doi: 10.56761/EFRE2022.C3-O-017802

Phase transformations under thermal treatment in Al-12%Si-Zr system with metastable structure synthesized by compression plasma flows impact

N.N. Cherenda[1,], N.V. Bibik[1], V.M. Astashynski[2], A.M. Kuzmitski[2]*

[1]*Belarusian State University, Minsk, Belarus*
[2]*A.V. Lyikov Heat and Mass Transfer Institute of the National Academy of Sciences of Belarus, Minsk, Belarus*
**cherenda@bsu.by*

Abstract. Phase transformations in Al-12%Si surface layer after alloying with Zr atoms by plasma impact and following thermal treatment at 450–550°C were studied in this work. Plasma impact resulted in formation of a metastable τ_1 phase with tetragonal structure $D0_{22}$ in the alloyed layer. The volume fraction of τ_1 diminished with growth of energy density absorbed by the surface layer and increase of temperature during annealing. The decomposition of the τ_1 phase and the formation of $ZrSi_2$ upon annealing for 30 min was observed at a temperature of 550°C.
Keywords: compression plasma flows, silumin, trialuminides, phase transformations.

1. Introduction

Eutectic silumins (Al-12%Si alloys) are widely used in the automobile industry due to its high thermal conductivity, corrosion resistance, high casting properties, etc. However, due to low strength characteristics, most of the silumins used in industry are complexly alloyed by other elements. Materials surface alloying by preliminary deposition of coating containing alloying elements and following treatment by ion, electron, plasma and laser beams is a prospective approach of surface properties enhancement [1, 2]. This process is of special interest in producing nonequilibrium, immiscible and metastable compounds. At the same time, metastable structure of the modified layer may be not effective for materials working at the high temperature. Thus, investigation of the effect of thermal treatment on the structure, phase composition and properties of surface layers alloyed under this approach should be necessary for possible industrial application of such materials.

Active research is carried out now on the formation of new types of aluminum alloys, including those based on Al-Si system with high strength properties and high heat resistance. One of the research directions is the formation of composites in which transition metals trialuminides are used as hardening particles. Intermetallides like Al_3Zr, Al_3Ti and Al_3Nb have a high melting point, low density, high modulus of elasticity, good resistance to oxidation, and low ability to coalescence [2].

Thus, alloying of eutectic silumin by compression plasma flows treatment of Zr/Al-12%Si system and investigation of alloyed layer structure and properties changes under heat treatment were the main aims of this work.

2. Experimental

Samples of eutectic silumin of the following composition: 87.37 Al, 12.55 Si, 0.08 Fe (at %) were investigation objects. A zirconium coating with a thickness of ~2 µm was deposited on silumin samples by vacuum-arc deposition. The samples were exposed to compression plasma flows (CPF) generated by a magnetoplasma compressor in the “residual gas” mode, in which the previously evacuated chamber was filled with nitrogen working gas to a predetermined pressure of 400 Pa. The discharge duration was ~100 µs. The samples were treated with three pulses. The density of the energy absorbed by the surface in one pulse (Q) was changed in the range of 15–35 J/cm^2 by varying the distance between the cathode and the sample. The samples treated with CPF were subjected to isochoric annealing in air for 30 min at temperatures of 450, 500, and 550 °C.

The phase composition was studied by X-ray diffraction (XRD) analysis using a RIGAKU Ultima IV diffractometer in the geometry of a parallel beam in Cu Kα radiation. Samples surface and cross-section morphology were studied using scanning electron microscopy (SEM) on a LEO1455VP microscope. The elemental composition of the samples was determined by X-ray spectral microanalysis using an Oxford Instruments detector coupled to a scanning electron microscope. The microhardness of the samples was measured by the Vickers method using the 402MVD Instron Wolpert Wilson Instruments equipment at the load of 10 g.

