

Crystallization process on amorphous Mg–Ga–Sn system

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The crystallization processes on $\text{Mg}_{81.09}\text{Ga}_{18.91}$ and $\text{Mg}_{80.50}\text{Ga}_{17.76}\text{Sn}_{1.67}$ amorphous samples were studied by means of X-ray diffraction and electrical resistivity isothermal measurements. A small amount of Sn added to the binary eutectic was found to modify the crystallization products and the evolution time. Crystallization activation energies were estimated.

1. Introduction

The Mg–Ga system has a total glass forming composition range around the Mg– Mg_5Ga_2 eutectic composition (19.13 at.% Ga) [1]. Its glass transition temperature has been estimated as 117 °C [2]. A metastable phase (M) has been obtained as a first step crystallization product and its local order has been correlated to the $\text{Mg}_{80.87}\text{Ga}_{19.13}$ amorphous short range order [1]. Liquid Mg–Ga has already been studied [3] and a strong associative tendency has been observed at 700 °C. The amorphous short range order has been correlated to that of Mg_2Ga .

Several works [4, 5, 6, 7] explore the influence that a strong associative tendency in the liquid has on the glass forming ability, when rapid quenching from the melt is employed. On the other hand, the improvement of the glass forming ability by the addition of Sn has been reported [8, 9, 10] on Mg– X systems ($X = \text{Cu}, \text{Zn}$), where a strong associative tendency of Sn towards Mg exists in the liquid.

The addition of Sn to the Mg– Mg_5Ga_2 eutectic has already been studied [11] and no additional phases were reported, leaving Sn in solid solution in the above mentioned phases, at least up to 1.67 at.% Sn.

The aim of this work is to analyse the influence that a small amount of Sn added to the Mg– Mg_5Ga_2 eutectic has on the stability of the amorphous phase and on the crystallization process.

2. Experimental procedure

$\text{Mg}_{81.09}\text{Ga}_{18.91}$ and $\text{Mg}_{80.57}\text{Ga}_{17.76}\text{Sn}_{1.67}$ (at.%) alloys were prepared from 99.99% pure materials, under Ar atmosphere, in graphite crucibles. Their homogeneity was checked by metallographic inspection.

Samples in near circular form were obtained by rapid quenching (RQ) from the melt at 590–600 °C employing the piston and anvil technique [12] under Ar atmosphere.

As cast alloys as well as RQ samples were analysed by X-ray diffraction at room temperature (20 °C) with

CuK_α radiation. The electrical resistivity was measured on RQ samples with a four probe d.c. device along isothermal annealings performed at five different temperatures (Table I).

3. Results

X-ray diffractograms were obtained along isothermal annealings performed at 20 °C. The most important features on the X-ray diffractograms from the $\text{Mg}_{81.09}\text{Ga}_{18.91}$ and $\text{Mg}_{80.57}\text{Ga}_{17.76}\text{Sn}_{1.67}$ amorphous samples are shown in Fig. 1 and Fig. 2. Each amorphous structure evolves towards different crystalline phases at room temperature. The evolution time (in hours) is also mentioned at each X-ray diffraction pattern. The first diffractogram from each sample was obtained two to three hours after the sample had been quenched. An amorphous halo and, also the presence of incipient crystalline phases are observed. Three peaks corresponding to the Mg_5Ga_2 and Mg equilibrium phases were identified.

The crystallization product on binary amorphous samples is the metastable phase M. In the crystallization process on ternary amorphous samples, the equilibrium phases grow in a first stage and, after an incubation time, the metastable phase M is also observed. The diffraction peaks corresponding to the crystalline phase patterns are reported in Figs 1 and 2.

The electrical resistivity normalized to the initial value, R/R_0 , measured at several temperatures on amorphous $\text{Mg}_{81.09}\text{Ga}_{18.91}$ and $\text{Mg}_{80.57}\text{Ga}_{17.76}\text{Sn}_{1.67}$ samples versus the evolution time t , are reported in Fig. 3 and Fig. 4. The R/R_0 asymptotic values ($t \rightarrow \infty$) are not constant, they depend on the different fraction of crystalline phases contained in the samples when annealing began.

