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Effect of nanoparticles on the critical cooling rate for glass formation in Mg–Zn alloys

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Abstract

In previous works it has been shown that the glass forming ability of metallic alloys can be modified by the addition of nanoparticles that perturb the alloy crystallization. In this work previous results are compared with results from new samples produced with a higher cooling rate. The results are interpreted in terms of a kinetic model that predicts that nanoparticles modify the nucleation rate with a very sensitive dependence on the particle volume fraction and size. It is shown that the effect of the particles is to change the critical cooling rate by about one order of magnitude and that the particle concentration must be adjusted within a narrow range. © 1997 Elsevier Science B.V.

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1. Introduction

In previous works it has been shown [1–4] that glass formation of metallic alloys can be induced by the addition of particles that perturb the alloy crystallization. A kinetic model [5,6] predicts that these particles strongly modify the nucleation rate but the growth rate is only slightly affected.

The experimental procedure used to generate the perturbing particles consists of adding an element with a strong tendency to associate with one elemental component of the alloy. In this manner those associations yield coherent perturbing particles (PP). Before the addition of the third element the alloy is called original binary alloy (OBA), and the matrix resulting after the formation of the associations was called remnant matrix (RM).

In the previous works [1–4] nanoparticles of Mg_2Sn were observed when tin was added to a Mg–Zn binary alloy. The same particles were formed by adding Mg to a Sn–Zn alloy [7]. Similar particles (Mg_2Pb) were formed when Pb was added to a Mg–Zn alloys [7]. Although no direct determination of the particle size was possible, an upper bound of less than 2 nm was estimated from Mössbauer spectra and X-ray diffraction [7].

The formation of the particles relies on the simple fact that the tendency of Sn and Pb to associate with Mg is so strong that clusters of Mg_2Sn or Mg_2Pb already exist in binary and ternary melts [8–12]. In fact, in the ternary as-cast samples Sn is detected only in the Mg_2Sn phase and in the rapidly cooled samples it was established from the Mössbauer spectra that Sn was located in a Mg_2Sn-type environment, even in the

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samples where the phase was not identified by X-ray diffraction [1,2]. The experimental evidence for the existence of Mg_2Sn particles, in the ternary MgZnSn system, is presented by Sirkin et al. [2]; moreover, tin atoms are detected only in this phase.

In Ref. [5] it was shown that if the number density of particles is high enough so that the crystalline nuclei of the matrix necessarily touch or embed a particle the latter's presence adds a surface energy term to the Gibbs free energy of the crystalline nucleus. This term is proportional to the volume fraction of particles (*f*), inversely proportional to the particle radius (r_0) and increases with the interfacial energy between the perturbing nanoparticles and the crystalline phase that is being hindered [5].

The effect of the particle size (assumed spherical of radius r_0) and the interfacial energy is represented by an unique parameter α defined as

$$\alpha = \frac{R_0 p}{2r_0} \tag{1}$$

where

$$p = \frac{\sigma_{\mathrm{cp}} - \sigma_{\mathrm{lp}}}{\sigma_{\mathrm{lc}}} \tag{2}$$

σ_{cp}, σ_{lp} and σ_{lc} are, respectively, the crystal/particle, liquid/particle and liquid/crystal surface energy densities and R_0 is a parameter that depends on the remnant matrix. As the parameter α increases, the critical cooling rate for glass formation decreases [5–7]. The critical cooling rate is defined as the minimum cooling rate such that the cooling curve does not touch the TTT curve for the formation of at most one part per million of the crystalline phase.

In the kinetic model [5–7] it was shown that the critical cooling rate is reduced nearly exponentially with the volume fraction of Perturbing Particles (*f*) and with the parameter α. For the alloys used in the previous investigations [1–3] and in this work, a decrease of one order of magnitude in the critical cooling rate was estimated.