3. Results

Aluminium and silicon were the main phases in the analyzed by XRD sample layer before Zr coating deposition (Fig.1a). The impact of CPF on coated samples leads to melting of the surface layer, liquid-phase mixing of the elements of the "coating-substrate" system and further crystallization under conditions of ultrafast cooling [1, 2] leading to changes in the structural state of the surface layer (Fig.1b–1e). Plasma impact resulted in Si primary crystals partial dissolution and formation of new τ_1 phase with tetragonal structure $D0_{22}$. This metastable phase, which can be designated as $(Al,Si)_3Zr$, $(Al_{1-x}Si_x)_3Zr$ or (Al,Si,Zr) in various references [3–6], is formed under conditions of rapid cooling in Al-Si alloys and differs from the equilibrium Al_3Zr with tetragonal $D0_{23}$ structure with reduced lattice parameter – *c*. The lattice parameters for Al_3Zr phase are: $a = 0.4014$ nm and $c = 1.7321$ nm. The lattice parameters of τ_1 in the sample treated at 35 J/cm^2 were: $a = 0.3873$ nm and $c = 0.8791$ nm. Increase of the energy absorbed by the surface layer led to diminishing of τ_1 lattice parameters (Fig.2) due to Si concentration increase in τ_1 lattice. Besides that formation of surface δ-ZrN with fcc cubic crystalline lattice was found. Nitrogen diffusion from the residual atmosphere of the vacuum chamber to the surface layer during its cooling was the main reason of this effect [7]. The intensity of τ_1 and δ-ZrN phases is decreasing with the growth of the energy absorbed by the surface layer indicating diminishing of Zr content in the alloyed layer. The reasons of this effect were discussed earlier: growth of melted layer thickness and intensification of surface erosion [1, 2].

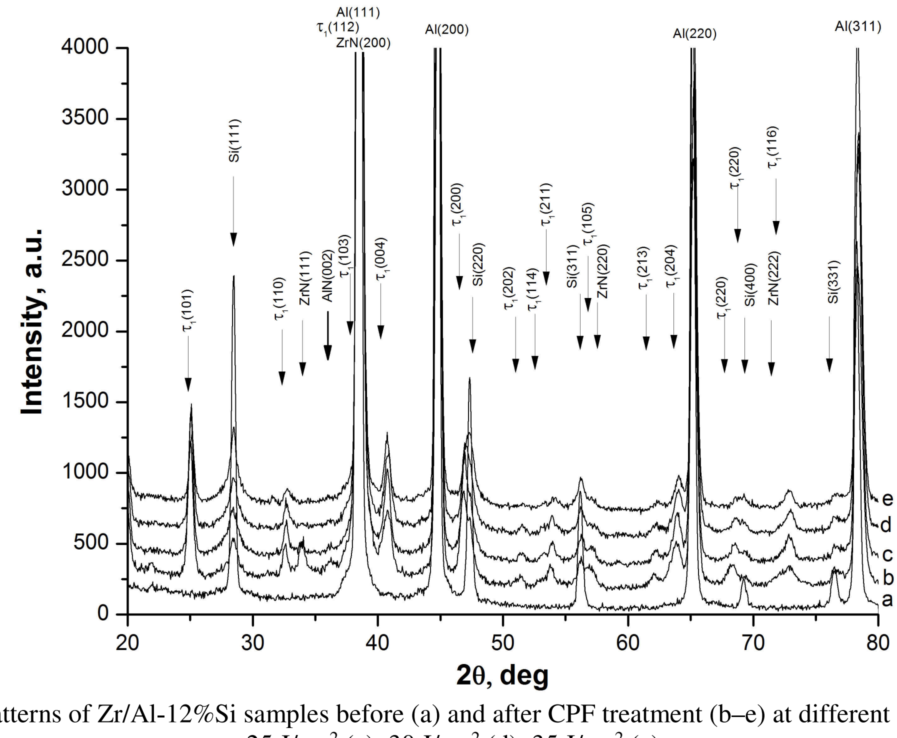

Fig.1. XRD patterns of Zr/Al-12%Si samples before (a) and after CPF treatment (b–e) at different Q: 15 J/cm^2 (b), 25 J/cm^2 (c), 30 J/cm^2 (d), 35 J/cm^2 (e).

