Pulse photon processing of amorphous alloys of the system Al-Fe-Ni-La

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Abstract. Multiphase nanocomposite gradient structure (for phase composition, hardness) at the pulse photon processing with gas-discharge lamp radiation treatment (IFO) is obtained in aluminum amorphous alloys (Al=85 at. %) alloyed with transition (Ni=5÷7 at. %, Fe=4÷7 at. %) and rare-earth (La=3÷4 at. %) elements. IFO critical parameters when crystallization at subsurface layers of amorphous ribbons at the radiation treatment side starts are defined (fluence F=10 J/cm²; duration τ~0,5 sec). It is shown that alloy composition alteration within the bounds of the indicated alloying elements content does not have significant influence on IFO critical parameters. Through-thickness crystallization of the amorphous ribbons (25-micron thickness) was observed after IFO with F≥20 J/cm². Hardness of alloys after IFO with different parameters is determined. Alloys’ phase composition was analyzed after the IFO with various parameters.

1. Introduction
The analysis of numerous modern works shows that a promising direction of the new aluminum-based alloys development is their alloying with transition and rare earth metals. High-strength conditions formation in aluminum alloys due to the large number of multicomponent intermetallic phases of various types in the nanoscale size range formation is provided by such alloys fast crystallization and their subsequent processing under various technological schemes. Amorphization of the alloys by high-speed quenching from the liquid state with subsequent photon treatment under the conditions of gas-discharge lamps radiation is one of the production methods of multiphase nanocomposites with controlled phase composition and grain size.

2. Material and techniques
The flow turning method is used to produce amorphous ribbons from aluminum-based (85 at. %) alloys doped with transitional Ni=5÷7 at. %, Fe=4÷7 at. %) and rare-earth (La=3÷4 at. %) elements. Polycrystalline alloys of the same compositions are obtained by quenching from the melt under cooling conditions close to equilibrium (in air). The alloys structure in the initial condition and after the pulsed photon processing (IFO) under parameters: fluence F=10-30 J/cm², processing time τ=0,5…1,5 sec was analyzed using the following techniques: transmission electronic microscopy (TEM), X-ray phase and micro-X-ray spectral (MRSA) analyses. Utilized equipment includes the following items: Titan 80-300 electron microscope with spherical aberration corrector lighting system,
equipped with an energy dispersive microprobe (EDRM) (EDAX, USA); ARL XTRA X-ray diffractometer (radiation of copper). Polycrystalline specimens were subjected to shear deformation under the 8 GPa pressure (IPD) on Bridgman anvils before the IFO; deformation degree corresponded to one movable anvil turn φ=360°. Mechanical properties were estimated by the results of microhardness measurement on the 401/402 – HVD Wolpert Wilson Instruments hardness-testing machine at a load of 10 g, 10 s. Differential scanning calorimetry (DSC) of the alloy was carried out on the SETARAM calorimeter with a heating/cooling rate of 20°/min.

3. Results and its discussion

Initial condition. Alloys Al₈₅Ni₃Fe₇La₃ and Al₈₅Ni₇Fe₄La₄ in the initial state have an X-ray amorphous structure, which is characterized by an asymmetrical double-humped halo (figure 1). The initial microhardness of alloys Al₈₅Ni₃Fe₇La₃ and Al₈₅Ni₇Fe₄La₄ is 456 HV and 406 HV respectively.

The results of differential scanning calorimetry studies of the initial amorphous alloy Al₈₅Ni₃Fe₇La₃ are presented in table 1. Three exothermic heat release peaks corresponding to multiphase crystallization of the amorphous matrix (P1-P3 peaks) were observed during heating. Crystallization begins at a temperature of 282 °C with the aluminum release, then intermetallic compounds are released which have paired heat release peak.

|            | Al₈₅Ni₃Fe₇La₃ | Al₈₅Ni₇Fe₄La₄ |
|------------|--------------|---------------|
|            | P₁           | P₂            | P₃           | P₁           | P₂           |
| Tₓi, °C    | 282          | 305           | 305          | 286          | 399          |
| T𝐩i, °C    | 364          | 364           | 399          | 295          | 381          |
| H, µV.s/mg | 5.4          | 14.0          | 12.0         | 15.0         |

**Notes:** H – thermal effect; Tx, Tp – crystallization start and peak temperatures respectively; 1, 2, 3 – crystallization stages corresponding indexes.

