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Kinetics of Mg_6Ni nanocrystallization in amorphous $Mg_{83}Ni_{17}$

T. Spassov [a,*], St. Todorova [a], V. Petkov [b]

[a] Department of Chemistry, University of Sofia "St.Kl.Ohridski", 1 J. Bourchier str., 1164 Sofia, Bulgaria
[b] Deptartment of Physics, Dow 203, Central Michigan University, Michigan, USA

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ABSTRACT

A comprehensive crystallization kinetics study was carried out in order to understand the mechanism of formation of a Mg-rich nanocrystalline Mg_6Ni phase in a metallic glass with similar overall composition, $Mg_{83}Ni_{17}$. Adequate description of the transformation kinetics was obtained by the JMKA equation with an integer Avrami exponent $n = 4$, associated with nucleation and three-dimensional linear growth crystallization mechanism. To study the nanocrystals growth mechanism separately a controlled heat treatment of the amorphous alloy was applied and thus a three-dimensional growth with a constant rate was obtained ($n = 3$) for the pre-annealed alloys. For all transformation curves the dependence of n on the degree of transformation α, $n(\alpha)$, was analyzed and the regions with constant n were defined. The correct separation of the processes of nucleation and crystal growth allowed reliable values for the activation energies of both nucleation and growth processes to be determined.

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1. Introduction

The thermal stability and crystallization of Mg–Ni-based metallic glasses have been intensively studied [1–6] due to their applicability for hydrogen storage as well as because of the possibility to produce nanocrystalline microstructures with attractive chemical and physical properties. The crystallization, microstructure and hydriding properties of magnesium rich Mg–Ni amorphous alloys with various compositions have been investigated as well [3,6–11]. Depending on the amorphous alloy composition different crystallization mechanisms (eutectic, primary, polymorphous) were determined [2–5,12,13]. Formation of a metastable Mg_6Ni phase with cubic structure (F43m) with high thermal stability was found in Mg-richer Mg–Ni and Mg–Ni–RE alloys [3,5,6]. It has to be pointed out that according to Sommer et al. [5] the composition of the metastable phase is slightly different, i.e. $Mg_{\sim 5.5}Ni$. The formation of Mg_6Ni is inhibited by the increase of the hydrogen concentration introduced into the ribbon [3,6]. During continuous heating this metastable phase transforms to the equilibrium αMg and Mg_2Ni [3]. The thermal stability of the Mg_6Ni phase was found to depend on the alloy composition, as the highest transformation temperature of about 350 °C was detected for $Mg_{83}Ni_{17}$ and $Mg_{87}Ni_{12}Y_1$ [3,13].

The crystallization of the metastable Mg_6Ni phase in amorphous $Mg_{83}Ni_{17}$ alloy was studied and a nucleation with subsequent three-dimensional crystal growth mechanism was found [13]. The activation energy of this transformation, determined by the Kissinger method, was estimated to be 160 ± 10 kJ/mol. An average grain size of about 30 nm was determined before the transformation of this phase to the equilibrium αMg and M_2Ni [13]. In contrast, annealing of the $Mg_{82}Ni_{18}$ amorphous alloy leads to the formation of Mg_2Ni and Mg [5]. The crystallization of this glass is governed by nucleation and three-dimensional growth mechanism [5].

Based on a comprehensive crystallization kinetics analysis the present study aims to elucidate upon the Mg_6Ni nanocrystallization reaction mechanism in a glass with an overall composition very close to Mg_6Ni (i.e. $Mg_{83}Ni_{17}$).

2. Experimental part

The alloy was prepared by melting of high purity Mg (99.95) and Ni (99.99) in an induction furnace under pure argon atmosphere. From the master alloy ingots ribbons were produced by melt-spinning with an approximate quenching rate of 25–30 m/s. The chemical composition of the alloys was examined by SEM with an energy dispersive X-ray analysis (EDX).