It was reported earlier [5, 6] that τ_1 phase is stable up to the temperature of 500 °C, however, there are still few experimental studies carried out in this direction. Thus plasma treated samples of silumin were subjected to isochoric annealing in the temperature range of 450–550 °C for 30 min in order to study the thermal stability of τ_1 phase. Annealing at the temperature of 450 °C leads to an increase in the τ_1 lattice parameters up to the values of $a = 0.3885$ nm and $c = 0.8888$ nm (Fig.3). With a further increase of a temperature up to 550 °C, a monotonic increase of the τ_1 lattice parameters is observed up to the values of $a = 0.3895$ nm and $c = 0.8981$ nm. Increase of the lattice parameters indicates that the release of Si atoms from the solid solution on the base of τ_1 phase can occur. It should be noted that the intensity of the τ_1 lines decreases with an increase in the annealing temperature from 450 to 550 °C (Fig.4). Growth of the annealing temperature up to 500 °C leads to the appearance of a "shoulder" on the Al(200) diffraction peak, which can be attributed to $ZrSi_2$(131). With further increase of temperature up to 550 °C, a partial decay of τ_1 phase and the appearance of diffraction peaks related to $ZrSi_2$ are observed. Besides that annealing of silumin samples in the temperature range of 450–550 °C results in formation of Al_8Fe_2Si phase in the analyzed by X-ray layer. Al_5FeSi was the main intermetallide phase in the initial sample. Plasma impact leads to dissolving of this phase precipitates in the melted layer giving rise to Al_8Fe_2Si formation during annealing.

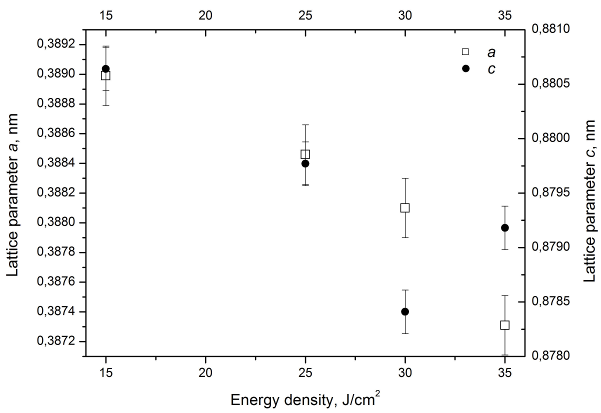

Fig.2. Dependence of τ_1 phase lattice parameters on Q during plasma impact.

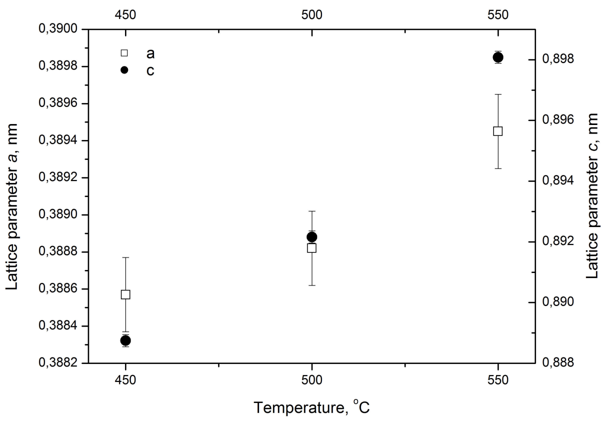

Fig.3. Dependence of τ_1 phase lattice parameters on annealing temperature in the sample treated by CPF at 35 J/cm^2.

Results of SEM investigations correlate with XRD data. In the SEM image, the formation of finely dispersed inclusions τ_1 with a size of 200–300 nm is observed on the sample surface after plasma treatment (Fig.5a). During isothermal annealing for 30 min at a temperature of 450–500 °C, coagulation of this phase is observed (Fig.5b and 5c). An increase of the annealing temperature up to 550 °C leads to significant changes in the morphology of precipitates (Fig.5d), which transform it shape to plates. According to energy dispersive analysis these plates contain Zr and Si, the concentration of silicon is 2 times higher than the concentration of zirconium, which suggests that they belong to $ZrSi_2$ phase, which is consistent with the previously obtained XRD results.

Cross-section analysis showed that the microstructure of the initial sample consists of regions of coarse eutectic, as well as separate primary inclusions of silicon and aluminum grains. The size of silicon inclusions was up to 10 µm. The depth of the surface layer alloyed by Zr under the action of compression plasma flows on the Zr/Al-12%Si system is 35–60 µm (Fig.6a). An analysis of the intensity distribution of the Zr and Si characteristic X-ray radiation showed a uniform distribution of these elements over the entire depth of the modified layer (Fig.6b). In the samples subjected to annealing, a uniform distribution of zirconium over the depth of the modified layer is retained; however, coagulation of silicon is observed (Fig.6d).