4. Discussion

Amorphous crystallization is described by the Johnson–Mehl–Avrami equation [13]

$$X_c(t) = 1 - e^{-(kt)^n} \quad (1)$$

TABLE I Annealing temperatures employed on thermal treatments

Samples	Temperature (°C)				
Mg _{81.09} Ga _{18.91}	30±2	35±2	41±2	48±2	53±3
Mg _{80.57} Ga _{17.76} Sn _{1.67}	35±2	40±2	45±2	52±3	60.5±3

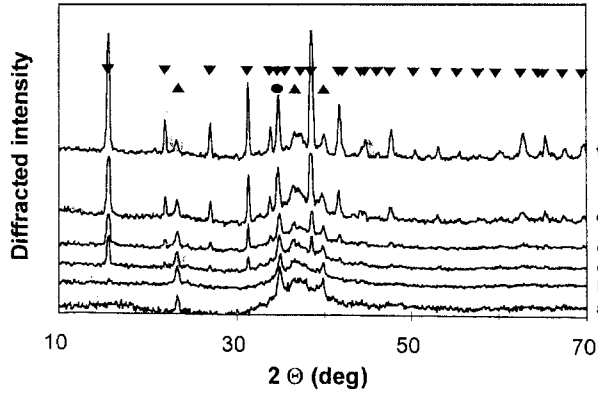


Figure 1 X-ray diffractograms, obtained with $\text{CuK}\alpha$ radiation, of the amorphous $\text{Mg}_{81.09}\text{Ga}_{18.91}$ samples under isothermal annealing at room temperature. The evolution times are (a) 2–3 h, (b) 3–4 h, (c) 7–8 h, (d) 11.5 h, (e) 14.5 h and (f) 480 h. As a reference, the diffraction lines of the crystalline phases Mg (●), Mg_5Ga_2 (▲) and metastable M (▼) are also reported.

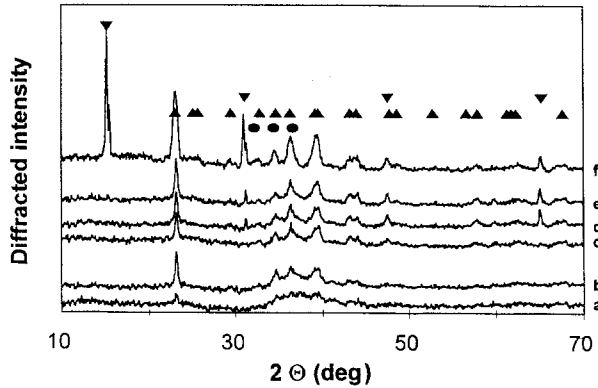


Figure 2 X-ray diffractograms, obtained with $\text{CuK}\alpha$ radiation, of the amorphous $\text{Mg}_{80.57}\text{Ga}_{17.76}\text{Sn}_{1.67}$ samples under isothermal annealing at room temperature. The evolution times are (a) 2–3 h, (b) 24 h, (c) 120 h, (d) 168 h, (e) 192 h and (f) 1000 h. As a reference, the diffraction lines of the crystalline phases Mg (●), Mg_5Ga_2 (▲) and metastable M (▼) are also reported.

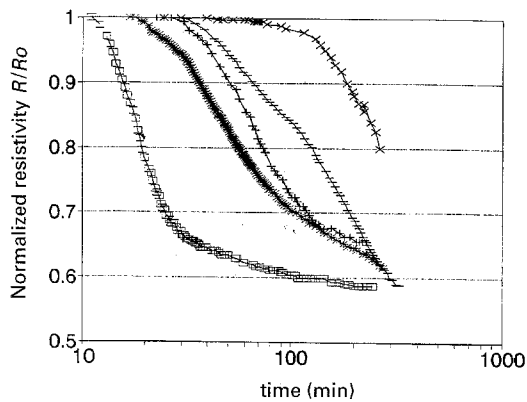


Figure 3 Normalized electrical resistivity R/R_0 change of the $\text{Mg}_{81.09}\text{Ga}_{18.91}$ sample under isothermal annealing at several temperatures (× 30°C, − 35°C, + 41°C, * 47°C and □ 53°C).

where $X_c(t)$ is the crystalline fraction depending on time t , k is the rate constant and n is an exponent that depends on the crystallization mode.

