Changes in the Glass Forming Ability of MgZnSn Alloys Due to the Presence of an Intermetallic Compound

M. Mingolo, B. Arcondo, E. Nassif, and H. Sirkin

Departamento de Fisica, Facultad de Ingenieria, UBA, Paseo Colón 850, 1063, Buenos Aires, Argentina

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X-ray and Mössbauer studies are performed on $(Mg_{70}Zn_{30})_{100-x}Sn_x$ rapidly colled alloys with different tin contents. The third element (Sn) added to $Mg_{70}Zn_{30}$ modifies the glass forming ability (GFA) of the binary alloy. It is shown that this occurs because of the appearance of an intermetallic compound (Mg_2Sn) that perturbs the crystallization of the remnant MgZn. The large affinity of the added element (Sn) to one of the components (Mg) appears to be the key to the improved GFA. Structural similarities were found between the obtained glass and amorphous $Mg_{70}Zn_{30}$.

Introduction

Structural studies on amorphous $Mg_{70}Zn_{30}$ indicated the presence of a strong short range order (SRO) [1], [2]. Besides, Rudin [2] concluded that a topological similarity exists between the crystalline and the amorphous state of the $Mg_{70}Zn_{30}$ alloy, and that the structural data of the crystallized system are consistent with the structure of the $Mg_{51}Zn_{20}$ compound [3]. This compound is a stable phase located near the eutectic of the phase diagram of MgZn [4], [5 a] and is usually designated as Mg_7Zn_3.

The $Mg_{100-x}Zn_x$ material was also studied by other authors [6–8]. The range in which they obtained amorphous samples is represented in Fig. 1 b, d, and e.

It is well known that the addition of a third element to binary alloys modifies the GFA [9]. A mechanism giving rise to an improvement of the GFA of MgZn by the addition of tin is studied in this work.

Experimental

The master alloy $Mg_{70}Zn_{30}$ was prepared by induction melting of the constituents (4 N) in alumina crucibles in fused silica under Ar pressure. The ternary alloys investigated were prepared by adding tin to the $Mg_{70}Zn_{30}$ alloy under conditions that prevent it from oxidation of the samples. The Scanning Electronic Microscope (Philips EM 500) and Energy Dispersive Analyzer of X-rays studies confirmed that the samples were homogeneous and had the desired composition.

Ternary alloys of the type $(Mg_{70}Zn_{30})_{100-x}Sn_x$ were obtained with $x = 2.5$, 5, 7.5, 10, 12.5 and 15 at.%.

The as-cast samples were rapidly quenched from 800 °C by the piston and anvil technique (PAT) [10], keeping the melt under Ar atmosphere.

The splat quenched foils, with thickness between 60 and 90 μ, as well as the as-cast alloys were

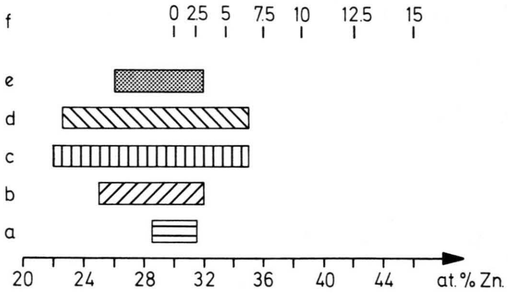

Fig. 1. The axis indicates the at.% Zn content of the binary MgZn: a) Approximate Mg_7Zn_3 region of the equilibrium phase diagram. b) Experimental glass forming range of MgZn (between 25 and 32 at.% Zn) obtained by Calka [6] with the Pond-Madin melt spinning method. c) Semiempirical glass forming range calculated using the Donald and Davies criterium. d) Experimental glass forming range of MgZn (between 22.5 and 35 at.% Zn) obtained by Matsuda [8] with a gun type splat cooling device. e) Boswell experiences [7] made with a gun type splat cooling device. (In this case only samples with 26 at.% Zn resulted amorphous). f) Composition of the RM of MgZn for the given tin content.

