Mg–Cu–Gd layered composite plate synthesized via the spray forming process

K.F. Chang\textsuperscript{a}, M.-L.T. Guo\textsuperscript{a}, R.H. Kong\textsuperscript{a}, Chi Y.A. Tsao\textsuperscript{a,∗}, J.C. Huang\textsuperscript{b}, J.S.C. Jang\textsuperscript{c}

\textsuperscript{a} Department of Materials Science and Engineering, and Frontier Material and MicroNano Science and Technology Center, National Cheng Kung University, 1 Da-Shieh Road, 70101 Tainan, Taiwan, ROC
\textsuperscript{b} Institute of Materials Science and Engineering, National Sun Yat-Sen University, 70 Lien-Hai Road, 804 Kaohsiung, Taiwan, ROC
\textsuperscript{c} Department of Materials Science and Engineering, I-Shou University, Section 1, Hsueh-Cheng Road, Ta-Hsu Hsiang, Kaohsiung County 840, Taiwan, ROC

Received 5 February 2007; received in revised form 12 September 2007; accepted 13 September 2007

Abstract

A layered composite plate of Mg–Cu–Gd was produced by spray forming with dimensions of 300 mm in diameter and 12 mm in maximum thickness, with a Gaussian distribution and a weight of 510 g. The deposit comprised of a nearly complete glassy structure at the bottom, glassy/crystalline structure in the middle (up to 6 mm from substrate), and a completely crystallized structure at the deposit top. The porosity of the spray-formed Mg–Cu–Gd layered composite plate varied from the near substrate interface to the near free surface. The chemical composition of the spray-formed Mg–Cu–Gd layered composite plate varied from near the substrate to near free surface, with increasing Cu + Gd concentration towards the substrate because segregation during melting. The glass forming ability of the spray-formed Mg–Cu–Gd layered composite plate was studied. The hardness of the spray-formed Mg–Cu–Gd layered composite plate varied due to variations in the local microstructures and phases, and porosity.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Spray forming; Bulk metallic glass; Glass forming ability; Mg–Cu–Gd alloy; Layered composite

1. Introduction

Mg–Cu–Y bulk metallic glass (BMG) ingots produced via mold casting process were first synthesized by Inoue et al. [1]. They demonstrated that Mg-based BMG alloys, e.g. Mg–Cu–RE, Mg–Ni–RE, exhibit high specific strength and excellent corrosion resistance. Therefore, many studies have been performed on these alloys over the years. Because of the high glass forming ability (GFA) of Mg–Cu–Y ingots, it is possible to produce them at critical cooling rates as less as 100 K/s. Substituting Y element with Gd element has also been found to offer a beneficial effect on GFA, and studies of the Mg–Cu–Gd alloy system have indicated that Mg\textsubscript{65}Cu\textsubscript{25}Gd\textsubscript{10} (numbers in subscripts indicate at.% throughout the text) ingots have the highest GFA in this type of alloy system [2–4]. Mg\textsubscript{65}Cu\textsubscript{25}Gd\textsubscript{10} ingots have been synthesized successfully up to a maximum diameter of 8 mm by copper mold casting.

The spray forming process has name characteristics of a rapid solidification process, and has been successfully used in making Al amorphous/crystalline hybrid composites [5–6]. In this study, a Mg\textsubscript{65}Cu\textsubscript{25}Gd\textsubscript{10} plate was produced by spray forming, during which high pressure nitrogen gas was used to atomize the melt into droplets that were collected into a deposit on a rotational copper substrate. Subsequently, the latent and specific heat contained in the deposit was dissipated by conduction the substrate, and convection to the atomizing gas in an attempt to attain further rapid solidification [5–8].

The objective of this study was to study the feasibility of spray forming an amorphous Mg plate, and the devitrification behavior of the spray-formed Mg–Cu–Gd metallic glassy plate. The devitrification led to a layered composite structure consisting of amorphous and crystalline phases. Additionally, the macro-segregation because of relatively dense solutes (like Cu,
and Gd) caused the variations in the local GFA in the layered composite.

### 2. Experimental methods

Cu–Gd master alloy ingots were prepared by arc melting of Cu (99.99%) and Gd (99.9%) in a water-cooled copper crucible under a Ti-gettering argon atmosphere. These ingots were then melted with pure Mg chunks (total charge is 1.1 kg) in an induction furnace under a purified argon atmosphere. During spray forming, the nozzle bore size is 6 mm in diameter; gas flow rate is 17.3 m³/min and metal flow rate is 7.3 kg/min; pouring temperature is 700°C. A Cu substrate of 5 mm thick was used producing a Mg–Cu–Gd deposit that was a Gaussian-shaped plate of 300 mm in diameter, 12 mm in maximum thickness and 510 g in mass. The cross-sectional regions of the deposit from bottom to top were characterized by X-ray diffractometry (XRD) using Cu Kα radiation. The thermal behavior of the material including the glass transition temperature ($T_g$), supercooled region, crystallization temperature ($T_x$) and liquidus temperature ($T_l$) were analyzed by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. Chemical compositions and the porosity in various regions of the deposit were analyzed by electron probe microanalysis (EPMA) equipped with wave-dispersive spectrometry (WDS) and scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectrometry (EDS). The hardness of the deposit in various regions was investigated by a micro Vickers ($\mu$HV) hardness tester at a load of 300 g and a dwell time of 10 s. Ten points were measured for one location in the deposit. The porosity of the spray-formed layered composite is measure by image percentage calculation of Optimas© software.

