Journal of Thermal Analysis and Calorimetry, Vol. 75 (2004) 373–378

NANOCRYSTALLIZATION OF HYDROGEN-CHARGED $Mg_{76}Ni_{19}Y_5$ AMORPHOUS ALLOY

*V. Rangelova, T. Spassov** *and N. Neykov*

University of Sofia, Department of Chemistry, 1126 Sofia, Bulgaria

(Received June 28, 2003; in revised form August 25, 2003)

Abstract

The crystallization of a hydrogen-charged melt-spun $Mg_{76}Ni_{19}Y_5$ amorphous alloy was studied in order to understand the influence of hydrogen absorbed on the crystallization kinetics and mechanism. Hydrogenation does not affect the thermal stability, but decreases significantly the enthalpy of crystallization. The glass transition, which is well manifested in the hydrogen-free alloy, is not observed after hydrogen charging. The main crystalline phases in the H-free and H-charged alloys are the same after complete transformation, but with finer microstructure for the hydrogenated samples.

Analysis of the crystallization kinetics reveals that during annealing of hydrogen charged $Mg_{76}Ni_{19}Y_5$ growth of nanocrystals surrounded by amorphous phase takes place just in the beginning of the transformation, followed by grain growth in fully crystallized material, which is the main process.

Keywords: amorphous materials, kinetics, Mg-alloys, nanocrystallization

Introduction

Magnesium based alloys for hydrogen storage continue to attract the interest of many investigators. Rapidly solidified amorphous and nanocrystalline alloys are among the promising materials for such application. Besides high hydrogen storage capacity (maximum amount of stored hydrogen) and fast hydrogen absorption/desorption the microstructural stability of the alloys during H-charging is an important feature. In the amorphous materials the hydrogenation shows an influence on the devitrification process, therefore together with a heat treatment it can be used for the controlled modification of the microstructure.

The present study continues a previous work [1], where a significant difference in the influence of hydrogen on the crystallization of $Mg_{76}Ni_{19}Y_5$ and $Mg_{78}Ni_{18}Y_4$ was found and aims in studying the mechanism of this influence on the devitrification of $Mg_{76}Ni_{19}Y_4$ by means of detailed differential scanning calorimetry (DSC) and X-ray diffraction. DSC at isothermal and continuous heating conditions is a particu-

---

* Author for correspondence: E-mail: tspassov@chem.uni-sofia.bg

1388–6150/2004/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

larly suitable method for studying quantitatively the kinetics of crystallization of metallic glasses [2, 3].

Experimental part

The pre-alloys were prepared by induction melting of high purity Mg, Ni and Y under the protection of argon. From the master alloy ingots ribbons were produced by melt-spinning in a helium atmosphere. The microstructure of the melt-spun materials as well as the crystalline phases in the heat-treated and hydrogenated alloys were characterized by X-ray (CuK_α) diffraction. The crystal sizes were calculated from the broadening of the X-ray diffraction profiles. The chemical composition of the alloys was examined by scanning electron microscopy (SEM) with an energy dispersive X-ray analysis (EDX).

Thermal stability and crystallization of the as-quenched and hydrogen charged alloys were studied by means of DSC (Perkin Elmer DSC2 and DSC7) at scanning (with heating rate 10 K min^{-1}) and isothermal conditions, as samples (ribbons) about 3 mg were heated in closed Pt pans under pure Ar atmosphere.

Hydrogen charging was carried out electrolytically under galvanostatic conditions in 0.5 M KOH at 25°C and a current density of 10 A m^{-2}. The hydrogen content was measured from the increase in mass after hydrogenation by a microbalance (Perkin Elmer TGS2) with an accuracy of 1 μg.

Results and discussion

The as-quenched alloy was found to be nanocrystalline/amorphous, consisting of small nanocrystals (2–3 nm) embedded in a large amount of amorphous phase [4]. DSC analysis of hydrogen-free alloy reveals a two-step devitrification process, Fig. 1. The first crystallization reaction (formation of hexagonal Mg_2Ni) at about 460 K has much larger enthalpy (56 J g^{-1}) and the second follows immediately the first one, as the total enthalpy is 84 J g^{-1} [4].