Two asymmetrical peaks of heat generation partitioned at the temperature scale associated with the two-staged crystallization development were observed at the calorimetric curve lines during continuous heating (20°/min rate) of an Al₈₅Ni₇Fe₄La₄ alloy in amorphous condition. Crystal aluminum is evolved simultaneously with the intermetallic compounds from the alloy at the first crystallization stage.

Multistage crystallization development during heating of the alloys under investigation is associated with their multi-component doping. Al₈₅Ni₃Fe₇La₃ and Al₈₅Ni₇Fe₄La₄ alloys crystallization is completed at 454°C and 406°C respectively.

Al₈₅Ni₇Fe₄La₃ alloy structure after IFO. In the frame of the project amorphous ribbons after the high-speed hardening undergo pulsed photon processing with the aim to find optimal irradiation modes to obtain nanocrystalline composite with the enhanced properties. IFO was carried out at the scientific equipment shared utilization center, Voronezh State University.

With the X-ray phase and transmission electronic microscopy techniques the alloy Al₈₅Ni₇Fe₄La₃ structure after IFO with different radiation doses was certified. After irradiation at a dose of energy F=10 J/cm² no significant changes in X-ray diffractograms were found (figure 1). The first intensity peaks from the crystalline phases were observed after treatment with F=15 J/cm² due to the crystallization development with the crystalline aluminum release. Crystallization develops in the surface layer from the irradiation side with an amorphous crystal structure formation. The volume fraction of crystallization is small as shown by electron microscopic studies, it explains the absence of intensity maxima from intermetallic compounds in the crystal state on X-ray diffractograms. The halos presence on diffractograms and electron microscopic diffractions indicate that the main structural
component is a solid aluminum solution in the amorphous state. The depth of crystallization penetration across the ribbon section is small.

An amorphous nanocrystalline structure with a grain size of ~10 nm is formed in the surface layer of the alloy after the IFO with a dose of 15 J/cm². Such a structure corresponds to a multi-ring diffraction with multiple point intensity maxima. The phase composition of the amorphous-nanocrystalline composite includes amorphous and crystalline solid solution based on aluminum and aluminides, which in addition to the aluminum include transition (Ni, Fe) and rare earth (La) metals. High-resolution electron microscopy confirmed the nanocrystalline phases presence, which should have a significant impact on the mechanical properties of nanocomposites. Crystallization is not complete entirely. Intermetallic compounds \( Al_{11}La_3 \) and \( Al_9Fe_{23}Ni_9 \) were detected in the crystal structural constituent after the IFO with \( F=15 \) J/cm² by electron-microscopic analysis. At low radiation doses nanocrystallization develops on one side of the ribbon facing the energy source, it allows to create nanocrystalline coatings on the surface of amorphous ribbons, to regulate the ratio of the volume fractions of the crystalline and amorphous components, which will probably determine the mechanical properties of the nanocomposite after processing.

Transparent multiple phase crystallization over the ribbon section was observed during electron microscope investigation after the IFO with \( F=20 \) J/cm². An amorphous matrix along with the crystalline phases is fractionally preserved in the structure according to the X-ray crystal structure analysis; it is indicated by the blurred halo observed at diffraction patterns. Average crystal grains sizes presenting \( Al, Al_{11}La_3 \) and \( Al_9Fe_{23}Ni_9 \) phases mixture is 130 nm. Grains have the form of polyhedrons. The major part of the volume is occupied by crystal aluminum generating diffraction peaks of maximum intensity at the X-ray examination and \( Al_9Fe_{23}Ni_9 \) intermetallic compound.

The structural state of the alloy changes significantly after IFO with \( F=25…30 \) J/cm². The average grain size grows sharply and the morphology of the phases changes. Both X-ray and electron microscopic diffraction patterns have multiple intensity maxima from crystalline aluminum and \( Al_{11}La_3 \) and \( Al_9Fe_{23}Ni_9 \) intermetallic compounds. The amorphous component in the alloy is practically absent. Intensities redistribution between the peaks of different crystal phases was observed on the diffractograms of samples after the IFO with the maximum values of \( F \). The intensity of the peaks obtained by the reflection from the crystalline aluminum decreases due to the crystalline solid aluminum solution volume fraction share decrease. Peaks intensity associated with \( Al_{11}La_3 \) and \( Al_9Fe_{23}Ni_9 \) intermetallic compounds increases sharply. Electron-microscopic images of the structure confirm the fact that the main bulk component in the structure are triple intermetallic grains having an egg-shaped form. Their size reaches 1 micron. Amount and grains sizes of the primary \( Al_{11}La_3 \) intermetallic compound are dramatically increased. The light-field structure images of its grains have a dark contrast and elongated cylindrical shape with aspect ratio of 2:1.

