Spark Plasma Sintering of Mg-Based Amorphous Ball-Milled Powders

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In the present study, we report the formation of the Mg-based bulk metallic glass (BMG) samples by spark plasma sintering of the amorphous powders prepared by ball-milling. The sintering was performed in the supercooled liquid region \((T_T - T_g)\) and fully glassy Mg-based samples were successfully sintered at 398 K. The deformation on the surface associated with Vickers indentation hardness tests of the compacts reveals the presence of the semi-circular shear-bands around the indents and also reveals inhomogeneous nature of plastic deformation.

Keywords: bulk amorphous alloy, magnesium base alloy, ball-milling, amorphization, spark plasma sintering (SPS)

1. Introduction

In recent years, much effort has been devoted to prepare a number of Mg-based alloys with a wide supercooled liquid region \((\Delta T_g)\) exceeding 20 K.¹⁻⁶ These new alloys are expected to expand the application fields of bulk metallic glasses (BMGs) due to their high specific strength–strength to weight ratio, and relatively low cost. Mg-based BMGs are generally prepared by high-pressure die-casting or mould casting method. The fabrication of bulk amorphous alloy by consolidation of amorphous powders provides an advantage since it enables the production of complex shapes without limitations in sample shape and dimension. Many studies have been performed on the consolidation of amorphous powders by various techniques such as hot pressing,⁷,⁸ equal channel angular extrusion,⁹ warm extrusion,¹⁰,¹¹ and rolling.¹² Spark plasma sintering (SPS) technique has been recently employed, because of its promising potential to obtain a fast densification with nearly no crystallization during the consolidation of amorphous powders.¹³,¹⁴

In the present study, Mg-based BMGs were produced by spark plasma sintering of the amorphous powders, prepared by ball-milling process. The structure and thermal stability of the as-milled and bulk samples were analyzed with X-ray diffractometry and differential scanning calorimetry.

2. Experimental Procedure

2.1 Specimen preparation

Elemental metals of Mg (99.9 mass%), Cu (99.99 mass%), Y (99.9 mass%) and Gd (99.9 mass%) were weighed to yield the desired composition \(\text{Mg}_{55}\text{Cu}_{30}\text{Y}_{15}\) and \(\text{Mg}_{55}\text{Cu}_{30}\text{Gd}_{15}\), respectively. The master alloy has been prepared by induction melting under argon atmosphere. Amorphization reaction by ball-milling depends directly on the local conditions during the milling.¹⁵ Twenty grams of the alloy powders mechanically crushed and sieved (with 250 µm in diameter), and two hundreds grams of hardened steel balls (with 10 mm in diameter) were filled in milling jar. Milling was performed under an inert atmosphere (argon) in a Retsch planetary ball mill (PM 100). To prevent in-situ nano-crystallization due to the ball-to-ball impacting and keep milling temperature below the crystallization temperature,¹⁶ a low rotational speed ranged from 250 to 300 rpm was used. Milling was interrupted after every 2 hours for 30 minutes, to cool down the jar and a small amount of the powder was extracted to examine the progress of the amorphization reaction. The obtained powders were pre-compacted, and then sintered. The sintering of the powders was carried out in a vacuum using a SPS apparatus (Model SPS 3-20MK-IV, Sumitomo Coal Mining Co. Ltd., Japan). The sintering was performed in the supercooled liquid region \((\Delta T_g)\). The details of the sintering procedures,¹⁷ temperature measurement and control, and loading pressure control in the SPS process have been given elsewhere.¹⁸,¹⁹

2.2 Structural analysis

The structure of both the initial crystalline and amorphous powder specimens was analyzed by X-ray diffraction (Rigaku Denki RINT1100, Cu Kα). Thermal analysis was performed using differential scanning calorimetry (TA Instruments DSC-Q100) at which the samples were heated from room temperature to 650 K at constant heating rate of 20 K/min. The hardness was measured at room temperature by a Vickers micro-hardness tester with a 0.98 N (100 gf) load.

3. Results and Discussion

3.1 Characterization of ball-milled powder samples

Figure 1 shows the X-ray diffraction patterns of the \(\text{Mg}_{55}\text{Cu}_{30}\text{Y}_{15}\) and \(\text{Mg}_{55}\text{Cu}_{30}\text{Gd}_{15}\) alloys after different milling time. At the early stage of milling, some sharp diffraction peaks were observed and identified as belonging to CuMg₂, YCu₂ and MgY in \(\text{Mg}_{55}\text{Cu}_{30}\text{Y}_{15}\) powder samples. The peak intensities decreased with increasing milling time. On further ball milling up to 10 h, a broad diffraction peak at \(2θ = 30°-45°\) is the main feature of these XRD patterns, indicating that the milled powders are predominantly amorphous. Homogeneously amorphous powders were successfully prepared after 30 h and 18 h of milling, for \(\text{Mg}_{55}\text{Cu}_{30}\text{Y}_{15}\) and \(\text{Mg}_{55}\text{Cu}_{30}\text{Gd}_{15}\) samples, respectively.