The influence of hydrogen absorbed on the thermal stability and crystallization of the amorphous alloy depends on its concentration in the alloy. Small amount of hydrogen absorbed (about 1 mass%) leads to not so well manifested glass transition and to more pronounced overlapping of the crystallization peaks (Fig. 1, curve b). At essentially larger amount of hydrogen (about 3.5 mass%), the glass transition DSC effect completely disappears, indicating that a partial crystallization has already taken place during hydrogenation. Whereas the hydrogen charged alloy (with about 3.5 mass% hydrogen) crystallizes at about the same temperature (only slightly higher), the crystallization peak is wider with substantially lower enthalpy ΔH_{cr}=33 J g^{-1} (Fig. 1, curve c), compared to the hydrogen free sample. The second peak is also reduced after hydrogenation. It is interesting to be mentioned that in some magnesium glasses obtained by rapid solidification (e.g. $Mg_{78}Ni_{18}Y_4$ [4], $Mg_{87}Ni_{12}Y_1$ [5], Mg–Ni–Pd [6]) the hydroge-

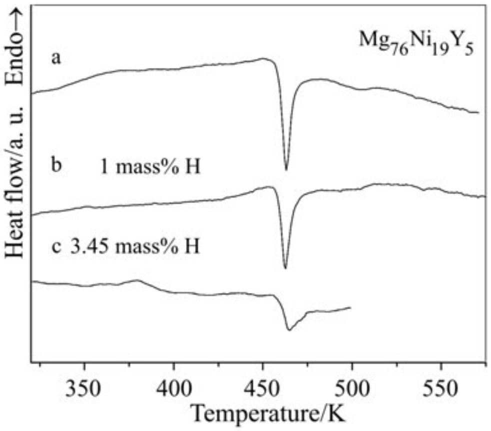

Fig. 1 DSC scans of as-quenched and hydrogen charged $Mg_{76}Ni_{19}Y_5$ alloy (scanning rate 10 K min^{-1})

nation increases the thermal stability. It is not still clear whether this effect is connected with the formation of the metastable Mg_6Ni [4].

The sample charged with a large amount of hydrogen shows a low temperature endothermic peak at about 380 K, which has to be connected with hydrogen desorption. Obviously this hydrogen, dissolved in the amorphous phase, is weakly bounded and releases before the crystallization. The larger (main) amount of hydrogen absorbed releases after the crystallization process at about 520 K [4].

X-ray diffraction analysis does not show noticeable difference between the H-free and H-charged melt-spun alloys. During heating the same crystalline phases (αMg and Mg_2Ni) are formed. The intermediate metastable Mg_6Ni also exists in both alloys below about 570–580 K. Figure 2 shows the X-ray diffraction patterns of sam-

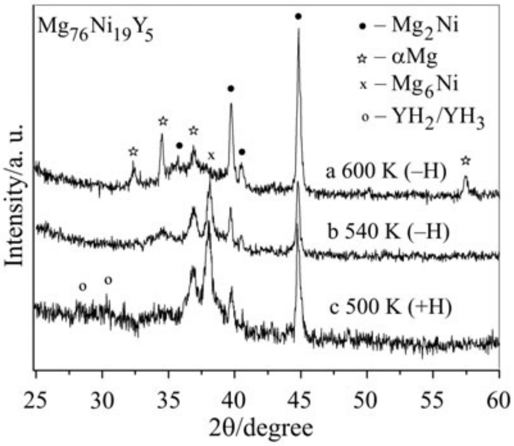

Fig. 2 X-ray diffraction of heat treated H-free and H-charged $Mg_{76}Ni_{19}Y_5$ rapidly solidified alloys: a – 600 K, b – 540 K and c – 500 K

ples with and without hydrogen after the DSC crystallization peaks and after higher temperature annealing (600 K). The hydrogenated alloy shows after crystallization at 500 K the existence of YH_2/YH_3, but no traces of Mg_2NiH_x or MgH_2 can be observed. The microstructure of H-charged and then crystallized samples is finer, which is seen from the broader diffraction peaks as well as from the nano-/amorphous halo superimposed on the diffraction peaks between $2\theta=35–40°$.

In order to study the influence of hydrogen on the mechanism of crystallization an isothermal DSC analysis of the devitrification was carried out. In contrast with the H-free samples, where the crystallization kinetics obey the JMA model [7, 8] with Avrami exponent exactly equal to 2.5 [9], in the case of the hydrogenated alloy just a decreasing DSC signal is observed at all temperatures studied (438–455 K), Fig. 3. The enthalpy decrease determined from the isothermal calorimetric curves corresponds to the enthalpy change obtained at scanning conditions. The shape of the calorimetric signal indicates growth of already existing nanocrystals formed during hydrogenation. Most probably the nanocrystals formed during hydrogenation with high density occupy the entire volume of the sample for short time and then grain growth process takes place. If we assume that during heating in DSC just a grain growth proceeds, according to Chen and Spaepen [10] the time evolution of the grain radius can be obtained from the isothermal differential calorimetry. The evolution of the nanograin radius with the time of isothermal annealing at two different temperatures is shown in Fig. 4. The average size of the nanocrystals determined by X-ray (from the broad diffraction peak) at several annealing times at constant temperature confirms those obtained by the kinetic analysis. The nanocrystals growth at both temperatures can be satisfactorily described by the kinetic law $r(t)=r_0+kt^{1/n}$, where r_0 is the initial radius of the nanocrystals (before the isothermal annealing to start), k is a temperature dependent constant and n is a time exponent. The initial growth kinetics (up to about $r\approx3$ nm) is best described with time exponent $n=2$, which value is predicted from the most grain-growth theories based on bulk diffusion. In the advanced stage of

