystallized alloys and the disappearance of the SME in the 40Cu alloy. It is shown that this is due to the formation of brittle Ti-Cu phases in the alloy structure. A decrease in the duration of heat treatment from 300 s to 100 s leads to insignificant changes in the structure of the alloys, accompanied by a slight increase in plasticity and the magnitude of the SME.

High-rate electro-pulse treatment makes it possible to almost completely block the formation of Ti-Cu phases in alloys with a high copper content, which makes it possible to realize a noticeable SME in such alloys.

Acknowledgments
The study was carried out at the expense of a grant from the Russian Science Foundation (Project No. 19-12-00327).

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