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The effect of changes in Al-based amorphous phase structure on structure forming upon crystallization

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ABSTRACT

The influence of heat treatment and deformation on structural changes of Al-based amorphous alloys in the amorphous state and at early stages of crystallization has been studied using the methods of X-ray diffraction, differential scanning calorimetry and transmission electron microscopy. It is shown that isothermal annealing and multiple cold rolling bring about formation of an inhomogeneous amorphous phase with the areas of different chemical composition. The formation of an inhomogeneous amorphous phase accelerates the process of nanocrystallization of Al-based alloys. The conditions of treatment of the amorphous alloy in the amorphous state affect the size and fraction of nanocrystals forming in the amorphous phase upon subsequent heating. The size of nanocrystals in the case of preliminary deformation is smaller than that upon preliminary isothermal annealing. We discuss the reasons for the formation of nanostructures containing smaller nanocrystals in the case of thermal and deformation treatments before the onset of crystallization.

A great quantity of papers [1–8] considers investigations of amorphous and amorphous-nanocrystalline materials of different composition. The interest to these materials is due to their unusual structure and physical properties that often surpass those of conventional materials of the same composition [9–12]. Nanomaterials are most commonly produced using ball milling of ordinary crystalline materials or through controlled crystallization of amorphous alloys. The latter may involve either heat treatment or deformation. A nanocrystalline structure was first produced by heat treatment of iron alloys and later it was obtained in great number of other alloys. The nanocrystalline structure forming upon crystallization of most of iron-, aluminum-, nickel-, zirconium-based amorphous alloys represents nanocrystals of main metal alloy component (or a solid solution on its basis) randomly distributed in an amorphous matrix [4,13–16]. Formation of nanocrystals upon heat treatment of these amorphous alloys occurs by the primary crystallization reaction, and precipitated nanocrystals have a chemical composition different from that of the matrix. The process takes place by the diffusion mechanism, the remained amorphous matrix is usually enriched with more refractory alloy components which increase its heat stability. The amorphous matrix with a changed composition remaining between the nanocrystals stabilizes the nanocrystalline structure preventing growth and coalescence of the precipitated nanocrystals. A multiphase nanocrystalline structure is formed upon crystallization in some amorphous alloys; crystallization of such materials occurs by the eutectic crystallization mechanism [17,18], and structure stability is conditioned by the fact that nanocrystals of one phase are in immediate contact with nanocrystals of the other phase, which prevents growth of each of them. However, alloys of by no means all compositions may crystallize with formation of a nanostructure; that is why the other method of production of nanostructures, namely, severe plastic deformation was developed later [19–22]. This method enables to create nanostructures in the materials if they are not formed by conventional heat treatment [22,23]. Severe plastic deformation may be carried out at room or at elevated temperatures and be combined with heat treatment. Nanostructure parameters are naturally determined by an alloy composition and a type of treatment (heat or mechanical one). The structure change upon the deformation was studied for different alloys [24–28]. As a result of deformation that may be carried out in different ways, renovation of the structure may also take place [29]; such renovation leads to considerable change in properties, particularly, in increased plasticity. Currently,

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there is no complete concept of the nanostructure formation processes under different treatment conditions. The present work considers the influence of different structural states of an amorphous phase in light metallic alloys (presence or absence of separation of amorphous phase) on the parameters of a nanocrystalline structure formed during crystallization.

Partly crystalline (amorphous/nanocrystalline) light alloys exhibit good mechanical properties. High strength combined with relatively low specific weight makes this material attractive for practical application. Mechanical properties of the material essentially depend on grain size [12,30], precipitation morphology, nanocrystalline phase fraction. The best properties are achieved with some intermediate crystal size depending on the chemical composition of the alloy. In order to obtain materials with an optimal complex of properties, it is necessary to find out the principles of nanocrystalline structure formation. One of the ways of structure control may be treatment of a metallic glass in the amorphous state purposed to produce inhomogeneous amorphous structure. In such a case it would be natural to expect that the areas of different chemical composition and with different types of short-range order will crystallize in different crystallization ways. The Ni-Mo-P system has demonstrated [31] that after decomposition of the amorphous phase the amorphous regions of different chemical composition crystallize with formation of different crystalline phases; the scale of decomposition may vary significantly [31,32]. Therefore, the combined treatment involving formation of an inhomogeneous amorphous structure as the first stage would provide control over the structure forming upon subsequent crystallization.

As was mentioned above, the parameters of the structure forming upon crystallization of amorphous alloys depend on the state of the amorphous phase just before the onset of crystallization. Heat treatment in the amorphous state which does not result in crystallization may lead to the formation of crystals with different sizes, the changes in the sequence of crystalline phase precipitation, and the crystallization mechanism or formation of crystalline regions only in a certain part of the sample upon subsequent heat treatment. In this respect it would be of interest to investigate the influence of preliminary treatment of the amorphous phase on the specific features of the nanocrystalline structure formation upon its subsequent crystallization. In this work we address our research to the influence of different structural states of light amorphous metallic alloys (in the presence or absence of amorphous phase decomposition) on the parameters of the nanocrystalline structure induced by crystallization.