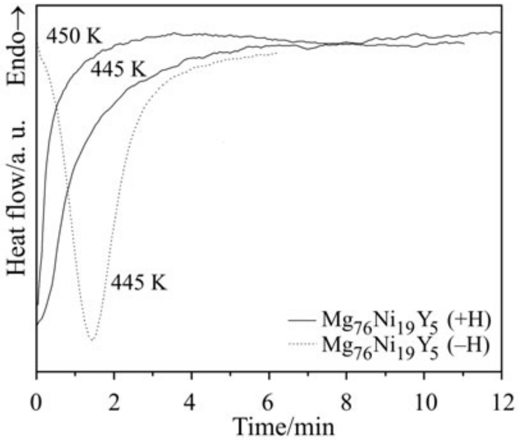

Fig. 3 DSC isotherms of primary crystallization in H-free and H-charged (about 2 mass% hydrogen) $Mg_{76}Ni_{19}Y_5$

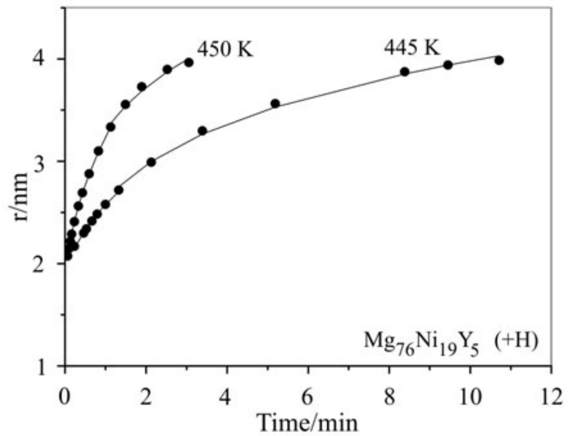

Fig. 4 Development of the average nanograin size with the time of isothermal annealing in H-charged (about 2 mass% hydrogen) $Mg_{76}Ni_{19}Y_5$

growth n changes from 2 to higher values, i.e. the growth slows down, indicating a change in the diffusion mechanism. For instance, values of $n=3$ are most frequently found in the experimental works on grain growth kinetics [11, 12].

The values for the parabolic rate constant k (at $n=2$) determined at two temperatures allowed a rough estimate for the activation energy of grain growth to be determined, $Q=210$ kJ mol^{-1}, which is close to that reported for nanocrystals growth in $CoZr_2$ and $FeZr_2$ [11].

Conclusions

Although the hydrogenation does not show strong influence on the thermal stability of rapidly solidified nano-/amorphous $Mg_{76}Ni_{19}Y_5$ it decreases essentially the enthalpy of devitrification suppresses the glass transition DSC effect. The crystalline phases in the H-free and H-charged alloys are the same with finer microstructure for the hydrogenated samples.

The isothermal crystallization shows that during annealing of hydrogen charged $Mg_{76}Ni_{19}Y_5$ alloy only growth of already formed nanocrystals takes place. The kinetic analysis reveals that just in the beginning the nanocrystals probably grow in amorphous surrounding, afterwards grain growth in completely crystallized material proceeds.

* * *

The authors are very grateful to the Alexander von Humboldt Foundation (Germany) for the donation of the DSC-7 calorimeter.

References

1 V. Rangelova, N. Neykov and T. Spassov, Ann. Univ. Sofia, Fac. Chim., 2003, in press.
2 J. J. Suñol, M. T. Clavaguera-Mora and N. Clavaguera, J. Therm. Anal. Cal., 72 (2003) 347.

3 J. J. Suñol, M. T. Clavaguera-Mora and N. Clavaguera, J. Therm. Anal. Cal., 70 (2002) 173.
4 T. Spassov, V. Rangelova and N. Neykov, J. Alloys Comp., 334 (2002) 219.
5 T. Spassov and U. Köster, J. Alloys Comp., 287 (1999) 243.
6 S. Yamamura, H. Kim, H. Kimura, A. Inoue and Y. Arata, J. Alloys Comp. 339 (2002) 230.
7 A. N. Kolmogorov, Izv. Akad. Nauk USSR. Ser. Matem., 3 (1937) 355.
8 M. W. A. Johnson and K. F. Mehl, Trans. Am. Inst. Min. Metall. Pet. Eng., 135 (1939) 416.
9 V. Rangelova and T. Spassov, J. Alloys Comp., 345 (2002) 148.
10 L. C. Chen and F. Spaepen, J. Appl. Phys., 69 (1991) 679.
11 T. Spassov and U. Köster, J. Mater. Sci., 28 (1993) 2789.
12 M. P. Anderson, D. J. Srolovitz, G. S. Grest and P. S. Sahni, Acta Metall., 32 (1984) 783.