Formation of composite structure of amorphous alloy after treatment of different types

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Abstract. The dependence of structure and microhardness of aluminium amorphous alloy were investigated and determined on samples after deformation, heat treatment and irradiation with fast carbon ions.

1. Introduction
Aluminum alloys are widely utilized as light, high-strength, temperature-resistant and corrosion-resistant materials for aviation and aerospace equipment. Aluminum doping with transition and rare-earth metals allows to receive amorphous structure during highspeed quenching from liquid state. Amorphous structure is an intermediate stage for amorphous-nanocrystalline composites preparation. Different methods of such structures preparation are known: heat treatment, severe plastic deformation (SPD), pulsed photonic irradiation, laser irradiation, radiation exposure. Ample quantity of scientific work is devoted to amorphous nanocrystalline structures preparation methods consideration. In such a way high deformation rates in event of severe plastic deformation [1-5] provide fine grained structure in alloys including nanoscale multiphase structure with increased strength performance. Scientific work results issued over the last years give an evidence of intense interest both to the new aluminum alloys development and to the formation behavior research of submicro- and nanocrystalline structures in the aluminum-based alloys doped with transition and rare-earth metals [3-11]. Amorphous alloys irradiation by high-energy ions is reviewed as one of the nanocrystalline composites preparation methods. Information presented in scientific literature about irradiation influence on amorphous alloys structures is limited and commonly contradictory, irradiation parameters vary in types of particles, energies and fluence.

Amorphous alloys structure modification is considered now as a method of simultaneous mechanical properties (such as strength and ductility) enhancement. As aluminum alloys doped with transition metals are embrittled due to bulk large-sized intermetallic compounds allocation, best available compositions pulverization technology development is an actual task for research studies.

2. Material and techniques
Different types of structure are formed at the Al₈₅Ni₇Fe₄La₄ alloy depending on processing type. Amorphous structure was obtained in the sample pieces presented in the form of ribbons with 25 µm thickness and 1 mm width after high-rate quenching (spinning method) at a rate of 10⁶ K/s. Structure of amorphous ribbons is metastable and any high-energy influence (high-temperature processing, plastic deformation, charged particles and laser irradiation, etc.) can lead to significant structural
changes. Al₈₅Ni₇Fe₄La₄ alloy amorphous ribbons are treated according to the following scheme: 1) annealing was conducted in the temperature range from 150 to 400ºC with the 50 ºC interval and 15 and 30 min exposure at each temperature with further cooling at the air; 2) severe plastic deformation was conducted at the ambient temperature in the Bridgman chamber at 8 GPa of hydrostatitical pressure and at the rotation angle of movable anvil φ=360°×n (where n=1, 3, 6); 3) irradiation with carbon C ions with 38 MeV energy and Φ=5·10¹⁶ particles/cm² fluence.

Comprehensive analysis of amorphous alloys structure in initial condition and after various types of processing with modern research techniques engagement (high-resolution electron microscopy, transmission scanning microscopy, energy dispersive analysis of X-rays, X-ray phase analysis) allows receiving of experimental findings in alloys structural and phase rating.

The following types of equipment were utilized for structural and ultimate composition research after above mentioned processing types:

1) dual-beam scanning electron-ion microscope (FEI, USA) equipped with energy-dispersive X-ray microanalysis system with film-type silicon drift detector of 40 mm diameter (EDAX, USA);

2) Titan 80-300 TEM/STEM (FEI, USA) electron microscope with illumination system spherical aberration corrector equipped with energy-dispersive X-ray microanalyzer (EDAX, USA), ring-shaped dark-field detector for wide angle scattered electrons (Fischione, USA), energy-dispersive X-ray microanalyzer system (EDAX, USA) and characteristic electronic energy loss spectrometer (Gatan, USA);

3) dual-beam electron-ion microscope Helios (FEI, USA). Utilization of reduced accelerating voltage at samples preparation allows to avoid their substantial heating which may result in structural and constitutional change in alloys not associated with the processes under consideration. Research on ionic thinning (by Ar⁻ ions) influence in wide range of parameters on phase transformation in amorphous alloys [12] was conducted earlier by the authors to determine optimum polishing regime.

