Modification of properties of the rapidly quenched TiNiCu alloy under laser irradiation

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Abstract. The work deals with the study of the influence of combined action of thermomechanical and laser treatments of rapidly quenched TiNiCu thin ribbons on the properties of two-way shape memory effect. It was shown that increasing of the energy density of the laser radiation and the external mechanical stress leads to growth of the reversible strain of the received amorphous-crystalline composite in the interval of martensitic transformation.

1. Introduction

Progress of knowledge intensive technologies in most industrial branches has been caused by miniaturization, rise of economy and response speed of actuator elements. In last decades microelectromechanical systems (MEMS) find rapidly their ways into a wide range of applications, such as aviation, automobile, nano-technological or biomedical devices [1-3]. That leads to a necessity of development and investigation of new functional materials, being capable of operating at the micro- and nano level and creating new principles of design of microsystems.

Efficiency of the use of alloys with the shape memory effect (SME) for making of different-type microdevices was demonstrated recently [4-8]. Practical use of SME alloys in micromechanical devices assumes, as a rule, a reversible change of shape in a heating-cooling cycle. Our recent demonstration has revealed [9, 10], that laser treatment of surface of thin TiNiCu ribbons, produced by melt quenching, results in forming amorphous-crystalline composite, that is capable of doing cyclic work due to realization of the two-way SME. This work has been aimed at research of the effect of the combined action of thermal-mechanical and laser treatment of the quenched TiNiCu alloy on its thermal deformational characteristics on realization of two-way SME.

2. Materials and techniques

The work had to do with the alloy of quasi-binary TiNi-TiCu system at 25% of the copper atomic content, produced in the form of amorphous ribbons of 40 μm thick and 2 mm wide with using rapid quenching from the liquid state [11-16]. Crystallization of the amorphous ribbon and specific shape setting were conducted through isothermal annealing in a muffle furnace at temperature of 500°C in
the course of 5 minutes. It has been revealed previously [17], that such process of heat treatment leads to the formation of submicrocrystalline structure with the average size of grain from 400 to 600 nm and manifestation of the pronounced SME.

The technique for forming the two-way shape memory effect (TWSME) through combined action of thermal-mechanical and laser treatment of the ribbon out of the rapidly quenched TiNiCu alloy is schematically shown in Fig.1. The ribbon is first endowed with memory of rectangular shape with using a special mandrel (Fig.1a). Then it is lengthened in the longitudinal direction under the mechanical load, $\sigma$, in the process of forward martensitic transformation (MT) up to a certain strain, $\xi$. Next the ribbon surface is subjected to the action of short pulse of laser radiation at the energy density, ample for heating of the sample surface layer above the melting temperature. As it was revealed in [9], as a result, a laminated structural composite with the interface, separating the amorphous and crystalline states into layers, is being formed. If this composite would be heated above the temperature $A_s$ of the start of the reverse MT in alloy, then, due to SME realization, the crystalline layer would strive to compression, which gives rise to composite bending at a certain radius $R_{min}$, like a bimetallic plate (Fig. 1b). On cooling below the temperature $M_f$ of the end of the forward MT the ribbon is partially straightened up to the bending radius $R_{max}$ due to elasticity of the amorphous layer, acting as a restoring force. Owing to the transformation plasticity effect [18], with the cooling during the forward MT, monodomain formation of martensite variants takes place in the crystalline layer and large strains, oriented along the direction of the applied elastic force of the amorphous layer, are accumulated. So, significantly lesser forces are required to deform the crystalline layer, and in which connection the amorphous layer thickness can be much less (a few times or even one or two orders), than that of the crystalline layer. Later on in the heating-cooling cycle reversible bending strains of the sample happen, i.e., the amorphous-crystalline composite ribbon, produced by this technique, is capable of showing evidence of TWSME.

