Effect of aluminum alloying on the structure and properties of rapidly quenched TiNiCu alloy

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Abstract. The efficiency of shape memory alloys for the MEMS technology has been recently demonstrated. Quasibinary intermetallic TiNi-TiCu alloys produced by rapid quenching from liquid phase in the form of thin (about 40 μm) ribbons are an attractive material for the fabrication of micro-actuators due to their narrow temperature hysteresis of the shape memory effect (SME) and relatively large recoverable strain. In order to broaden the functionality of SME microdevices, in this work we have alloyed TiNiCu containing 25 at.% copper with aluminum. The results have shown that alloying with 0.6 at.% Al increases the cast characteristics of the composition and favors its amorphization. Upon crystallization by isothermal annealing or electropulse treatment the resultant microstructure and SME properties of the Al containing alloy change but slightly in comparison with the original alloy however there is a significant shift (by more than 15°C) of the SME temperature range toward lower temperatures.

1. Introduction

Shape memory alloys (SMAs) are a bright example of the so-called smart functional materials [1, 2]. The ability of SMAs to retain their unique properties on a microscopic scale allows fabricating high-efficiency devices on their basis for microelectromechanical systems (MEMS) [3-5] which is one of the most rapidly developing innovative technologies today. Alloys of the TiNi-TiCu quasibinary intermetallic system produced by rapid quenching from the liquid phase in the form of thin (about 40 μm) ribbons are an attractive material for the fabrication of micro-actuators due to their narrow temperature hysteresis of the martensitic transformation (MT) which is the basis of the shape memory effect (SME) and relatively large recoverable strain [6-10]. We recently developed a series of microtweezers – a micromechanical tool for gripping and holding of micro- and nanoscale objects for their further spatial manipulation and preparation [11-13]. Thereby we experimentally showed the possibility of fabricating composite amorphous-crystalline microgrippers with SME using the pulse laser treatment technique and demonstrated the operation of the devices and their compatibility with most of the existing micro- and nanopositioning systems.

An efficient way to broaden the functionality of SME microdevices is to provide new alloys with modified properties. It is well-known that even a slight change in the chemical composition of TiNi-based alloys causes major changes in their thermomechanical properties [14]. For example, an increase in the Ni content in binary TiNi alloys by only 1 at.% relative to the equiatomic composition...
leads to a considerable decrease in the MT critical temperatures and a strong change in the alloy structure (phase composition). On the other hand, addition of third component, e.g. hafnium, to TiNi alloys allows shifting the MT temperature range by decades of degrees toward higher temperatures. Research is currently underway into the effect of alloying of ternary TiNiCu alloys with fourth component (aluminum) on the alloy structure, phase MT characteristics and SME parameters.

2. Experimental
The test material was the quasibinary TiNi–TiCu alloy containing 25 at.% copper (hereinafter referred to as 25Cu) and the 25Cu alloy with 0.6 at.% Al addition (denoted as 0.6Al). The alloy compositions and notations are summarized in Table 1.

| Alloy  | 25Cu       | 0.6Al        |
|--------|------------|--------------|
| Composition (at.%) | Ti<sub>50.2</sub>Ni<sub>24.8</sub>Cu<sub>25</sub> | Ti<sub>50.2</sub>Ni<sub>24.8</sub>Cu<sub>24.4</sub>Al<sub>0.6</sub> |

The alloys were produced by rapid quenching from the liquid phase (the planar flow casting technique) [15, 16] in the form of 30–50 μm thick ribbons at a melt cooling rate of 10<sup>6</sup> K/s which was maintained constant for both the alloys.

The alloys were heat treated by two methods: isothermal annealing at 500°C for 300 s and electropulse method, i.e., passing a short electric current pulse with preset duration and amplitude through the specimen for specimen heating to the specified temperature due to Joule heat release. To calculate the required parameters of electropulse crystallization of the amorphous specimens we used the current density to electric pulse duration relationship derived by us earlier [8].

The structure of the alloys was studied by metallography, electron microscopy and X-ray diffraction. For the metallographic study of ribbon specimens we prepared their cross-sections using Buehler equipment. Final polishing was conducted using an acid-containing mixed suspension with an abrasive grain size of 50 nm. The cross-section microstructure of the specimens was studied under a FEI Quanta 600 FEG scanning electron microscope (SEM). X-ray diffraction analysis was carried out with Bragg-Brentano focusing and a hybrid monochromator on a PANalytical Empyrean X-ray diffractometer in Cu-Kα radiation.