### 3. Results and discussion

The melt of Mg–Cu–Gd was spray-formed into a Gaussian-shaped plate of 300 mm in diameter, 12 mm in maximum thickness and 510 g in mass, as shown in Fig. 1.

#### 3.1. XRD and DSC

Fig. 2 shows XRD patterns obtained from the cross-section of the spray-formed Mg$_{65}$Cu$_{25}$Gd$_{10}$ layered composite. In the bottom region, 1 mm distance from the substrate, a typical single broad peak for amorphous structure is shown. In the middle region, 6 mm distance from the substrate, a similar amorphous broad peak is shown together with several weak characteristic peaks, indicating some crystallization of the amorphous matrix. In the top region, 11 mm distance from the substrate, more characteristic peaks are shown. Therefore, the inherent structure of the deposit is amorphous at the bottom, partially crystallized in the middle, and completely crystallized at the top, which becomes a layered amorphous/crystalline composite. The devit...
Thermal properties and GFA parameters (Table 1) at various locations of as-spray-formed Mg100−x−yCu,Gd layered composite

<table>
<thead>
<tr>
<th>Position</th>
<th>$T_g$ (K)</th>
<th>$T_x$ (K)</th>
<th>$T_l$ (K)</th>
<th>$T_{ig}$</th>
<th>$\Delta T = T_x - T_g$</th>
<th>$\gamma = T_x/(T_g + T_l)$</th>
<th>$\text{Mg}_{100-x-y}\text{Cu}_x\text{Gd}_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom</td>
<td>412.1</td>
<td>459.8</td>
<td>699</td>
<td>748.4</td>
<td>47.7</td>
<td>0.551</td>
<td>0.396</td>
</tr>
<tr>
<td>Middle</td>
<td>447.5</td>
<td>486.1</td>
<td>691.6</td>
<td>796.3</td>
<td>38.6</td>
<td>0.562</td>
<td>0.391</td>
</tr>
<tr>
<td>Top</td>
<td>N/A</td>
<td>N/A</td>
<td>708.1</td>
<td>728.4</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

3.2. Microstructural characterization

Fig. 4 shows micrographs of a cross-sectional area from the as-spray-formed deposit, which clearly shows that the microstructure varies from the top to the bottom of the deposit, forming a layered “composite”. There are mainly two reasons causing this layered structure. The solidification and cooling rates are highest at the bottom due to the cold substrate used. The top region in this thin deposit has lower solidification and cooling rates compared with the middle region. Therefore, the amorphous phase is formed more easily in the bottom region, while the top region contains more crystalline phase in addition to the amorphous phase, to form the layered structure. In addition, it was found that the compositions of the deposit varied from the bottom to the top. Table 2 shows the chemical composition of various layers in the vertical direction of the deposit, which is now therefore designated as Mg100−x−yCu,Gd (x ~ y) accordingly. The variations in the compositions in the deposit were mainly due to gravity effects during melting. Since there were large differences in density among Mg (1.73 g/cm³), Cu (8.9 g/cm³), and Gd (8.4 g/cm³), the Mg–Cu–Gd melt underwent gravity-induced element segregation during melting prior to spray forming. Heavier element, such as Cu and Gd segregated towards the bottom, and Mg towards the top of the melt. As the melt was bottom-poured to be spray-formed, the melt with more Cu and Gd was spray-formed first to form the bottom part of the deposit, containing more Cu and Gd. For a conventional cast amorphous ingot, the melt weight used is very small, about 100 g, so that the segregation effect is usually insignificant. For the spray forming in this study, however, the melt weight of ~1000 g was much larger, and the segregation was significant. Consequently, the compositions of the spray-formed deposit varied with distance from the substrate, which can again be referred to as a layered composite. It is important to note that the GFA also changes appreciably with composition. Therefore, the GFA of the layered structure must vary from top to bottom, as indicated previously.
Fig. 4 shows that the bottom region, due to its best glass-forming ability, yields an amorphous structure with some white spots of pure Gd. Subsequently, at the region 3 mm from the substrate, the relatively low GFA and low cooling rate might lead to partial devitrification of any glassy phase. The gray spots correspond to crystallized areas. In the region 5–6 mm from the substrate, the sizes of the gray spots decrease but they agglomerate to form large crystallized areas, which have distinct boundaries from the adjacent featureless amorphous regions. In the region 7–10 mm from the substrate, the whole deposit was completely crystallized. However, in the region 11 mm and above from the substrate, close to the free surface, thermal dissipating rate gradually increased due to strong gas convection over the top surface of the deposit, which led to an increasing cooling rate. Therefore, an amorphous region might coexist with a crystalline region near the free surface (11–12 mm). However, the volume fraction of the amorphous phase was too small to be measured in the DSC traces shown in Fig. 3.