Figure 2 shows the DSC curves of mechanically milled \(\text{Mg}_{55}\text{Cu}_{30}\text{Y}_{15}\) and \(\text{Mg}_{55}\text{Cu}_{30}\text{Gd}_{15}\) powder samples after different milling time. It can be seen that the amorphous powders exhibited change in heat capacity due to the glass...
transition; followed by a sharp exothermic peak, indicating a successive transformation from a supercooled liquid state to crystalline phases. The glass transition temperature ($T_g$) and the crystallization temperature ($T_x$) are 425 and 458 K, respectively, in the case of Mg$_{55}$Cu$_{30}$Y$_{15}$ and 428 and 452 K, respectively in the case of Mg$_{55}$Cu$_{30}$Gd$_{15}$ ($T_g$ and $T_x$ are defined as the onset temperatures of the respective reaction in the DSC scan). The corresponding width of the supercooled liquid region $\Delta T_x$ is 33 K and 24 K, respectively.

### 3.2 Characterization of spark plasma sintered specimens

Figure 3 shows the XRD patterns taken from the Mg$_{55}$Cu$_{30}$Y$_{15}$ samples sintered at $T_s = 373$, 398, 423, and 448 K, respectively. The XRD patterns show a typical broad halo peak in the $2\theta$ range of 30–45°, a characteristic of the amorphous structure. The amorphous structure was retained during SPS sintering process at 373 K while after sintering at 398 K, some Bragg peaks were identified as belonging to CuMg$_2$, YCu$_2$, and MgY phases. Figures 4(a) and 4(b) correspond to the Mg$_{55}$Cu$_{30}$Y$_{15}$ compacts sintered at 373 and 398 K, respectively. A number of voids (pores) are seen in Fig. 4(a),
indicating that the sintering at 373 K gives lower density compared to sintering performed at 398 K (Fig. 4(b)). In the latter case only a few voids can be identified, suggesting that the plastic deformation of the amorphous powders occurred during SPS process, leading to almost complete densification.

Figure 5 shows Vickers micro-hardness and density of the compacts as a function of the sintering temperature for both Mg$_{55}$Cu$_{30}$Y$_{15}$ and Mg$_{55}$Cu$_{30}$Gd$_{15}$ alloys. The densities of the Mg-based compacts consolidated at 423 and 448 K of 3.6 and 4.4 Mg/m$^3$, respectively, are similar to that of the as-cast Mg$_{55}$Cu$_{30}$Y$_{15}$ and Mg$_{55}$Cu$_{30}$Gd$_{15}$ BMG alloys.$^2$ Vickers hardness of the consolidated samples (Fig. 5) increases monotonously from 385 (sample sintered at 373 K) to 895 MPa (sample sintered at 448 K) and from 325 (373 K) to 710 MPa (448 K) for Mg$_{55}$Cu$_{30}$Y$_{15}$ and Mg$_{55}$Cu$_{30}$Gd$_{15}$ samples, respectively. For comparison Vickers hardness test performed on compacts of Mg$_{55}$Cu$_{30}$Y$_{15}$ sample sintered from initially crystalline powders at 423 K showed much lower value $H_v = 106$ MPa.$^{20}$ Thus, initially amorphous powder samples show better sintering behaviour and higher hardness.

The inset in Fig. 5 shows the optical micrograph of the Vickers test indentation obtained for the Mg$_{55}$Cu$_{30}$Y$_{15}$ amorphous alloy sintered at 398 K. Shear bands developed along the edges have a semi-circular shape. It was reported that this pile-up was seen as a number of discrete steps in the BMGs due to the inhomogeneous nature of plastic deformation.$^{21}$ No noticeable cracks can be observed in the consolidated sample, indicating a rather high fracture toughness of the material.$^8$

## 4. Conclusions

In this paper we studied the amorphization behaviour of Mg$_{55}$Cu$_{30}$(Y, Gd)$_{15}$ alloy powders synthesized by mechanical milling technique. The initial crystalline powders of the Mg$_{55}$Cu$_{30}$Gd$_{15}$ and Mg$_{55}$Cu$_{30}$Y$_{15}$ alloys became amorphous after 18 h and 30 h of milling, respectively. No significant difference was observed between these two compositions. The thermal stability of amorphous powder was investigated by differential scanning calorimeter. The $T_g$, $T_x$ and $\Delta T_x$ values of the Mg$_{55}$Cu$_{30}$Y$_{15}$ alloy are about 425 K, 458 K, and 33 K, respectively; while in the case of Mg$_{55}$Cu$_{30}$Gd$_{15}$ the corresponding values are 428 K, 452 K and 24 K, respectively. Dense Mg$_{55}$Cu$_{30}$Gd$_{15}$ and Mg$_{55}$Cu$_{30}$Y$_{15}$ bulk metallic glassy samples were successfully prepared by spark plasma sintering. It was found that the amorphous phase retains in Mg$_{55}$Cu$_{30}$Y$_{15}$ powders during consolidation at the applied temperature ranging from 373 to 448 K. The deformation upon Vickers indentation hardness tests on the surface of the Mg-based alloy compact reveals the presence of the semi-circular shear-bands around the indents. It reveals inhomogeneous nature of plastic deformation.

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