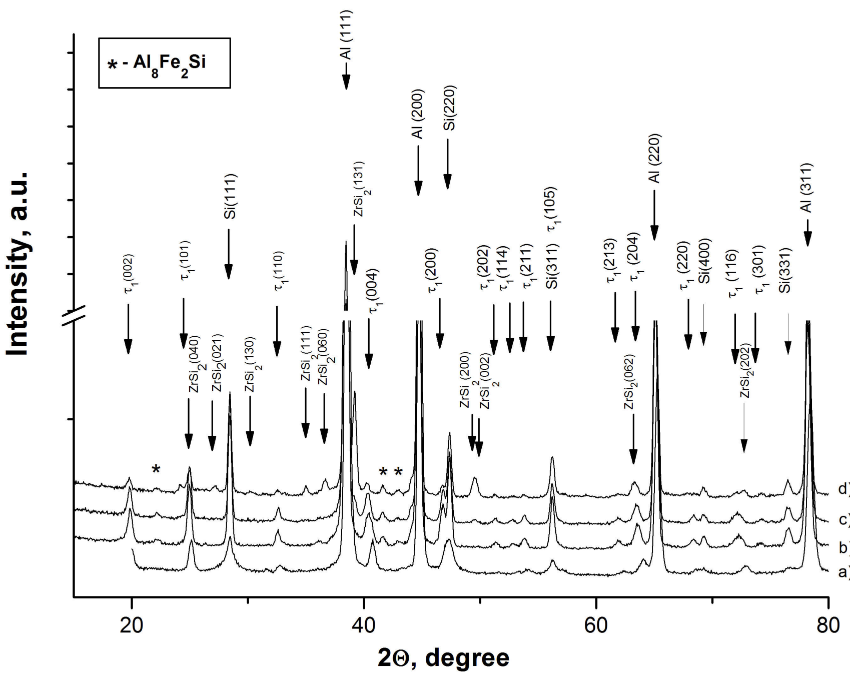

Fig.4. XRD patterns of Zr/Al-12%Si samples treated by CPF at 35 J/cm² before (a) and after annealing at 450 °C(b), 500 °C (c) и 550 °C (d).