The characteristic temperatures and enthalpy of the MT in the alloys were determined using differential scanning calorimetry (DSC) on an STA 449 F1 Jupiter calorimeter by heating and cooling cycles in the 20 to 100°C range with 5°C/min steps.

The SME in the alloys was studied by bend testing [17]. A ribbon specimen with thickness d having a preset straight shape memory was bent by 180° in the martensitic state and placed between a stable and a movable pressure plates. The distance D between the plates was set so the ribbon acquire the preset initial strain $\xi_i = dl/D$ providing for the maximum specimen surface strain. After the removal of the load and subsequent heating to above the reverse MT finish temperature $A_f$ the SME occurred in the specimen to recover the preset straight shape, either completely or partially, thus returning part $\xi_{sme}$ of the accumulated strain which characterizes the SME magnitude. As shown earlier [17], $\xi_{sme}$ is determined by the relationship $\xi_{sme} = \xi_i (180°-\alpha)/180°$, where the angle $\alpha$ is in degrees. The changes in the specimen shape and the angle $\alpha$ were traced using a special video control system and data processing software.

3. Results and Discussion
The initial structure of the rapidly quenched ribbons of the test alloys was studied using X-ray phase analysis both at the contact (oriented towards the quenching wheel) and the noncontact (free) surfaces of the ribbon (Fig. 1). The room-temperature X-ray diffraction patterns for the ribbon free sides of the 25Cu alloy contained clearly expressed diffraction peaks of both the austenitic phase $B2$ (CsCl type
bcc lattice) and the martensitic phase $B19$ (AuCd type orthorhombic lattice) whereas those patterns for the 0.6Al alloy contained a smeared halo near $2\theta = 42$ deg indicating its amorphous state. Electron microscopic studies of the alloy microstructure for the ribbon cross-sections showed that this difference between the alloys is caused by the formation of a $\sim 3\ \mu m$ thick surface crystalline layer at the 25Cu alloy ribbon free side during quenching (Fig. 2d) whereas such a crystalline layer did not form on 0.6Al ribbons (Fig. 2a). The non-typical positions of the most intense reflections in the X-ray diffraction patterns of the $B2$ and $B19$ phases are accounted for by the formation of textures on the formed crystalline layer. It should be noted that the contact surfaces of both alloy ribbons had neither crystalline layers nor structure-related peaks in the X-ray diffraction patterns. Thus study of the 0.6Al alloy showed that additional aluminum alloying of the 25Cu alloy leads to its complete amorphization.

![Figure 1](image1.png)

**Figure 1.** X-ray diffraction patterns for contact and free surfaces of 25Cu and 0.6Al alloys in as-quenched state (at room temperature).

![Figure 2](image2.png)

**Figure 2.** Cross-sectional SEM images of rapidly quenched ribbons of 0.6Al (a, b, c) and 25Cu (d, e, f) alloys, in the initial state (a and d), after isothermal crystallization (b, e) and after electropulse crystallization with 5 ms pulse duration (c, f)
Analysis of the cross-sectional SEM images of the ribbons after isothermal crystallization from the amorphous state showed that a submicron crystalline structure forms both in the 25Cu and in the 0.6Al alloys with an average grain size of 0.5-0.7 µm (Fig. 2b, c). Noteworthy aluminum alloying of the 25Cu alloy changes its structural morphology but slightly. X-ray study revealed that aluminum alloying does not either considerably affect the phase composition of the 25Cu alloy (Fig. 3a). It can be seen that the 0.6Al alloy is completely in the $B19$ martensitic state at room temperature which is confirmed by the presence of $B19$ phase reflections and the absence of strong peaks of other phases in the X-ray diffraction patterns.

The DSC curves of the 0.6Al alloy specimens after isothermal crystallization contained typical heat absorption peaks (during heating) and heat emission peaks (during cooling) in the 20 to 70°C range (Fig. 3b), indicating the single-stage polymorphic MT $B2 \leftrightarrow B19$. This suggests that the crystallization leads to the formation of a homogeneous single-phase structure. A similar MT behavior for the 25Cu alloy was reported in a number of earlier works [8, 16, 18]. However according to the DSC curves of the 0.6Al alloy its MT temperature ranges are noticeably shifted (by more than 15°C) toward lower temperatures in the 30 to 45°C range. This fact can be obviously used for broadening the functionality of the TiNiCu alloy with 25 at.% Cu for the fabrication of SME devices.