In the present work some compositional alloys were rapidly quenched by the melt spinning technique, that provides a cooling rate one order of magnitude higher than the splat cooling technique used for the samples of Refs. [1–3]. The effect of the perturbing particles on alloys produced by the two techniques is compared. Although the perturbing particles are not necessary in order to obtain an amorphous Mg–Zn alloy with the melt spinning technique, that technique complements the previous results [1–4] in addressing the following points:

1. Is the critical cooling rate reduced by about one order of magnitude due to the addition of the perturbing particles (PP), as predicted theoretically in Refs. [5–7]?
2. The addition of a third element also shifts the composition of the remnant matrix (RM). Can the critical cooling rate for glass formation be changed in a magnitude similar to that obtained by the presence of the PP, due to the shift in composition toward a more favorable region?
3. Considering that in previous works [2,3] the samples with the lowest tin content (2.5 at%) showed a high crystallinity, could a low PP concentration promote heterogeneous nucleation of the RM instead of producing an amorphous phase?

2. Experimental

High purity materials (4N) were employed in the preparation of the alloys. Scanning electron microscopy, employing an X-ray energy dispersive analyzer, provided information about the homogeneity and compositions of the samples. All the rapidly quenched and as-cast samples produced were structurally characterized by the X-ray diffraction technique ($\mathrm{Cu}K_\alpha$ radiation).

Melted bullets of the as-cast alloys were rapidly cooled by the melt spinning technique and ribbons 20 μm–30 μm thick were obtained, while samples described earlier [1–3] were produced by the splat cooling technique and resulted in discs 70 μm–80 μm thick. Although the cooling rate in the present experiments could not be measured, it can be roughly estimated from the resulting sample thickness, since in both production techniques the cold substrate is the same (polished copper). The cooling rate for this material obtained by the melt spinning technique was estimated to be one order of magnitude higher than for the splat cooling technique [13].

Fig. 1(a) was constructed for the purpose of showing the compositional differences between the samples prepared; the zinc concentration in the original binary

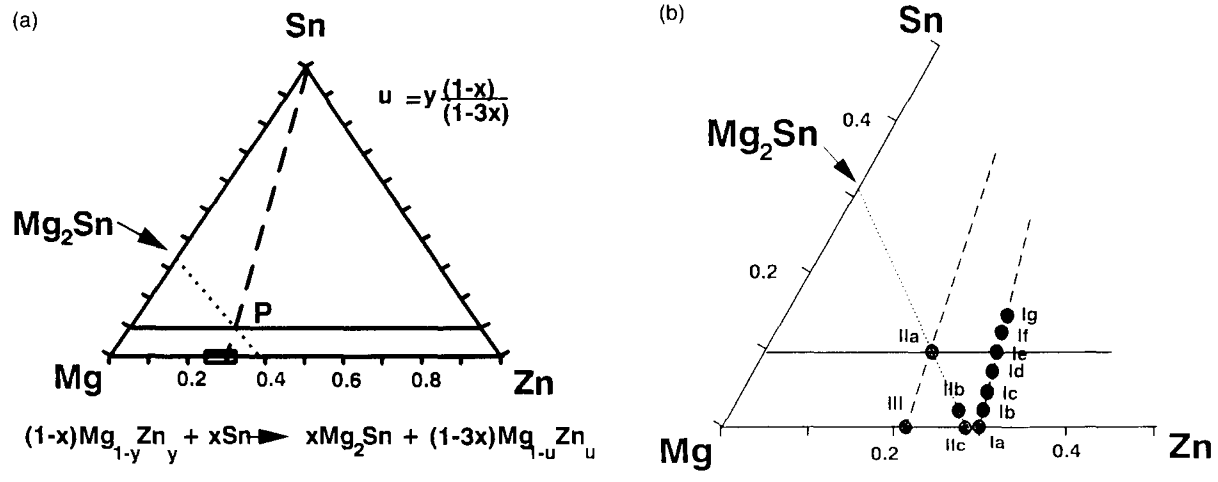

Fig. 1. Ternary diagrams showing the composition of the prepared alloys. (a) Diagram showing the resulting composition of the remnant matrix (RM) for the alloys prepared from an original binary alloy (OBA) after the addition of x(at.%) of Sn. The dashed line corresponds to the constant original binary alloy to which tin is added;the dotted line indicates constant remnant matrix with added Mg_2Sn; the solid line corresponds to constant 10% Sn content, (b) Compositions of the samples prepared. For details regarding y, x and u see Table 1.