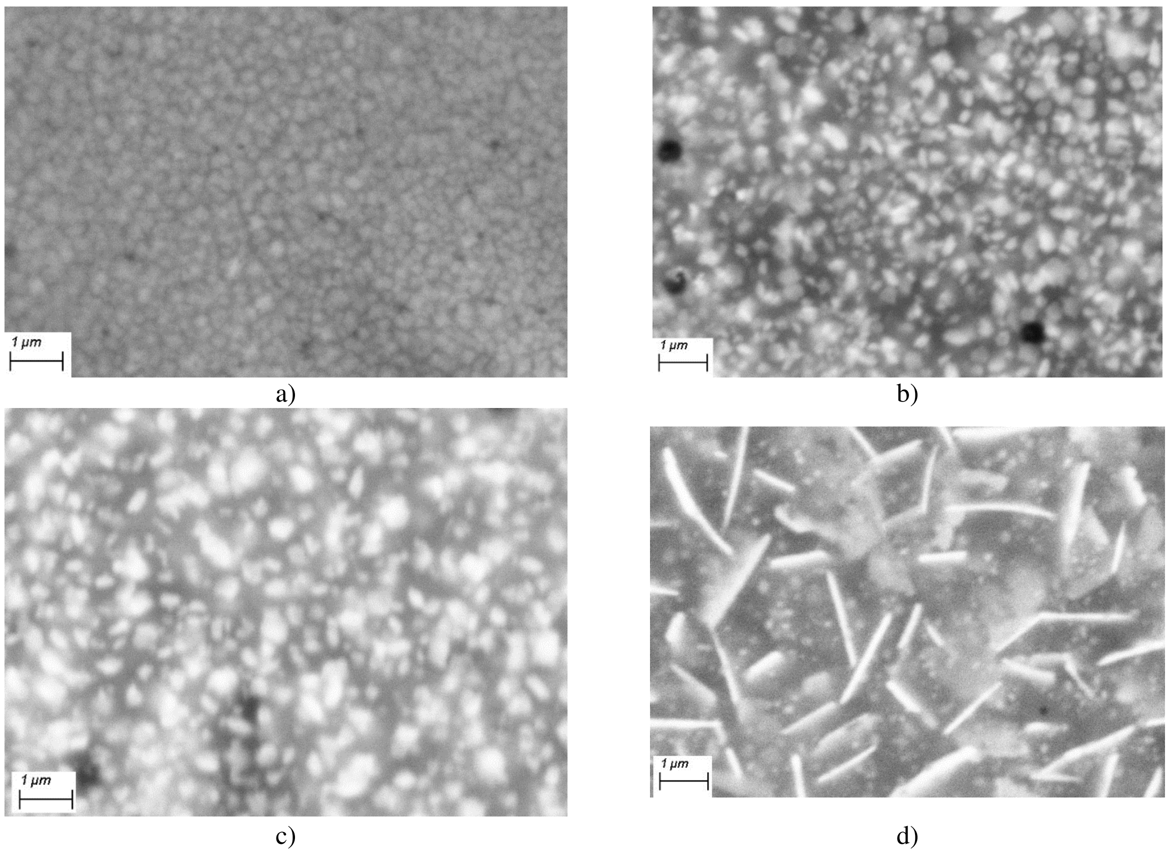

Fig.5. Surface morphology of Zr/Al-12%Si samples treated by CPF at 35 J/cm² before (a) and after annealing at 450 °C(b), 500 °C (c) и 550 °C (d).

Structural-phase transformations in the modified layer cause changes in the microhardness of the silumin alloy. The microhardness of the original sample of silumin is 0.55 GPa. The microhardness of the modified layer after plasma treatment at 35 J/cm^2 is 1.35 GPa. Hardening of the alloy is explained by the action of several factors simultaneously: the formation of inclusions τ_1, the formation of an aluminum-based solid solution, and the structure dispersion. Subsequent annealing at 450 °C leads to a decrease in microhardness to 1.01 GPa. At the same time, the microhardness of the original uncoated sample subjected to annealing at 450 °C also decreases to 0.52 GPa due to the ongoing processes of recovery and grain growth. As the annealing temperature increases, the microhardness of the modified layer decreases to 0.72 GPa at 550 °C, while the microhardness of the original sample annealed at this temperature is 0.50 GPa.

