Nanocrystal formation and structure rejuvenation in Al-based alloys

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Abstract. Studies of the structural evolution of the group of Al-based amorphous alloys of Al-Ni-RE (RE = La, Y, Gd) systems showed that, under the combined action of heat and deformation on the structure, one may obtain samples with different crystal sizes and different fractions of the nanocrystalline phase. Under crystallization of a heterogeneous amorphous phase, the size of the nanocrystals is smaller, and their fraction is larger than under crystallization of a homogeneous amorphous phase. The use of cryogenic cycling method allows rejuvenating the amorphous phase in partially crystalline alloys.

1. Introduction
Amorphous and nanocrystalline alloys belong to the group of materials being widely studied due to a combination of splendid physical properties: magnetic, strength, corrosion-resistant, and others [1-3]. Fe-based alloys have excellent magnetic properties: low coercivity (0.5 – 1 A/m) and high saturation magnetization, which exceeds 1.4 T. Superior hysteresis properties were obtained in Co-based alloys [3], which have almost zero magnetostriction. Good properties of the material are determined by its structure. One of the examples of promising amorphous-nanocrystalline materials are light Al-based alloys. They are high-strength, and the values of yield stress in Al-based alloys containing 6-15% of a transition metal (Fe or Ni) and a few percent of a rare-earth metal reach 1.6 GPa under sufficiently high plasticity [4-7]. The properties are structure-sensitive and may change significantly under a change in the structure [8, 9]. Structural changes may occur both in the amorphous state and under the formation of crystalline phases. It was established that the changes under heat treatment depend considerably on temperature: above or below the glass transition temperature [10]. Significant changes are observed also under plastic deformation: the formation of shear bands or the reduced density regions occurs in the amorphous phase. In these regions, the processes of diffusion mass transfer are accelerated, and a region with a thickness to 100 µm is formed near the shear band, the mechanical properties of which differ from the properties of the remaining amorphous matrix [11-13].

It is important to note that structural changes result in the formation of materials with a novel combination of properties. There are a lot of works devoted to the study of the structure and properties of amorphous and amorphous-nanocrystalline materials [14-18]. The present paper considers the possibilities of both creation of a partially crystalline structure with different structural parameters, as well as rejuvenation of an amorphous structure in partially crystalline samples.
2. Experimental

Al-Ni-RE (RE = La, Y, Gd) amorphous alloys were obtained in the form of ribbons with a thickness of about 30 µm and a width of about 1 cm by melt quenching. The obtained samples were subjected to heat treatment and deformation in a different order. Isothermal annealing in a furnace, heating in a calorimeter at a constant rate of 20°/min and thermal cycling in the temperature range of 77-373 K were used for heat treatment. The method of multiple rolling was used for deformation. After each stage of treatment, the structure was investigated with a Siemens D500 X-ray diffractometer using CoKα radiation and JEM 2100 and JEM-100CX electron microscopes. The microhardness was measured with a Micro-Vickers hardness tester with a load of 10 g. The nanocrystal size was determined by XRD analysis as well as by dark-field electron microscopy images. The nanocrystal size was estimated using the Scherrer formula [19]. The fraction of the nanocrystalline phase was determined by the ratio of the integral phase intensities according to [20-22].

3. Results and discussion

3.1. Formation of a nanocrystalline structure under combined heat treatment

One of the methods of exposure on the amorphous structure was carrying out combined treatments. It was established earlier [23, 24] that the use of the combined treatment “annealing + deformation” and “deformation + annealing” allows changing significantly the structural parameters and properties of the material. Figure 1 demonstrates an X-ray diffraction pattern of the Al_{88}Ni_{8}Y_{4} alloy heated in a calorimeter up to a temperature corresponding to the maximum of the first peak on the DSC curve after preliminary (before DSC heating) 50% deformation (1) and preliminary (before DSC heating) annealing at 100 °C during 3 h (2). The structure of the samples is two-phase and consists of Al nanocrystals and an amorphous matrix. Although the X-ray diffraction patterns are similar, the structural parameters turn to be different. After heating, the average nanocrystal size in the preliminarily annealed sample is 11 nm, and the fraction of the nanocrystalline phase is 10%; the same values for the preliminary deformed sample are 9 nm and 12%, respectively. Similar values were obtained for other alloys. For instance, in an alloy containing La, the average nanocrystal size is 30 nm in the case of preliminary annealing at 150 °C during 3 h and then heating in the calorimeter up to the temperature corresponding to the maximum of the first peak on the DSC curve, and it is 26 nm in the case of preliminary 50% deformation and then heating in the calorimeter up to the same temperature; the fraction of the nanocrystalline phase is also greater in the case of preliminary deformation. In the case of crystallization of the samples without preliminary treatment the average nanocrystal size turns to be significantly larger and is 32 nm for an alloy containing La, 23 nm for an alloy containing Y, and 26 nm for an alloy containing Gd. The observed differences are related to the fact that the formation of a heterogeneous amorphous structure occurs under preliminary treatment [25-32].