The crystalline fraction is obtained, as a first approximation, from the linear relation

$$X_c(t) = [1 - R/R_0(t)] / (1 - R/R_{0\min}) \quad (2)$$

where $R/R_{0\min}$ is the minimum R/R_0 value.

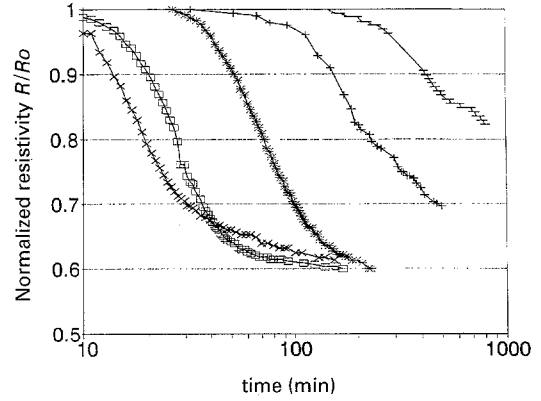


Figure 4 Normalized electrical resistivity R/R_0 change of the $\text{Mg}_{80.57}\text{Ga}_{17.76}\text{Sn}_{1.67}$ sample under isothermal annealing at several temperatures (− 35°C, + 40°C, * 45°C □ 52°C and × 60.5°C).

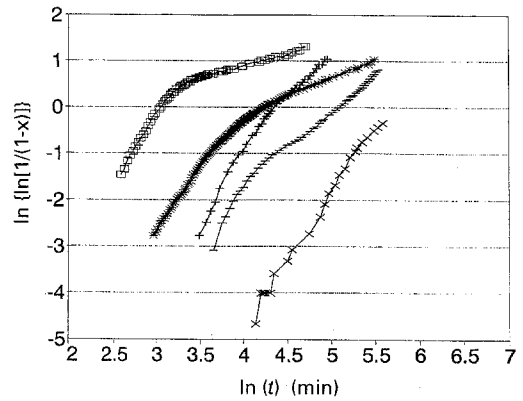


Figure 5 Plots of $\ln[\ln(1/(1-X))]$ versus $\ln(\text{time})$ at several temperatures (× 30°C, − 35°C, + 41°C, * 47°C, and □ 53°C) corresponding to the $\text{Mg}_{81.09}\text{Ga}_{18.91}$ sample. X is the crystalline fraction.

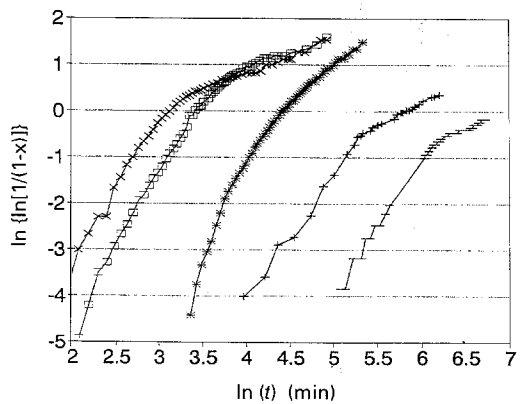


Figure 6 Plots of $\ln[\ln(1/(1-X))]$ versus $\ln(\text{time})$ at several temperatures (− 35°C, + 40°C, * 45°C, □ 52°C and × 60.5°C) corresponding to the $\text{Mg}_{80.57}\text{Ga}_{17.76}\text{Sn}_{1.67}$ sample. X is the crystalline fraction.

TABLE II Johnson-Mehl-Avrami exponents n_1 and n_2 , obtained by linearizing Equation 1, corresponding to two different modes in each crystallization process

Mg _{81.09} Ga _{18.91}			Mg _{80.57} Ga _{17.76} Sn _{1.67}		
T (°C)	n ₁	n ₂	T (°C)	n ₁	n ₂
30	2.91	1.81	35	2.76	0.81
35	2.77	1.55	40	2.66	0.98
41	3.46	1.71	45	3.29	1.54
47	2.74	0.80	52	3.35	1.32
53	3.09	0.51	60.5	2.88	0.65
average n	3.1 ± 0.3	1.3 ± 0.5	average n	3.0 ± 0.3	1.1 ± 0.4