**Figure 1.** Diagrammatic representation of the technique for forming TWSME through the combined action of thermal-mechanical and laser treatment of the SME alloy ribbon: (a) – the treatment of the ribbon, (b) TWSME in the ribbon.
In accordance with the preliminary calculations the TiNiCu alloy ribbons were treated with using a single pulse (its duration - 20 ns) of radiation of the CL7000-series excimer laser with gas mixture KrF, with the wavelength - 248 nm, the laser energy density thereat was varied from 5 to 17 mJ/mm².

Metallographic cross-sections of the ribbons in hand were manufactured on BUEHLER® firm equipment: precise cutting-off machine «Isomet 1000», automatic hydraulic press for shrink fitting «Simplimet 1000», grinding-buffing machine «EcoMet 250+AutoMet 250».

Microstructure of the cross-section of the samples produced was studied by scanning electron microscope (SEM) «FEI Quanta 600 FEG» with field-emission cathode and integrated attachment for energy-dispersion X-ray microanalysis EDAX.

X-ray structural analysis was performed with the sliding X-ray beam method on diffractometer D8 Discover. X-ray lines profiles were obtained by survey in Cu Kα₁ radiation with pyrolytic graphite monochromator.

3. Results and discussion

According to the technique, proposed for the formation of TWSME, prior to the laser radiation action the ribbon with memory given to have rectangular shape, is extended lengthwise up to a certain strain ξ. To gain the maximum value of ξ the mechanical load σ is applied due to the suspension of a pertinent weight, P, to the ribbon, its heating above the temperature Aᵣ, and its subsequent cooling below the temperature Mᵣ. The process of the forward MT results in monodomain formation of the alloy (alignment of martensite domains along the load σ direction), which provides accumulation of the strain being maximum for the used magnitude of σ. By thermal cycling at the MT interval under loading the ribbon changes reversibly its length. If in the initial state it has the length l₀, on the cooling below Mᵣ it is extended to l₁, but by the heating above Aᵣ it decreases to l₂, then, the magnitude of the reversible strain makes up ξᵣ = (l₁−l₂)/l₀. In so doing, at the great σ the ribbon can, when heating, not restore some strain ξₒ = (l₃−l₀)/l₀ because of plastic deformation.

Shown in Fig. 2 is the dependence of ξᵣ and ξₒ on the magnitude of the applied mechanical stress σ by thermal cycling at the MT interval. As is seen, at small stresses (σ<60 MPa) the ribbon restores the strains practically fully, however, with increasing σ up to 120 MPa the magnitude of residual deformation ξₒ is getting noticeable, which has a negative effect on ribbon operating capacity with SME realization.

The work dealt with the rapidly quenched ribbon of the Ti₅₀Ni₂₅Cu₂₅ alloy, treated by a single pulse of laser radiation with different energy density E from 5 to 17 mJ/mm², the value of tensile mechanical stress thereat varied in the range 20 to 120 MPa.

For the study on microstructure, metallographic cross-sections of the ribbons subjected to the action by the laser pulse of different power, were made. Representative electron microscope images of the cross-sections are given in Fig. 3 (for $E = 5$ mJ/mm² and $E = 17$ mJ/mm²). It can be seen that at the ribbon surface the modified (amorphous) layer, separated by a sharp boundary from the rest of the
crystalline ribbon bulk, is formed, as it was evident in previous works too [9, 10]. With the increase of the laser energy density the thickness of the amorphous layer grows from 0.4 to 1.4 μm.

Figure 3. Metallographic cross-section of the ribbon treated by laser radiation at different energy density: 5 (a) and 17 (b) mJ/mm²

In the course of X-ray structural analysis at the ambient temperature, a series of diffraction patterns was obtained both of the initial untreated ribbon (Fig. 4a), and samples after the laser action at different energy densities (Fig. 4b). On the diffraction pattern of the untreated ribbon characteristic peaks of reflection of the martensite phase Β₁₉ are evident [17]. It can be seen, that with a growth of energy of the laser pulse an appreciable decrease in most intense reflection peaks takes place near the angle 2θ=42°. This is indicative of the reduction of a part of the crystalline phase in the area of the laser beam action due to partial amorphisation of the alloy and of the formation of the surface amorphous layer.