Electropulse (dynamic) heat treatment with 5 ms pulse duration dramatically changed the microstructure of the alloys as compared with isothermal annealing (Fig. 2c, f). The cross-sectional SEM images of the dynamically crystallized ribbons show an inhomogeneous distribution of crystals in the ribbon thickness: a columnar crystal structure forms near the ribbon surfaces whereas discrete or agglomerated large grains with typical sizes of 3 to 12 µm are observed in the ribbon bulk. The columnar crystals observed near the surface migrate inward to the crystals forming in the ribbon bulk. The transverse sizes of the columnar crystals at the contact and free sides of the ribbons are nearly the same, i.e., 0.5 to 2.0 µm, their heights ranging between 2 and 5 µm. It is well-known that annealing...
with an high-rate heating rate favors a decrease in the size of the forming crystalline features while retaining the same morphology and crystalline structure and should therefore lead to the formation of finer structures in comparison with conventional isothermal furnace annealing. As we noted earlier [19, 20], this considerable increase in the grain size for dynamically crystallized TiNiCu alloys can be caused by a decrease in the number of crystallization centers in the amorphous matrix with an increase in the copper content in the alloys or by the lack of a regular structure of the “frozen-in” crystallization centers.

The X-ray diffraction patterns show that by analogy with isothermal annealing, dynamically crystallized 25Cu and 0.6Al alloys are completely in the martensitic state at room temperature with the $B_{19}$ structure (Fig. 3a). Heating of the 0.6Al alloy to 70°C (above the temperature $A_f$) leads to the elimination of the $B_{19}$ phase peaks, and only the $B_2$ phase reflections remain, i.e., the alloy transits to the completely martensitic state as a result of the MT $B_{19} \leftrightarrow B_2$. It should be noted that the diffraction pattern of the 0.6Al alloy in the martensitic state contains quite an intense peak near $2 \theta = 40.8$ deg which is not eliminated upon the transition to the austenite state. This peak can be identified as the (110) reflection of the $B_{11}$ phase but one cannot affirm safely the presence of this phase in the alloy structure because the diffraction patterns do not contain visible reflections from other crystal planes of this phase.

The experimentally shown structural properties of the dynamically crystallized specimens have a significant effect on the DSC curve patterns of the alloys (Fig. 3b), i.e., splitting of the heat emission and absorption peaks. This is likely to be associated with the bimodal structure of the alloys which contain a grain structure in the ribbon bulk and columnar crystals near the ribbon surfaces (Fig. 2c, f). These structures may have different critical MT temperatures resulting in superposition of peaks from different structures and splitting of the common peak. Furthermore electropulse crystallization appreciably increases the MT critical temperatures (by more than 10°C) for the 0.6Al alloy; the same phenomenon was earlier found in other TiNiCu alloys [20].

Then we determined the SME parameters of the alloys by recording curves of the SME recovered strain $\xi_{sme}$ vs the initial strain $\xi_i$. The results showed that after isothermal annealing $\xi_{sme}$ increases in an almost linear manner with an increase in the strain $\xi_i$, whereas at $\xi_i > 5\%$ this growth becomes considerably slower which seems to be caused by the exceeding of the pseudoplastic strain for the TiNi-TiCu system alloys [10, 21] and the generation of a tangible plastic strain. The maximum measured deformation $\xi_{sme} \approx 5.1\%$ is almost the same for the 25Cu and 0.6Al alloys. However the dynamic crystallization of the specimens considerably increases their maximum strain $\xi_{sme}$ (to 6.4%). Thus aluminum alloying of the 25Cu alloy (0.6 at.%) does not compromise its SME parameters.

4. Conclusions
A quasibinary TiNi-TiCu system alloy with a copper content of 25 at.% in the form of a layered amorphous-crystalline ribbon was produced by rapid quenching from the melt (the planar flow casting technique). We showed that aluminum alloying to 0.6 at.% causes complete amorphization of the alloy during quenching.

Isothermal crystallization of both the initial and the alloyed alloys produces a submicron crystalline structure of orthorhombic martensite $B_{19}$ with an average grain size of 0.6-0.7 μm which transforms to the austenitic phase $B_2$ during heating as a result of the polymorphic martensitic transformation $B_2 \leftrightarrow B_{19}$. However aluminum alloying significantly (by more than 15°C) reduces the critical MT temperatures and hence shifts the SME temperature range toward lower temperatures. The maximum SME-recovered bending strain is 5.1% regardless of alloying.

High-rate electropulse crystallization with 5 ms duration dramatically changes the microstructure of the alloys as compared with isothermal annealing and increases the SME magnitude to 6.4% but also noticeably increases (by about 10°C) the critical MT temperatures.
Thus aluminum alloying of ternary TiNiCu alloys with SME allows one to broaden their functionality by varying the SME temperatures while retaining the high mechanical parameters of the SME.

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