1. Experimental

Amorphous alloys of nominal composition $Al_{87}Ni_8La_5$, $Al_{87}Ni_8Gd_5$ and $Al_{87}Ni_8Y_5$ were obtained as 30 μm thick and ~5 mm wide ribbons by rapid melt quenching. The samples were subjected to isothermal annealing in the temperature range 100–300°C for different time intervals and to heating at a constant rate of 20°C/min in a Perkin Elmer DSC-7 differential scanning calorimeter as well as to plastic deformation. Deformation was performed by multiple rolling at room temperature. Cold rolling of the samples was performed in a VEB Schwermaschinenbau four-roll mill by the multiple rolling technique, the run number being 50–150. The strain value was calculated by the formula $\varepsilon = \Delta h/h_0$ where h_0 and Δh are the original thickness and its deformation-induced change, respectively. The structure of the samples was controlled after each stage of heat treatment and deformation.

The structure of the samples was studied by the methods of X-ray diffraction and by transmission and scanning electron microscopy. For X-ray diffraction experiments Co K_α radiation with a step mode (step was 0.01 and 0.02°) was used. Using of soft Co K_α radiation enabled to stretch the X-ray diffraction pattern and, on the one hand, to see distortions of diffuse maxima more clearly, and, on the other hand, to determine their location more precisely. Computer programs were used for processing of the X-ray diffraction spectra (smoothing, background correction, etc.). At the early crystallization stages, the samples contained amorphous and nanocrystalline phases; therefore, separation of the overlapped peaks was made. The size of forming nanocrystals was determined both from dark-field electron microscope images and from the data of X-ray diffraction. Determination of nanocrystal size from half-width of a diffraction line was carried out using the Scherrer formula [33]. The accuracy of the crystal size determination was not worse than 1 nm.

2. Results and discussion

On quenching all the prepared samples were amorphous. The temperature intervals of crystallization were determined using the method of differential scanning calorimetry. Fig. 1 shows the DSC curve of $Al_{87}Ni_8La_5$ alloy. Its crystallization proceeds in three stages. It starts at 228° C when aluminum nanocrystals precipitate in the amorphous matrix. The second and the third stages of crystallization proceed almost simultaneously. The low intensity peak corresponding to the second stage of crystallization virtually merges with the third peak in the DSC curve. The DSC curve of the alloy with Gd looks alike (Fig. 2), but the second and the third stages are more pronounced and temperature-separated. The onset temperature of crystallization of this alloy is 216°C. Crystallization of the alloy with Y also proceeds in three stages, onset temperature of the crystallization being 170° C. Fig. 3 shows a X-ray diffraction pattern of $Al_{87}Ni_8Gd_5$ alloy after the first stage of crystallization. The first crystallization stages of all alloys in question involved precipitation of aluminum nanocrystals, the two subsequent stages corresponded to formation of intermetallics. On termination of the second crystallization stage the samples contain nanocrystals of aluminum and Al_3Ni intermetallics well as remained amorphous phase; at the following stages the formation of nanocrystals of the phases containing rare earth metals form. Fig. 4 presents the X-ray diffraction pattern of $Al_{87}Ni_8Gd_5$ alloy on termination of the third stage of crystallization when the sample contains Al, Al_3Ni, Al_2Gd, and a metastable phase with a Al_4NiY-type structure (the reflections corresponding

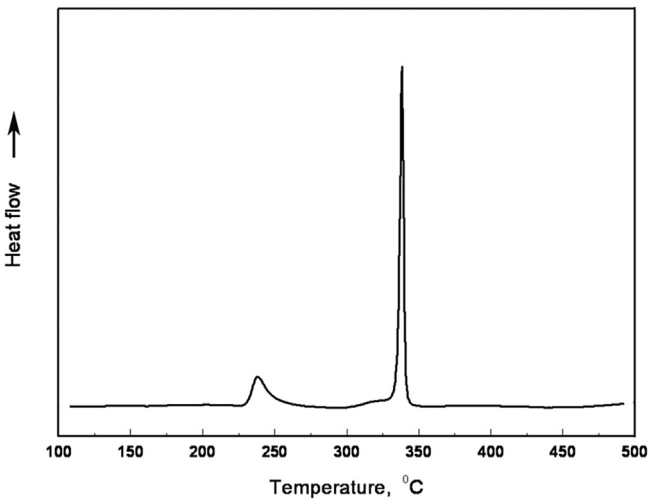

Fig. 1. The DSC curve of $Al_{87}Ni_8La_5$ alloy.