Application of laser radiation for creation of metamaterial based on rapidly quenched shape memory TiNiCu alloy

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Abstract. The work deals with application of laser radiation for creation of metamaterial – layered structural composite based on rapidly quenched TiNiCu thin ribbon. Structural properties of the composite were examined by transmission and scanning electron microscopy. Considerable two-way shape memory effect was achieved and studied.

1. Introduction
Advanced tasks from different areas of the natural sciences impose on functional materials the increasing demands for high speed and small size of devices based on them. Nanostructured thin ribbon of a shape memory TiNiCu alloy meet this set of requirements since this material saves its properties at nanoscale [1]. As a rule, application of shape memory alloys (SMAs) micromechanics requires reversible deformation in the heating-cooling cycle [2,3]. Traditional methods of obtaining two-way shape memory effect (SME) are aimed at combining the one-way SME with an external elastic force that will deform the sample during cooling [4]. In a number of works [5,6], effectiveness of a method of achieving two-way SME by means of impact of ultrahigh energy fluxes on surface of SMAs due to creating a structural composite was shown.

In this paper, we discussed the method of creation a micro-sized functional metamaterial on the base of shape memory Ti\textsubscript{2}NiCu alloy using laser radiation.

2. Experiment
Ti\textsubscript{2}NiCu alloy in the form of thin ribbon with a thickness of 40 \(\mu\text{m}\) and a width of 1.5 mm was obtained by melt spinning technique [7] in the amorphous state. Then, samples of the amorphous ribbon were isothermally crystallized at temperature of 500 °C for 240 s in a bent state with the bending radius of 1.5 mm. The crystalline samples were pseudoplastically unbent to the strain
of $\xi \sim 1.3\%$. Surface of the deformed samples was processed with a single pulse radiation of CL7000 series excimer laser based on KrF gas mixture (pulse duration $\tau = 20$ ns, wavelength $\lambda = 240$ nm and power density in the range $P = 10^{11} - 10^{12}$ W/m$^2$).

To describe processes taking place during laser treatment of the surface of the samples, the Stefan problem was solved [8], which is a form of boundary value problem of the heat equation describing motion of the phase boundary.

Metallographic cross-sections of the samples were manufactured on BUEHLER company equipment (precise cutting-off machine Isomet 1000, automatic hydraulic press Simplimet 1000, grinding-buffing machine EcoMet 250+AutoMet 250). Cross-section of the samples was examined using FEI Quanta 600 FEG scanning electron microscope (SEM) and JEM-2100 JEOL high-resolution transmission electron microscope (TEM) to determine microstructure. Lamella for TEM study was made by focused ion beams (FIB) technique using Strata-201 FEI scanning ion microscope equipped with a nanomanipulator of Omniprobe company.

3. Results and discussion

Depth temperature distribution of the samples after beginning of the laser pulse action was obtained by solving the Stefan problem (Fig. 1). It was shown that laser irradiation with power density $P = 10^{12}$ W/m$^2$ led to melting of the surface of the sample in depth of about 1 $\mu$m (melting temperature $T_m = 1420$ K). It was calculated from the obtained curves that surface temperature was more than 6000 K and the cooling rate of the melted layer reached $10^8$ K/s. As it was shown in [9-11], the cooling rates above $10^6$ K/s may cause amorphization of TiNiCu alloy.

![Figure 1](image_url)

**Figure 1.** Depth temperature distribution of the sample after 20, 50, 100, 200, 500, 1000 ns of laser treatment beginning ($\tau = 20$ ns, $P = 10^{12}$ W/m$^2$)

After laser treatment the samples were thermally cycled at the martensitic transformation interval. The results of video recording of this process are presented at Figure 2. The obtained samples acquired the two-way SME with reversible angular displacement up to 60 degrees and maximum strain of about 0.5%.

SEM investigation of the cross-section of the samples revealed a clearly visible interface between the modified surface layer and the primary crystalline part of the ribbon (Figure 3a, b). It was found that the thickness of the modified layer varies from 0.4 to 1.7 $\mu$m with the increasing of laser radiation power density from $10^{11}$ to $10^{12}$ W/m$^2$. 
Figure 2. Variation of shape of the irradiated Ti$_2$NiCu ribbon during thermal cycling  

$P = 10^{12}$ W/m$^2$

A lamella from the cross-section of the samples for TEM study was made by means of local ion milling. TEM image of the interface between the initial crystalline and irradiated phases and corresponding electron diffraction patterns are presented in Fig. 3c. According to the TEM data, amorphous structure was formed on the surface of the irradiated crystalline Ti$_2$NiCu ribbon.

Thus, during laser processing amorphous-crystalline layered structure, which exhibits the two-way SME with reversible strain of 0.5%, was formed.

Figure 3. SEM image of cross-section of the Ti$_2$NiCu ribbon irradiated at different laser power density: $10^{11}$ W/m$^2$ (a), $10^{12}$ W/m$^2$ (b) and TEM image of the interface between the initial crystalline and irradiated ($10^{12}$ W/m$^2$) phases and corresponding electron diffraction patterns (c)

4. Conclusion

The results are summarized as follows:

1. Amorphous Ti$_2$NiCu alloy ribbon of 40 $\mu$m thick and 1.5 mm wide was produced by the rapid quenching from a melt.

2. Micro-sized functional metamaterial was formed by the action of pulsed laser radiation (wavelength of 248 nm, pulse duration of 20 ns and power density from $10^{11}$ to $10^{12}$ W/m$^2$) at the surface of previously isothermally crystallized and pseudoplastically deformed ribbon.

3. It was shown that the irradiated ribbon has layered amorphous-crystalline structure and exhibits considerable two-way shape memory effect.

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