The microstructure of the melt-spun materials as well as the crystalline phases in the as-quenched and heat treated alloys were

* Corresponding author. Tel.: +359 2 81 61 236.
E-mail address: tspassov@chem.uni-sofia.bg (T. Spassov).

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characterized by X-ray diffraction (XRD) using both in house equipment (Cu-Kα; $\lambda = 1.54$ Å) and synchrotron radiation X-rays ($\lambda = 0.103$ Å) at the beamline 11IDB (Argonne National Laboratory). Thanks to the high energy/short wavelength of synchrotron radiation X-rays used XRD data were collected over quite a wide region (0–25 Å^{-1}) of reciprocal space vectors, Q. Here $Q = 4\pi\ (\sin\theta)/\lambda$, where θ is half the angle between the incoming and outgoing X-rays, and λ is the wavelength of the radiation used. Besides, the higher flux of synchrotron radiation X-rays and the usage of a large area detector yielded XRD data of a very good statistical accuracy. Experimantal struture functions are shown in Fig. 1(a), and their Fourier transforms – the experimental reduced atomic distribution functions, $G(r)$ – in Fig. 1(b).

Thermal stability and crystallization kinetics of the rapidly solidified alloys were studied by means of DSC (Perkin–Elmer DSC7) under pure argon atmosphere.

3. Results and discussion

As already mentioned in the introduction, in a series of our previous studies [3,4,12,13] the formation of the metastable Mg_6Ni phase in melt-spun amorphous Mg–Ni alloys was analyzed. The kinetics of its formation and its thermal stability depend on the amorphous alloy composition. For the one with an overall composition close to that of the metastable Mg_6Ni compound ($Mg_{83}Ni_{17}$) the kinetic analysis reveals nucleation with subsequent three-dimensional linear growth mechanism [13], although the microstructure of the Mg_6Ni formed is fine nanocrystalline (10–15 nm) and remains in the nanometer range (20–30 nm) during annealing up to the temperatures of its decomposition to αMg and Mg_2Ni (330–360 °C). Substantial grain growth of Mg_6Ni was not detected as well. Therefore, it was challenging to take a deeper look into the local range order of the as-cast amorphous $Mg_{83}Ni_{17}$ alloy. As can be seen in Fig. 1(a) the experimental structure function for as-cast $Mg_{83}Ni_{17}$ exhibits a sharp first peak followed by low-frequency, low-amplitude oscillations, a picture typical for metallic glasses. The $Q[S(Q) - 1]$ data for the Mg_6Ni phase show more and sharper peaks, reflecting the onset of (nano)crystallization. Correspondingly, the correlations between atoms in Mg_6Ni are defined better and extend to longer interatomic distances compared to those seen in as cast $Mg_{83}Ni_{17}$. This is well demonstrated by the fact that the atomic PDF for Mg_6Ni is much more structured than that for amorphous $Mg_{83}Ni_{17}$. (see Fig. 1b) which decays to zero already at approx. 20 Å.

The DSC analysis of the amorphous $Mg_{83}Ni_{17}$ (Fig. 2) shows a single crystallization reaction at 165 °C ($T_{max} = 175$ °C), resulting in nano-Mg_6Ni formation (see Fig. 1), with an enthalpy of crystallization of 70 J/g and confirms our preliminary results [13]. The transformation of the metastable Mg_6Ni phase into the equilibrium αMg and Mg_2Ni takes place with a low velocity in the temperature range of 300–350 °C and therefore the thermal peak associated with this reaction is very broad and weak. Compared to other Mg based metallic glasses, which also transform to the stable crystalline state through the metastable Mg_6Ni phase, the thermal stability of the Mg_6Ni phase in the studied alloy is higher.

It is interesting to note that the Mg_6Ni phase, formed by annealing the $Mg_{83}Ni_{17}$ glass up to a temperature immediately after the single crystallization peak (180 °C), is extremely fine nanocrystalline (3–4 nm). Experimental XRD and RDF data clearly show that the short-range atomic order in the nanocrystallized alloy extends to about 3.0 nm (Fig. 1(b)). In addition, the (nano)crystallization involves a modification/change of the immediate/local atomic/chemical order in the glass as indicated by the change in the shape of the first peak in the corresponding atomic RDFs.