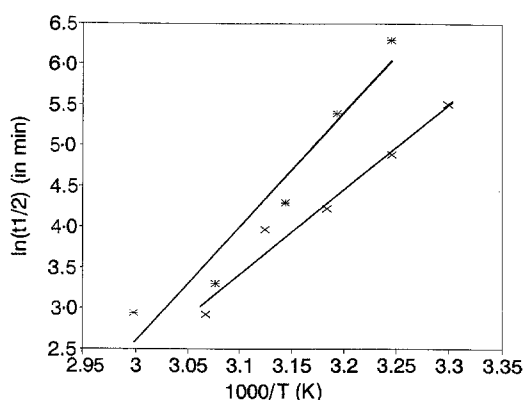


Figure 7 Arrhenius plot of $\ln(t_{1/2})$ versus $1000/T$ corresponding to the Mg_{81.09}Ga_{18.91} (*) and Mg_{80.57}Ga_{17.76}Sn_{1.67} (x) samples.

Linearizing Equation 1, $\ln\{\ln[1 - X_c(t)]^{-1}\}$ versus $\ln(t)$ plots are obtained (Fig. 5 and Fig. 6) corresponding to Mg_{81.09}Ga_{18.91} and Mg_{80.57}Ga_{17.76}Sn_{1.67} crystallization processes. Each plot consists of a broken line, corresponding to a two stage crystallization process, from which slopes n_1 and n_2 , obtained by a least square fitting, are reported in Table II. The average n values on each stage are also reported in Table II.

The n values obtained are not influenced by the presence of Sn. Those values show that the growing process is controlled by the interface [13]. The two stage crystallization process may be associated with the nearly plane shape of the samples. In the first stage, crystallization is a three-dimensional process with a decreasing nucleation rate. After a time, growing becomes a two-dimensional process while the number of crystalline nuclei saturates.

Provided that the temperature range is small enough, the temperature dependence of the rates of crystallization obeys an Arrhenius type equation i.e. a linear relation exists between the logarithm of the rate constant and the reciprocal of the absolute temperature T [14]. This applies also to $t_{1/2}$, the time needed to reach a resistivity change fixed in 50% of the total change. In these circumstances it is possible to define an empirical activation Ea by the equation

$$t_{1/2} = t_0 e^{(Ea/RT)} \quad (3)$$

where R is the gas constant and t_0 is a constant factor.

The $t_{1/2}$ values are reported in Table III. Linearizing Equation 3, Ea/R is the slope in a $\ln t_{1/2}$ versus $1/T$ graphic. Ea and t_0 , estimated by a least square fitting, are also reported in Table III.

TABLE III The time needed to reach a resistivity change fixed in 50% of the total change, $t_{1/2}$, estimated on each isothermal annealing process, the empirical activation energy Ea and the time factor t_0

Mg _{81.09} Ga _{18.91}		Mg _{80.57} Ga _{17.76} Sn _{1.67}	
T (°C)	$t_{1/2}$ (min)	T (°C)	$t_{1/2}$ (min)
30	246	35	541
35	132	40	218
41	68	45	73
47	52.5	52	27
53	18.5	60.5	19
Ea (kJ mol ⁻¹)	86 ± 8	Ea (kJ mol ⁻¹)	116 ± 15
t_0 (h)	5.7 × 10 ⁻¹⁵	t_0 (h)	1.4 × 10 ⁻¹⁹

5. Conclusions

A small addition of Sn to the binary eutectic composition samples generates more stable amorphous phases. The activation energy is about 35% greater and the evolution time increases up to four times on ternary samples.

The crystallization products on each transformation are different. The metastable phase M is obtained in the binary samples' crystallization process while the equilibrium phases are obtained in the ternary samples' crystallization process. The fact that after crystallization of the equilibrium phases the metastable phase nucleates in the ternary samples, suggests that Sn diffusion is a previous condition to crystallization of the M phase.

The increase in the activation energy as well as in the evolution time by the addition of Sn is a consequence of the different crystallization processes; a polymorphous crystallization in the binary samples and diffusion plus nucleation in the ternary samples' eutectic crystallization.

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