Alloy phase compositions were studied by X-ray diffraction method utilization: DRON-3M (Russia) diffractometer with Cu-Kα irradiance utilization (exposure mode U = 38 kV, I = 20 mA, slot 1x2x0.5 + Soller slot system). XPertPro (PANanlitical) diffractometer in Cu-Kα irradiance (40 kV, 15 mA, Ni-Kβ-filter, step angle 0.016 degree/s). PDF-2 (sets 1-52) data were used during X-ray photogram phase analysis.

PMT-3 measuring device as well as 402 MVD – Wolpert Wilson Instruments (Germany) microhardness tester were used for samples microhardness measuring at 10 g load and 10 sec exposure time.

3. Results and its discussion
Alloy in amorphous state has single-phase structure with high oversaturation by Ni, Fe, La doping elements-halo presence at the X-ray diagrams and electron-diffraction photographs is distinctive for this case. Amorphous alloy microhardness is conventionally exceeding microhardness of polycrystalline alloy and is 405 HV. Structure of amorphous ribbons is metastable and any high-energy influence (high-temperature processing, plastic deformation, charged particles and laser irradiation, etc.) can result in significant structural alteration.

Isothermal annealing of ribbons resulted in amorphous condition stability loss: crystallization with crystalline aluminum and intermetallic phases on the basis of Al–Ni, Al–Fe, Al–La formation is developed in the alloy at a temperature of 250 ºC and higher. Overall crystallization development behavior during annealing for the alloys of Al₈₅FeₓNiᵧLaₔ (where x=1÷4 at. %, y=7÷9 at. %, z=4÷5 at. %) system is described at [13]. Crystalline constituent amount is increasing in alloys during annealing temperature rising from 250 to 400 ºC. Large amount of peak amplitudes is put in appearance at the X-ray diagrams with that and the rings with large number of reflexes are formed at the submicroscopic diffractions. Alloy phase composition at 400 ºC includes crystalline aluminum solid solution with the grain sizes of about 100 nm and a large number of intermetallic compounds (Al₁₁La₃, Al₉Ni₉, Al₉Fe₄, Al₉Ni₉, Al₉Ni, Al₉Fe₂-xNiₙ, Al₉Fe₂-xNiₙLa, Al₉Fe₂) due to multicomponent doping process of an alloy. Relaxation and crystallization processes developed during annealing are reflected at the evaluations of
such structure-sensitive property as microhardness which is an important characteristic value of material resistance to plastic deformation for amorphous alloys. As far as annealing temperature increases microhardness is descending as much as 10-15 % at first and then as temperature reaches the values of crystallization commencement it goes upward and reaches the value of 509 HV. Microhardness alteration behavior is not depending upon retention time.

$\text{Al}_3\text{Fe} (\text{Al}_1\text{Fe}_4 \text{ analog})$ phase microhardness rate ranges from 800 to 1100 HV, $\text{Al}_3\text{Ni}$ phase – from 700 to 770 HV, and $\text{Al}_6\text{Co}_2$ phase ($\text{Al}_3\text{Fe}_2-\text{xNi}_\text{x} \text{ analog} [14]$) from 650 to 750 HV. $\text{Al}_3\text{Ni}_2$ phase has hardness of 1100 HV according to the data from [15]. Considerable accession of alloy hardness during annealing operation is determined by high hardness of intermetallic phases.

Multiple phase amorphous-nanocrystalline structure consisting of aluminum in crystalline and amorphous conditions and nanoscale intermetallic compounds ($\text{Al}_3\text{Fe}_4$, $\text{Al}_3\text{Ni}_2$, $\text{Al}_3\text{Ni}$, $\text{Al}_5\text{Fe}_{2-\text{xNi}_\text{x}}$, $\text{Al}_5\text{Fe}_2\cdot\text{Ni}_\text{x}\cdot\text{La}$) are formed in the alloys after severe plastic deformation as was shown by X-ray crystal structure analysis. At that stratification by spinodal decomposing type to two amorphous components and nanocrystallization in one of them (doped with nickel and lanthanum to a small extent) accompanying the crystallization is discovered in the structure by micro X-ray spectrum analysis. Amorphous-nanocrystalline fragmented structure of “collar” type with fragments sizes 10…20 nm with distinctive preservation of amorphous component at the center of the fragments and with the nanocrystalline well formation with the grain sizes of 3-6 nm at the boundary zones [16] is formed after severe plastic deformation which was shown by high-resolution electron-microscope investigation. It should be noted that contrast similar to the “collar” at the transmission electronic microscopy pictures is increasing due to samples thickness variations conditioned by preferential etching of amorphous regions with various chemical composition at samples preparation for transmission electronic microscopy research. With increase of degree of deformation, the volume ratio of nanoscale crystalline phases somewhat increases without noticeable changes of phase composition and nanocrystals sizes. Crystallization is not terminated along the whole investigated interval of deformation parameters. Structure formation mechanism after severe plastic deformation is extensively reviewed in scientific work [13]. Microhardness values after severe plastic deformation with $\Phi = (360^\circ \times 3) \times 2$ amounted up to 706 HV.