Figure 4. Diffraction patterns of the ribbon in the initial untreated state (a) and after the laser beam action with the different energy density (b).

Thus, structural investigations have revealed, that the Ti₅₀Ni₂₅Cu₂₅ alloy ribbons, subjected to the laser action, are the laminated amorphous-crystalline composite.

It was further established that the amorphous-crystalline composites produced have an ability to execute reversible angular displacements, as on Fig. 1b. For each composite, the bending radiiuses 𝐑ₘᵢ₉₉ (in the “hot” state above the temperature 𝐀ₙ) and 𝐑ₘᵢ₉₉ (in the “cold” state below the temperature 𝑀ₙ) were determined, as well as the relevant strains, 𝜀ₘᵢ₉₉ = 𝐷/2𝐑ₘᵢ₉₉ and 𝜀ₘᵢ₉₉ = 𝐷/2𝐑ₘᵢ₉₉, where 𝐃 is the thickness of the ribbon, were calculated. The reversible strain 𝐀𝜀 = 𝜀ₘᵢ₉₉ - 𝜀ₘᵢ₉₉ characterizes in essence the magnitude of the TWSME.
Presented in Fig. 5 are the bending strains $\xi_{\text{min}}$ and $\xi_{\text{max}}$, as well as $\Delta \xi$, of the amorphous-crystalline composite as a function of the stress $\sigma$ for the samples, treated at the three different values of the laser pulse energy density: 5, 11 and 17 mJ/mm$^2$.

It can be seen, with increasing the applied stress $\sigma$ the bending of the composite grows. The reason is that at the sample tension with a growth of $\sigma$, a greater strain is accumulated in the crystalline layer (Fig. 3), which it strives to return with heating, which, in its turn, results in the increase in $\xi_{\text{max}}$. However, with increasing $\sigma$ over 40 MPa, $\xi_{\text{min}}$ increases appreciably too, which is caused by the accumulation of residual strain. As a result, at greater values of $E$ (11 mJ/mm$^2$ and 17 mJ/mm$^2$) and, accordingly, the greater thickness of the amorphous layer, the reversible strain $\Delta \xi$ has somewhat greater values, but it does not essentially change with the growth of $\sigma$ in the range 60 to 100 MPa.

Besides, the influence of the laser radiation energy density $E$ on the composite strain was investigated at the fixed stress $\sigma$. The characteristic dependences $\xi_{\text{min}}, \xi_{\text{max}}$ and $\Delta \xi$ are shown in Fig. 6 at $\sigma = 80$ MPa. It was established, that with increasing energy density from 5 to 17 mJ/mm$^2$ the reversible strain $\Delta \xi$ is nearly doubled. This may result from the fact, that, as was mentioned above, the increase in the laser beam power give rise to the formation of the thicker amorphous layer, that deforms the crystalline layer to a greater extent with cooling.
Thus, the combined action of thermal-mechanical and laser treatments of the rapidly quenched TiNiCu alloy makes it possible to produce the laminated amorphous-crystalline composite having the TWSME properties. In so doing, combined variation of the tensile mechanical stress and the energy density of pulsed laser radiation enables to gain optimal parameters of the composite for a specific problem, both in the magnitude of reversible angular displacements, and in the range of angles, where these displacements take place.

4. Conclusion
The work has to do with investigation into the rapidly quenched ribbons of the Ti_{50}Ni_{25}Cu_{25} (at%) alloy, subjected to the combined action of external mechanical stress and pulsed laser radiation ($\lambda = 248$ nm, $\tau = 20$ ns). The interaction of laser radiation and surface of the alloy was simulated, which allowed choosing parameters of the combined action: the magnitude of the tensile stress was varied from 20 to 120 MPa, the laser radiation energy density – from 5 to 17 mJ/mm$^2$.

It has been revealed that after this treatment the laminated amorphous-crystalline composite with the distinct two-way SME is formed. It has been established, that greater amplitude of the reversible bending strain of the amorphous-crystalline composite at the MT interval can be gained both with the creation of high stresses in material, and the action of a high-power laser pulse.

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