alloy is denoted by y. To this alloy an amount x of tin is added. As was explained, after alloying, tin atoms appeared to associate only with Mg in a Mg_2Sn configuration leaving a remnant matrix containing Mg and Zn of shifted composition as compared to the OBA. The Zn concentration in the RM is labeled u and can be calculated from the initial Sn (x) and Zn (y) concentrations by the relation given in Fig. 1(a). A linear dependence is indicated between u and y and the slope depends on the concentration, x, of tin. The dashed line corresponds to original binary alloy of constant Zn/Mg ratio to which tin is added. The dotted line indicates constant remnant matrix with added Mg_2Sn. Within this region of the diagram tin was always found in the Mg_2Sn phase in the as-cast samples. The bar indicates the composition range (0.25 to 0.32 Zn atomic fraction) for which other authors [14,15] have obtained amorphous samples in the binary alloy. It is used to compare the resulting structure of remnant matrices from present work with the data of other authors.

The compositions of the samples prepared are listed in Table 1 and represented in a partial ternary phase diagram (Fig. 1(b)). Two series of samples were prepared. The series I(a–g) contains alloys with the same OBA (Table 1) and with increasing tin concentration. The series II(a–c) ensure fixed RM composition and varies the amount of PP formed. Alloys IIa and III have the same OBA.

Table 1
Compositions of the samples prepared, expressed in atomic fractions

Sample	y	u	x
Ia	0.30	0.30	0
Ib	0.30	0.316	0.025
Ic	0.30	0.335	0.05
Id	0.30	0.358	0.075
Ie	0.30	0.386	0.10
If	0.30	0.42	0.125
Ig	0.30	0.464	0.15
IIa	0.21	0.27	0.10
IIb	0.26	0.27	0.025
IIc	0.27	0.27	0
III	0.21	0.21	0

3. Results

The most representative X-ray diffraction spectra of series I(a–g) are shown in Fig. 2. The spectra of series II(a–c) and composition III, together with the diffraction spectrum of an as-cast sample of composition IIa, are shown in Fig. 3.

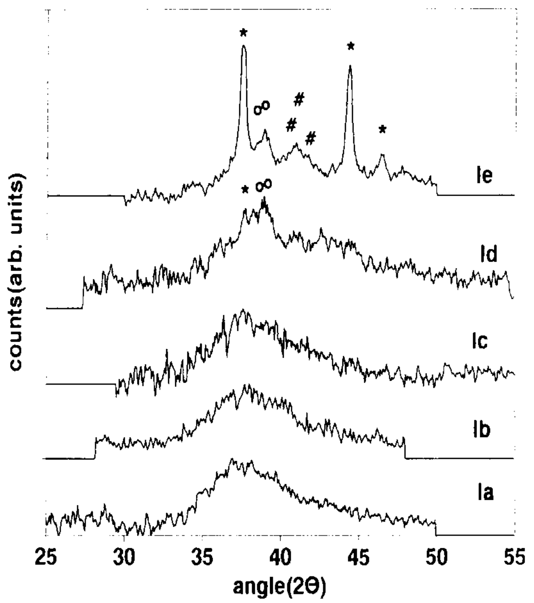

Fig. 2. X-ray diffraction spectra showing the most representative features for samples of series I(a–e) (see Fig. 1), produced with the melt-spinning technique. The positions of the peaks of the expected crystalline phases are indicated: (*) Mg_2Sn; (#) Mg_2Zn_3; (o) Mg_7Zn_3.

From Fig. 2 it can be seen that alloys Ib and Ic were substantially amorphous. Alloy Ia (no tin content) has a similar diffraction spectra to that of Ib and Ic. The spectrum of alloy Id (7.5 at.%Sn) shows several peaks barely above the amorphous halo, attributed to the Mg_2Sn and Mg_7Zn_3 phases. In alloy Ie (10 at.%Sn) the crystalline Mg_2Sn phase shows up clearly, and some of the lines attributed to the remnant matrix also appear. Note that the RM composition lies outside the binary alloy glass forming range [14,15]. Compositions If and Ig (not shown in the figure) yield crystalline samples.