Reprint requests to Dr. H. Sirkin, Dpto. de Física, Facultad de Ingeniería – UBA, Paseo Colón, 850 – 1063 Buenos Aires, Argentinien.

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studied by X-ray diffraction (Debye chamber, Cu K_α radiation) and Mössbauer spectroscopy (SnO_3Ba source at room temperature).

Results

The Donald and Davies criterium [11] provides a semiempirical amorphization range between 22 and 35 at.% Zn, for the MgZn alloy [4], [5a] (see e.g. Fig. 1c) whereas it does not predict the existence of a glass forming composition range for MgSn [5b].

As will be discussed later, in all the studied alloys (both rapidly quenched and as-cast samples) tin was only found associated with Mg in a Mg_2Sn type configuration. This leads us to assume that enough Mg is consumed to form Mg_2Sn leaving a remnant matrix (RM) containing only Mg and Zn, which shows no chemical interaction with the Mg_2Sn. The composition of such a RM can be easily computed and the results are given in Table 1. Those compositions are compared with the expected glass forming regions in Fig. 1f.

As cast alloys: In the $Mg_{70}Zn_{30}$ and $(Mg_{70}Zn_{30})_{100-x}Sn_x$ alloys, the intermetallic compound Mg_7Zn_3 was identified by X-ray analysis. In both alloys the RM crosses the region of one phase Mg_7Zn_3 (Fig. 1a, f) when they are cooled from the liquid state [4], [5a]. Such a phase is easily formed, as can be corroborated by the results obtained with the rapidly quenched samples, and it can be retained at room temperature because its transformation kinetics is sluggish [4]. In the alloy with $x = 2.5$ the Mg_2Sn phase was also identified.

In all our alloys with $x \geqq 5$ the decomposition $Mg + Mg_2Zn_3 + Mg_2Sn$ has been identified by X-ray analysis, but not the Mg_7Zn_3 compound.

Table 1. Concentrations x and u according to the transforformation $(Mg_{70}Zn_{30})_{100-x}Sn_x \rightarrow A\ Mg_2Sn + B\ (Mg_{100-u}Zn_u)$, where all the tin is associated to Mg, leaving a binary remnant matrix of MgZn.

x (at.%)	u (at.%)	$(100-u)$ (at.%)
2.5	31.62	68.38
5	33.53	66.47
7.5	35.9	64.1
10	38.6	61.4
12.5	42.08	57.92
15	46.36	53.64

The Mössbauer spectra for all the as-cast samples containing tin showed a single peak with an Isomer Shift (IS) around 1.85 mm/sec, which corresponds to crystalline Mg_2Sn, as shown in Figure 2.

Both X-ray and Mössbauer analyses indicate that tin is only bound to Mg to form Mg_2Sn. Supporting this, studies on liquid MgSn by Steeb and coworkers [12], [13] indicated that atomic clusters similar to the solid compound Mg_2Sn exist in the liquid state.

Rapidly Quenched Alloys: The PAT used in this work does not provide a high enough cooling rate to obtain completely amorphous $Mg_{70}Zn_{30}$. This fact proved advantageous to demonstrate that the GFA of MgZn is improved by the presence of Mg_2Sn. This is shown by the fact that with the addition of tin, samples with an important degree of disorder were obtained, even though the composition of the RM was shifted towards a more unfavorable region, according Boswell [7] rich in Zn.

The X-ray data showed that the $Mg_{70}Zn_{30}$ alloy, prepared with the PAT, was partially amorphous with a diffuse ring with q between 2.55 and 2.75 Å^{-1} superposed to a broadened line ($q = 2.59\ \text{Å}^{-1}$) and a few weak lines corresponding to more distant planes of $Mg_{70}Zn_{30}$. This indicates that at an intermediate cooling rate the formation of crystalline Mg_7Zn_3 competes with glass formation.

A similar observation is made in the $x = 2.5$ at.% Sn alloy, for which the RM lies within the composition range of the phase Mg_7Zn_3 (Fig. 1a, f). Contrarily with the as-cast sample, no phase containing tin was identified.