Fig. 5 shows a high-resolution transmission electron microscopy (TEM) image taken from material at 1 mm distance from the substrate. The microstructures are mainly amorphous phase with some quenched-in crystalline, about 5 nm in diameter, within the amorphous matrix.

### 3.3. Hardness testing

Table 4 shows the hardnesses at the positions of 1, 6 and 11 mm from the substrate are about 240, 260 and 160 μHV, respectively. Hardness might be influenced by both the inherent porosity and microstructures, but we assume porosity effect is the major one for as-deposited sample in this study. The porosity of the spray-formed layered composite varied with locations, as shown in Table 3. The porosity level is the lowest in the middle region, about 3.5%, and the largest at top region, about 8.5%. The level of the porosity is directly related to the depositing temperature. When atomized droplets are still in the liquid or semisolid

<table>
<thead>
<tr>
<th>Position (mm)</th>
<th>Hardness (μHV)</th>
<th>Porosity (%)</th>
<th>Microstructure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>240</td>
<td>3.9</td>
<td>Amorphous</td>
</tr>
<tr>
<td>6</td>
<td>260</td>
<td>3.5</td>
<td>Amorphous + crystalline</td>
</tr>
<tr>
<td>11</td>
<td>160</td>
<td>8.5</td>
<td>Crystalline</td>
</tr>
</tbody>
</table>
states, they can spread over to fill up the interstices between them upon deposition. The porosity formed from the crevices between them is thus reduced significantly. However, shrinkage porosity may be formed due to the shrinkage of excessive liquid phase during solidification. For potentially amorphous materials, when the solid phase is reheated above $T_g$ during spray deposition, it becomes supercooled liquid with very high viscosity. Therefore, the phenomena generated in the top semisolid layer of the deposit during spray forming become quite complex. As the cooling rate of the bottom layer was the fastest, the largest fraction of crevice porosity was generated. The cooling rate in the middle layer was the slowest, so the amount of crevice porosity generated was the lowest (Table 4).

The average hardness of the layered deposit is the highest in the middle region, 260 $\mu$HV, and the lowest in the top region, 160 $\mu$HV. The average hardness of the bottom region is about 240 $\mu$HV, as shown in Table 4. The low hardness at the top region is attributed to the larger amount of porosity. There are shear bands around the indentation for the bottom, which further verifies that the matrix is amorphous phase, as the deformation of amorphous phase is by propagation of shear bands. There are also cracks around the indentation. Around the indentation shown for the middle region, there are cracks extending from the sharp edges of the indentation, showing the brittle behavior of the material. During spray forming, the depositing droplets provided the heat input to the top of the deposit constantly, which caused further in situ devitrification of the partially amorphous phase in the deposit. The in situ devitrified structure is shown in Fig. 5, which has numerous quenched-in nuclei within the amorphous matrix. These particles serve as obstacles to shear band propagation in the as-spray-formed layered composite, which, therefore, gives the composite a higher strength but a lower ductility.

4. Conclusions

(i) A $\text{Mg}_{100-x-y}\text{Cu}_x\text{Gd}_y$ layered composite plate was spray-formed, consisting of amorphous structure with numerous quenched-in nuclei in the bottom region (0–2 mm from the substrate), partially crystallized structure in the middle region (3–6 mm), and completely crystallized structure in the top region (7–12 mm).

(ii) Gravity-induced solute segregation caused the composition of the melt to vary during spray forming, which generated a layered composite.

(iii) The glass forming ability of the spray-formed $\text{Mg}_{100-x-y}\text{Cu}_x\text{Gd}_y$ ($x \sim y$) layered composite decreased with decreasing $x$, $y$ values, and accounted for the variations of the structures from the top to the bottom of the layered composite.

(iv) The variation of the solidification and cooling rate during spray forming also caused a layered structure. The amorphous phase was easier to form at the bottom region where the cooling rate was the highest.

(v) The average hardnesses at the positions of 1, 6 and 11 mm from the substrate were 240, 260 and 160 $\mu$HV, respectively, which were strongly influenced by the inherent porosity and microstructures of the deposit.

(vi) Shear bands were formed around the indentation at the bottom region, which further suggested the matrix being substantially amorphous.

(vii) Quenched-in nuclei were formed within the amorphous matrix, serving as obstacles to shear band propagation in the layered composite, which gave the composite a higher strength but a lower ductility.

Acknowledgments

The authors would like to thank the financial support from the National Science Council, the technical supports from the Frontier Material and Micro/Nano Science and Technology Center at National Cheng Kung University, alloy preparation and DSC analysis from I-Shou University, and the JEOL 3010 TEM analysis at National Sun-Yat-Sen University.

References