From Fig. 3 it is seen that the spectrum of alloy III (whose composition is outside the glass forming range of the Mg–Zn alloy) presents peaks corresponding to αMg and a broad one characteristic of the amorphous phase. This result is in agreement with those obtained by Boswell [14]. When 10 at.% Sn is added to this alloy (sample IIa), the RM composition is shifted inside the glass forming range of the Mg–Zn alloy; a few weak peaks begin to appear above the amorphous halo, attributed to Mg_2Sn and Mg_7Zn_3, and the two lines are not identified. It may be noted that no crystalline αMg can be detected. For comparison the X-ray diffraction spectra of an as-cast sample of composition IIa is included in Fig. 3. Note that the background is almost flat and that all the lines corresponding to Mg_7Zn_3, αMg and Mg_2Sn are identified, this last being much stronger than the others.

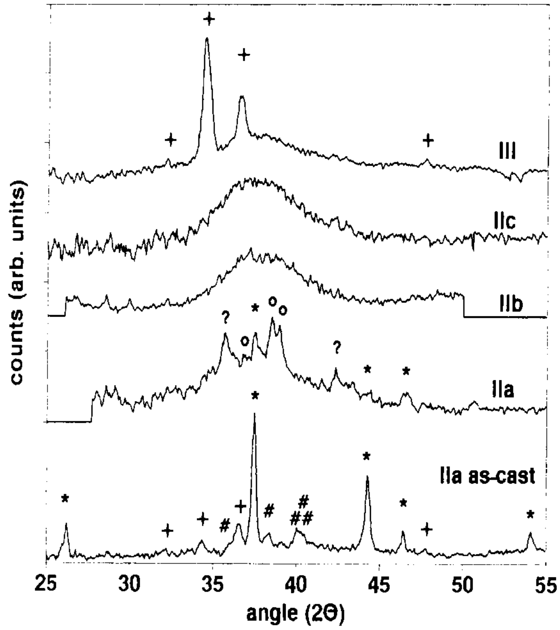

Fig. 3. X-ray diffraction spectra showing the most representative features for samples of series II(a–c) and III (see Figure 1), produced with the melt-spinning technique. A spectrum of an as cast sample is added for comparison. The positions of the peaks of the expected crystalline phases are indicated: (+) Mg; (*) Mg_2Sn; (#) Mg_2Zn_3; (o) Mg_7Zn_3 and (?) not identified peak.

The alloys IIb and IIc were substantially amorphous. This was expected since both remnant matrices have compositions that lie inside the amorphous range and the melt-spinning technique provides an adequate cooling rate.

4. Discussion

In samples produced by the two techniques, it was found that there exists a maximum tin content capable of promoting disorder in the Mg–Zn remnant matrix. The theoretical description given earlier [5,6] predicts a monotonous decrease of the critical cooling rate (easier glass formation) with an increase of the amount of perturbing particles.

This discrepancy can be understood with the following model. If it is assumed that in the liquid N_0 spherical particles of identical size preexist, and if F is the volume fraction of the particles and N is the number of particles that do not touch any other (estimated by $N_0 \exp(-8F)$], the volume fraction of particles that do not touch any other (f) can be evaluated by:

$$f = \frac{N}{N_0} F = F.e^{-8F} \quad (3)$$

The fraction $F = 1/8$ maximizes f. The resulting volume fraction of isolated particles is $f = 0.05$. As the kinetic model predicts a very sensitive dependence of the perturbing action of the particle on its size, it is a reasonable simplification to assume that only the isolated particles contribute effectively to the decrease in the critical cooling rate.

From the statistical model an optimum amount of PP is expected around a volume fraction $F = 1/8$. In the case of Mg_2Sn this fraction corresponds to alloying the Mg-Zn OBA to 3.4 at.%Sn. The excellent results obtained with 2.5 at% Sn and 5 at.% Sn are consistent with the model. It may be recalled [3] that in the previous study where the splat cooling production technique was used, sample Ic (5 at% Sn) produced amorphous and Ib (2.5 at%) crystalline phases, also consistent with the model.