To determine the mechanism of the crystallization reaction, leading to the nanocrystalline Mg_6Ni phase, a comprehensive isothermal kinetic study at different temperatures was carried out. Figs. 3 and 4 present the DSC isothermal curves and the corresponding transformation curves in the range 145–165 °C, which is the largest temperature interval in which the reaction kinetics

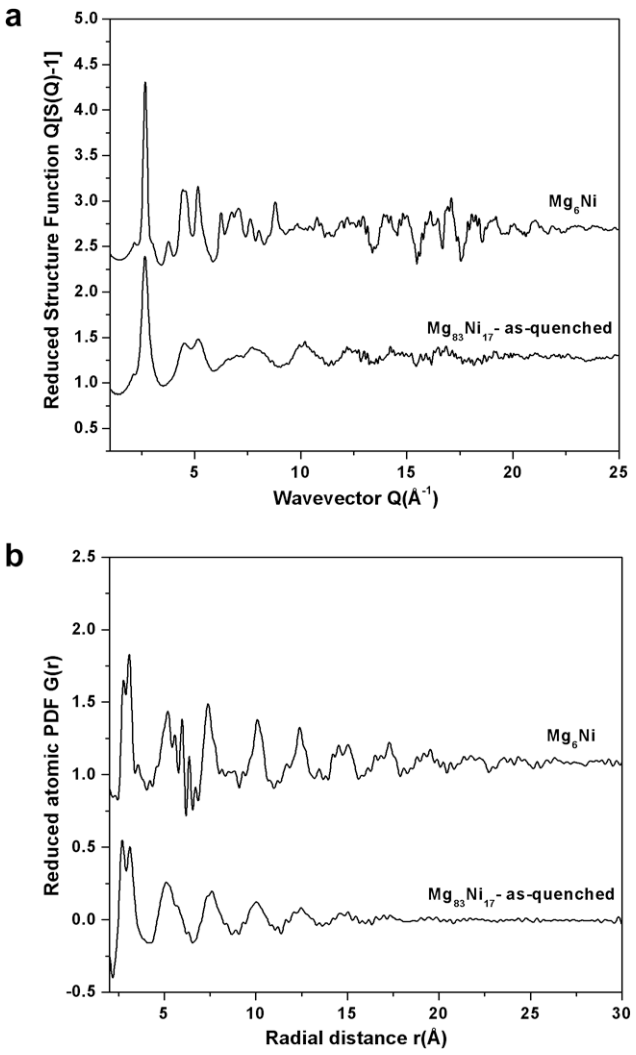

Fig. 1. Experimental structure functions of as-quenched $Mg_{83}Ni_{17}$ and Mg_6Ni phase (a) and their Fourier transforms (b).

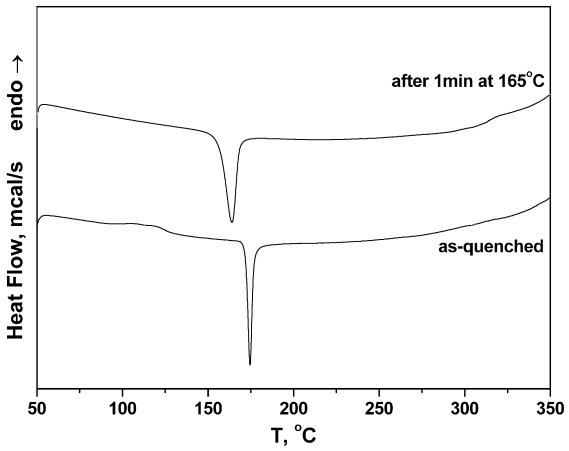

Fig. 2. DSC scans of as-quenched and pre-annealed $Mg_{83}Ni_{17}$.

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