Said intermetallic acquires a rounded shape by coagulation at the energy \( F \) increasing to 30 J/cm². The secondary intermetallic compound \( Al_{11}La_3 \) separations of round shape and different dispersity were observed in the volume of \( Al_9Fe_{23}Ni_9 \) intermetallic compound grains featuring a maximum volume concentration and the grain size. Their size is by an order of magnitude less than the grain size of the primary intermetallic compound of the same composition. Thus, transparent multi-phase crystallization in the amorphous ribbons with a thickness of 25 micron was observed after the IFO in the range of treatment parameters \( F \) 20…30 J/cm² and \( \tau=1…1.5 \) sec. The maximum ribbons microhardness 611.4 HV at 10 g load and 10 s loading time was obtained after the IFO with \( E=10 \) J/cm², which exceeds the microhardness in the initial after the hardening amorphous state (456 HV) by ~30%. E increasing to the values of 15-20 J/cm² leads to a slight microhardness decrease to 599 and 568 HV values respectively. This reduction is commensurate with the measurement error of ±12 HV.

Microhardness maximum ratings are in consistence with the multiphase amorphous nanocrystalline structure incorporating amorphous and crystalline solid aluminum solutions along with the three-component intermetallic compounds with the grain sizes not exceeding ~130 nm. Microhardness noticeable reduction to 484 and 475 HV values was obtained after the IFO with the 25 and 30 J/cm² energies affecting the sample. Fully crystallized structure is remarkable for its inequigranularity
associated with the multiple phase presence corresponds with the received values. $Al_{0.9}Fe_{2-x}Ni_x$ intermetallic compound phase has maximum grain size of ~1 micron.

![Figure 1. Al$_{85}$Ni$_7$Fe$_4$La$_4$ alloy diffractograms after the IFO with energy dose 25 J/cm$^2$: a) initial condition – amorphous; b) polycrystalline initial condition after the IPD $P=8$ GPa, $\varphi=360^\circ$. Notation: 1- Al, 2 - $Al_{11}La_3$, 3 - $Al_{0.9}Fe_{2-x}Ni_x$.](image)

Noticeable diffraction maxima due to the multiphase crystallization development during processing were observed the amorphous alloy $Al_{85}Ni_7Fe_4La_4$ X-ray diffractograms after the IFO with $F=25$ J/cm$^2$. Along with the intense maxima (111) and (200) Al, peaks belonging to the intermetallic phases are in place. Multiple supersaturation of the amorphous phase by Ni, Fe, La alloying elements leads to multiphase crystallization with the double and triple aluminides release at IFO process, it significantly complicates the unambiguous phases identification only on the basis of X-ray analysis.

Halo indicating the presence of an amorphous component is not preserved on X-ray diffractograms obtained by X-ray phase analysis (Fig. 1a). Transparent multiphase crystallization develops throughout the whole sample volume after the IFO with $F=25$ J/cm$^2$. Alloy phase composition includes crystalline aluminum and $Al_{0.9}Fe_{2-x}Ni_x$, $Al_{11}La_3$ intermetallic compounds. The microhardness of such a structure is 556 HV.

Polycrystalline alloy $Al_{85}Ni_7Fe_4La_4$ IFO with $F=25$ J/cm$^2$ after IPD 8 GPa with $\varphi=360^\circ$ leads to the phase transformations development with $Al_{11}La_3$ and $Al_{0.9}Fe_{2-x}Ni_x$ intermetallic compounds release and riveted structure static recrystallization. Diffraction maxima formed by crystalline aluminum planes (111) and (200) reflection has the maximum intensity on X-ray diffractograms. The microhardness of the samples after the IFO with $F=25$ J/cm$^2$ was 533 HV which is much lower than the microhardness of the amorphous-nanocrystalline alloys after the IFO.
4. Conclusions
Obtained results are important at utilization of high-strength aluminum alloys in the amorphous state to produce amorphous nanocrystalline multiphase composites with high strength characteristics under pulsed photon processing. IFO as a processing method is promising for the nanocrystalline coatings, gradient and nanocomposite structures creation in the products made of amorphous alloys.

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5. References
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