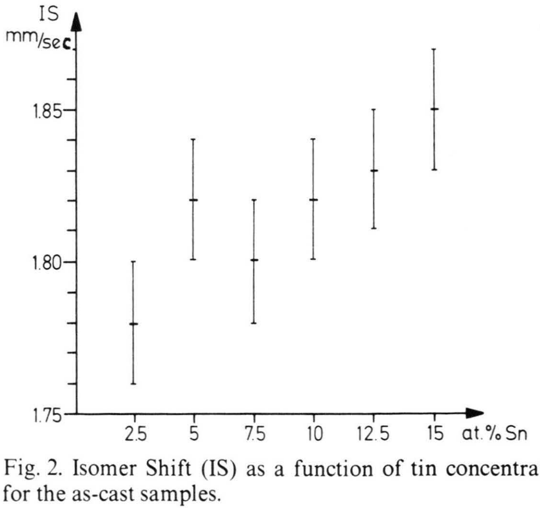

Fig. 2. Isomer Shift (IS) as a function of tin concentration for the as-cast samples.

The Mössbauer absorption spectra of this sample presented a 20% increase of the IS (2.10 mm/sec), as compared to the as-cast sample. It also presents a line broadening. This can be attributed to the presence of Mg_2Sn in a non crystalline configuration (probably clusters retained from the liquid state). Under this assumption we can infer the existence of a RM of similar composition to that of the as-cast sample.

The X-ray data for the sample with $x = 5$ at.% Sn showed a very intense diffuse ring with q between 2.43 and 2.67 $Å^{-1}$ and another one poorly defined in the region of the prepeak previously reported [1], [2], [6]. The principal line of the Mg_7Zn_3 was barely visible and appeared superposed with the diffuse ring. Two extremely weak lines corresponding to the most distant planes were also seen. Only the most intense line of Mg_2Sn (compared with the as-cast sample) still persists.

The Mössbauer spectra of this sample (Fig. 3a) presented a single line with an IS of 2.11 mm/sec also shifted with respect to the as-cast sample.

The X-ray data for the sample with $x = 7.5$ at.% Sn presented a large number of lines corresponding to Mg_2Sn and a weak broad line located about the position of the most intense line of Mg_7Zn_3. The broadening of this line indicates the loss of long range order (LRO). The disappearance of all lines of phases containing Zn, as compared to the as-cast samples, also supports the assumption of the presence of a disordered RM.

The Mössbauer spectra of this sample (Fig. 3b) were fitted by two single peaks, one with IS = 1.85 ± 0.02 mm/sec and another one with IS = 2.27 ± 0.03 mm/sec as shown in the figure.

The Mössbauer spectra of the alloy with $x \geqq$ 10 at.% Sn (see e.g. Fig. 3c) present a single narrow peak corresponding to the crystalline Mg_2Sn, with a sligth tendency to increase with tin content. The IS of the rapidly quenched samples was always larger than the corresponding one of the as-cast samples. The values were

x (at.% Sn)	10	12.5	15
IS (mm/sec)	1.85	1.88	1.9

A summary of the Mössbauer data is shown in Figure 3. These results suggests that, in all cases, tin is associated with Mg in a similar configuration. For $x \geqq 10$ this configuration is attributed to crystalline