It was found that, on increasing the tin content, a Mg_2Sn crystalline peak is detected. This result is also consistent with the statistical model, considering that, when an excess of PP over the optimum value is added, the probability of particles touching each other increases giving rise to the growth of Mg_2Sn and finally segregation of that phase. In terms of the kinetic model it is possible to observe that if the PP are large, for a fixed value of f, the coefficient α defined by the Eq. (1) decreases. Once the optimum tin content is exceeded, the particle size increases and the fraction of isolated particles decreases. The decrease in both parameters (f and α) explains why above an optimum value the excess of tin does not improve the glass-forming ability of the matrix.

The other point addressed in the case of low content of PP was the possibility of heterogeneous nucleation, that is related to the interfacial energy (coefficient p in Eq. (2)) and hence to the parameter α. It is not possible to evaluate experimentally the parameter α because it depends on the interfacial surface energy in the supercooled liquid, but some qualitative indication can be obtained from the lattice mismatch [16] between the crystalline phases of the Mg_7Zn_3 matrix and the PP (Mg_2Sn). In fact, the phase Mg_7Zn_3 has an orthorhombic structure with a nearest neighbor distance between Zn atoms of about 0.27 nm [17,18] while the Mg_2Sn phase is a FCC structure with a distance between Sn neighbors of 0.478 nm [17,19]. Hence, such a large mismatch indicates that the parameter p defined in the Introduction is positive, because the surface energy between the liquid and the particle should be smaller than the energy between the crystalline nucleus and the particle ($\sigma_{cp} > \sigma_{lp}$). No promotion of heterogeneous nucleation by the particle is then expected. This assumption is consistent with the fact that samples with low tin content did not show an increase in crystallinity.

At this point it is important to recall some of the previously reported results for comparison. Samples Ia and Ib were crystalline when produced by the splat cooling technique [1–3], and the possibility of heterogeneous nucleation with a small tin content could not be discarded in the previous works. The results obtained in this work with samples Ib and IIb can now be explained by the fact that in this case the amount of PP is less than the fraction required for compensating the less favorable composition. No indication of heterogeneous nucleation due to the PP is found.

The shift in the composition of the RM with respect to the OBA is also a relevant factor to take into account regarding the glass-forming ability. Comparing sample III with IIa it can be seen that the addition of tin to an OBA with excess of Mg prevents the segregation of this element. If the shift in composition is toward an unfavorable value (alloy Ie), the glass-forming ability is decreased. Hence sample IIa was a better glass former than Ie with the same amount of PP. In both cases the volume fraction of PP was $F = 0.35$, much larger than the optimum predicted.

Comparing the X-ray diffraction spectra of alloys Ic and IIa in Figs. 2 and 3 respectively, it can be seen that alloy Ic has a higher disorder than IIa in spite of the fact that the latter has a more favorable composition of the RM. Alloy Ic has a particle concentration F closer to the predicted optimum. It is inferred that, even at higher cooling rates, it is possible to enhance the glass formation by the addition of PP.

5. Conclusions

By comparison of the production technique used in this work (melt spinning) with that previously reported [1–3] (splat cooling) it is inferred that the effect of perturbing the crystallization by the addition of particles is equivalent to decreasing the critical cooling rate by approximately one order of magnitude. This result is consistent with the theoretical prediction [6,7].

It was also inferred that if the lattice mismatch between the particles added and the crystalline phase to be hindered is large, no heterogeneous nucleation is promoted.

Due to the exponential dependence of the change in the cooling rate with particle concentration predicted earlier [6] at low tin concentration no significant effect is detected. At high tin concentration, when the particles are segregated, the dominant effect is the shift in the composition of the remnant matrix. Hence the range of particle concentration effective in hindering the crystallization is relatively narrow, it can be estimated theoretically but must be determined more precisely experimentally. It was shown that the complementary effect of shifting composition can enhance the glass formation in a trivial way but without decreasing the critical cooling rate for the new composition.

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