Research of radiation exposure to amorphous alloys structural condition and mechanical properties is of certain interest. Increase in hardness during corresponding processing and magnetic characteristic alteration are mentioned in a number of works; there exists conflicting information about radiative effect on amorphous alloys structural and thermal stability. Amorphous aluminum alloys are not without interest in terms of new radiation-proof materials development for the space hardware. New experiments on amorphous alloys irradiation with high-energy carbon ions were conducted; they required calculations for irradiation conditions, samples holder development and irradiation performance experimental testing. Residual radioactivity after irradiation is substantially extended duration of the experiment due to samples prolonged subjection to withdraw this effect. Results of that experiments are resulted as follows.

Noticeable changes in amorphous alloy structure were discovered after irradiation with carbon $^{12}\text{C}^{+3}$ ions with 38 MeV energy and $\Phi = 5 \times 10^{16}$ particles/cm$^2$ fluence. Multiple narrow-width Bregg reflexes specific for polycrystalline condition were observed at the X-ray diffractogram after specified three-hour processing. Such diffractogram conversion is associated with multiphase nanocrystallization development at the initially amorphous single-phase structure. It has been established that crystallization in alloy after irradiation is developed with the solid solutions with face-centered cubic lattice development – Al, intermetallic compounds $\text{Al}_3\text{La}_3$, $\text{Al}_5\text{(Ni, Fe)}$, $\text{Al}_5\text{Fe}_{2-\text{xNi}_\text{x}}$, $\text{Al}_5\text{Fe}_2\cdot\text{Ni}_\text{x}\cdot\text{La}$. Besides that, peaks do appear at the diffractogram which can be associated with the graphite. Multiphase amorphous-nanocrystalline structure with the grain sizes 10-20 nm is formed in the alloy which was also determined by transmission electronic microscopy method. Detailed structure study of this sample by the high-resolution transmission electronic microscopy confirms data about amorphous alloy crystallization. Both face-centered cubic lattice Al grains and intermetallic compounds [17] were observed on transmission electronic microscopy pictures. Experiment conditions don’t allow
establishing of phase transformation sequence during the crystallization at irradiation exposure. Utilized experimental methodologies record only the final result of multiphase crystallization after three hours exposure of the sample. Nanocrystallization development is followed by substantial microhardness increasing up to 683 HV. Such irradiated sample hardness growth is provided (as in the case of nanocrystallization during annealing and severe plastic deformation) by the high content of the intermetallic compounds with increased strength and nanosized grains of crystalline aluminum.

4. Conclusions

Comparative analysis of the structures formed in the Al₈₅Ni₇Fe₄La₄ alloy shows the possibility of multiphase amorphous-nanocrystalline structures formation at the initially amorphous Al₈₅Ni₇Fe₄La₄ alloy under the conditions of severe plastic deformation, annealing and irradiation with carbon ions. Based on structural parameters attestation and results of hardness measurement optimum processing conditions were defined:

- amorphous ribbon isothermal annealing at T = 400 °C, 30 min (509 HV);
- severe plastic deformation of the amorphous ribbon by rotation under pressure: P=8 GPa, φ=(360°x3)x2 (706 HV);
- irradiation with carbon ¹²C⁺ ions with 38 MeV energy and Φ =5·10¹⁶ particles/cm² fluence of the amorphous alloy leads to hardness increasing up to 683 HV.

It has been established that the most perspective development method of the amorphous-nanocrystalline composite material with the advanced structural performance in amorphous alloy Al₈₅Ni₇Fe₄La₄ is severe plastic rotational deformation under pressure, as a result of its hardness values achieve maximum magnitude.

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