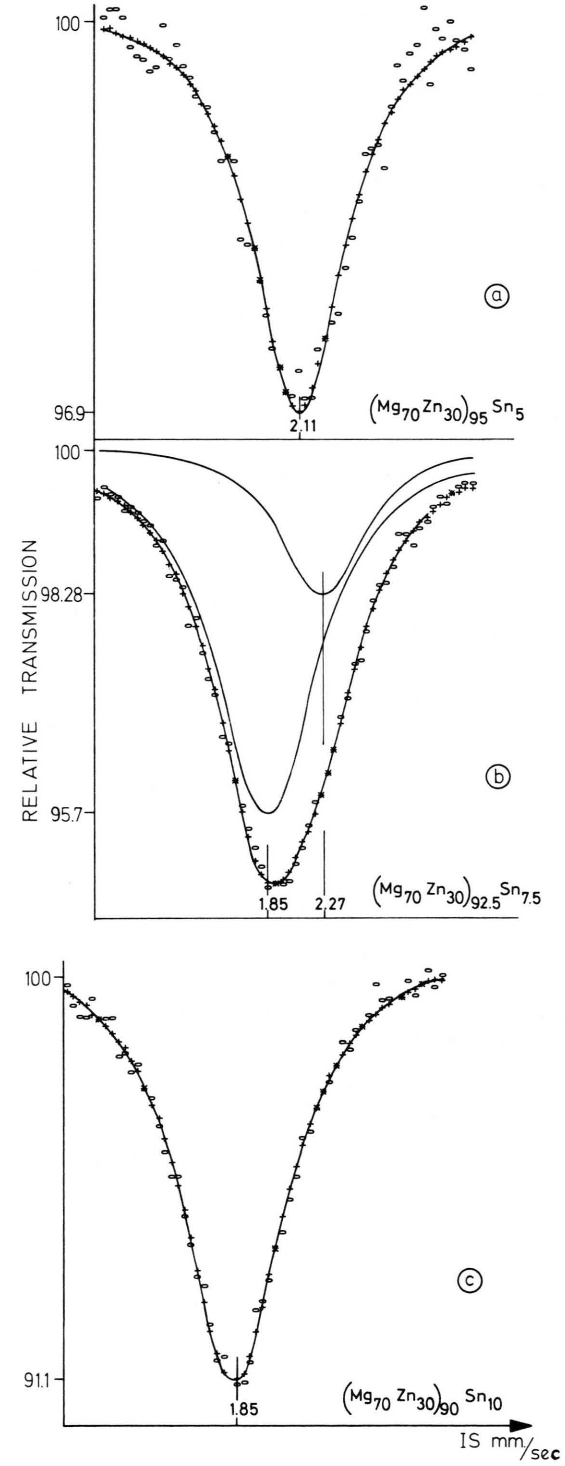

Fig. 3. Mössbauer spectra of the rapidly quenched samples of $(Mg_{70}Zn_{30})_{100-x}Sn_x$: a) $x = 5$ at.% Sn, b) $x = 7.5$ at.% Sn, c) $x = 10$ at.% Sn; ○ experimental data, +: fitted points.

Mg_2Sn, characterized by a covalent type of chemical bonding together with a strong metallic component that yields an effective number of s electrons $n_s = 1$ when calculated according to Flinn [14]. For $x \leqq 5$, the increased IS value can be explained by the existence of small Mg_2Sn associations that are distorted with respect to the crystalline phase due to the influence of the disordered RM. The IS measured are characteristic of metallic environments with $n_s = 1.11$.

Conclusions

The addition of tin to the $Mg_{70}Zn_{30}$ alloy gives rise to the appearance of Mg_2Sn clusters that modifies the GFA of the RM in two ways:

a) Introducing a higher disorder for a definite composition of the RM in comparison with that corresponding to the MgZn binary alloy of the same composition. This explains why the 5 at.% Sn alloy has a larger glass forming tendency than the $Mg_{70}Zn_{30}$, prepared with the PAT, even though it has a more unfavorable composition as shown by Boswell (7). This improved GFA can be attributed to the presence of large amounts of small configurations, chemically inert, of Mg_2Sn (15% of the atoms are in this configuration). Such clusters or microcrystals hinder the crystal growth, thus favoring amorphization.

b) Shifting the composition of the RM towards a region richer in Zn with respect to the original binary alloy. As for the case treated in this work such a shift is unfavorable for glass formation [7]; this mechanism competes with the one described in a. This explains why for richer tin alloys the GFA decreases again.

It is also important to notice that even though the RM has its composition shifted with respect to that of the intermediate phase Mg_7Zn_3, the glass obtained has a similar diffraction pattern as that obtained for the tin free alloy. This indicates that the topological SRO of the glass has not changed due to the shifted composition.

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