The properties of the samples depend considerably on the structural state. The studies have shown that the microhardness of this alloy is 270 MPa in the initial amorphous state and 440 MPa in the partially crystalline state. Figure 2 demonstrates the X-ray diffraction pattern of the alloy of the same system, but with a different ratio of Ni and Y. It is seen that with an increase in the annealing temperature, the fraction of the nanocrystalline phase increases along with an increase in the microhardness of the alloy: 280 MPa after annealing at 100 °C and 310 MPa after annealing at 170 °C (in both cases, the duration of annealing was 30 h). In all the investigated samples, the microhardness also increases with an increase in the fraction of the nanocrystalline phase. However, a significant decrease in microhardness is observed under the formation of a multiphase structure.

Thus, the use of combined treatments enables creating amorphous-nanocrystalline materials with different structural parameters (nanocrystal size, fraction of the nanocrystalline phase) and, consequently, with different properties.
3.2. Rejuvenation of the amorphous structure under cryogenic thermal cycling

Another way is the possibility of rejuvenation of the amorphous structure. It is well known that under crystallization of some amorphous alloys embrittlement occurs, and in this case, the revival of the amorphous structure is necessary for the plasticity recovery. To study the possibility of rejuvenation of the amorphous structure, the samples in the partially crystalline state were subjected to cryogenic cycling in the temperature range of 77 - 373 K. The idea of this treatment is based on the following assumption: since the coefficients of thermal expansion of the amorphous phase and nanocrystals are different, stresses will be accumulated in the structure under the multiple cycles “heating-cooling”, which should lead to structural changes. This idea was tested earlier for heterogeneous amorphous alloys [33, 34]. Its testing on amorphous-crystalline samples (with a greater difference in values of the coefficients of thermal expansion) should lead to larger structural changes [35].

The mentioned treatment was carried out on partially crystalline samples, where the amorphous-nanocrystalline structure was created by annealing or deformation. Figure 3 shows X-ray diffraction patterns of the Al$_{88}$Ni$_{10}$Y$_2$ alloy before (1) and after (2) cryogenic thermal cycling. Al-reflections are marked with crosses. The inset illustrates the decomposition of the X-ray diffraction pattern in amorphous (a) and crystalline (c) components. It is seen that the fraction of the nanocrystalline phase decreases during cryogenic thermal cycling. No signs of a crystalline phase were observed in the X-ray diffraction patterns with an increase in the number of cycles to more than 100.

Figure 1. X-ray diffraction pattern of the Al$_{88}$Ni$_{10}$Y$_6$ alloy heated in the calorimeter after preliminary deformation (1) and preliminary annealing (2).

Figure 2. X-ray diffraction pattern of the Al$_{88}$Ni$_{10}$Y$_2$ alloy annealed during 30 h at 100 °C (1) and 170 °C (2).

Figure 3. X-ray diffraction patterns of the Al$_{87}$Ni$_8$Gd$_5$ alloy before (1) and after (2) cryogenic thermal cycling.
Thus, the application of cryogenic cycling to partially crystalline alloys allows decreasing the fraction of the nanocrystalline structure component and, under certain conditions, rejuvenating completely the amorphous phase.

4. Conclusions
Studies of the structural evolution of a group of Al-based alloys of Al-Ni-RE (RE = La, Y, Gd) systems have shown that using the combined heat and deformation influence on the structure, it is possible to obtain samples with different crystal sizes and different fractions of the nanocrystalline phase. The application of the cryogenic cyclic method enables rejuvenation of the amorphous phase in partially crystalline alloys.

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