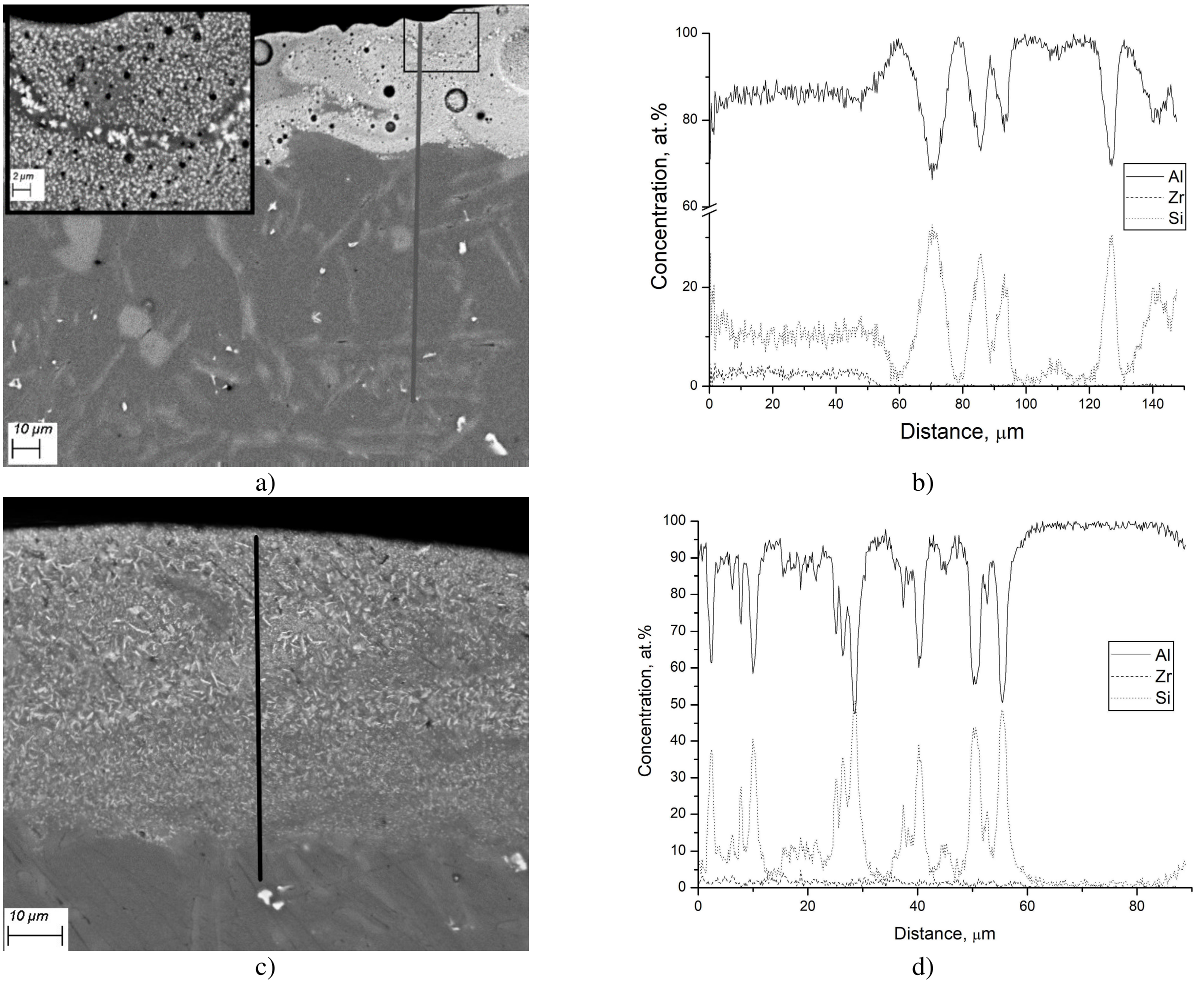

Fig.6. Cross-section morphology (a, b) and characteristic X-ray distribution of elements along line (c, d) in Zr/Al-12%Si samples treated by CPF at 35 J/cm2 before (a, b) and after annealing at 550 °C (c, d).

4. Conclusion

The impact of compression plasma flows on the Zr/eutectic silumin system with an energy density absorbed by the surface of 15–35 J/cm^2 makes it possible to form an alloyed by Zr layer with dispersed microstructure and the thickness of up to ~60 μm. Alloyed layer contains metastable τ_1 phase with tetragonal structure $D0_{22}$. Size of τ_1 phase precipitates is 200–300 nm. Besides that formation of surface δ-ZrN with fcc cubic crystalline lattice was found. The volume fraction of τ_1 and δ-ZrN phases is decreasing with the growth of the energy density indicating diminishing of Zr content in the alloyed layer. The volume fraction of the τ_1 phase decreases with an increase of the annealing temperature from 450 to 550 °C. The decomposition of the τ_1 phase and the formation of $ZrSi_2$ upon annealing for 30 min is observed at a temperature of 550 °C.

Structural-phase transformations in the modified layer cause changes in the microhardness of the silumin alloy. The microhardness of the Zr alloyed layer is 2.5 times higher than that of initial silumin sample. Even after 30 minutes annealing at 550 °C alloyed layer microhardness was 1.4 times higher than that of initial sample.

5. References

[1] Cherenda N.N., Basalai A.V., Shymanski V.I., Uglov V.V., Astashynski V.M., Kuzmitski A.M., Laskovnev A.P., Remnev G.E., *Surf. Coat. Tech.*, **355C**, 148, 2018; doi: 10.1016/j.surfcoat.2018.02.048

[2] Cherenda N.N., Bibik N.V., Astashynski V.M., Kuzmitski A.M., *High Temp. Mater. P.-US*, **26**(2)**,** 91, 2022; doi: 10.1615/HighTempMatProc.2022043681

[3] Gao T., Li D., Wei Z, Liu X., *Mat. Sci. Eng. A.*, **552**, 523, 2012; doi: 10.1016/j.msea.2012.05.081

[4] Gao T, Cui X., Li X., Li H., Liu X., *Cryst. Eng. Comm.,* **16**, 3548, 2014; doi: 10.1039/C3CE42548G

[5] Hirano T, Ohtani H., Hasebe M., *High. Temp. Mat. Pr.-Isr.*, **29**(5–6), 347, 2010; doi: 10.1515/HTMP.2010.29.5-6.347

[6] Guo J.Q., Ohtera K., *Mater. Lett.*, **27**, 343, 1996; doi: 10.1016/0167-577X(96)00002-X

[7] Cherenda N.N., Shimanskii V. I., Uglov V.V., Astashinskii V.M., Ukhov V.A., *J. Surf. Investig.,* **6**(2), 319, 2012; doi: 10.1134/S1027451012040088