Journal of Metastable and Nanocrystalline Materials Vols. 24-25 (2005) pp 687-690
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doi:10.4028/www.scientific.net/JMNM.24-25.687
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Ca-Mg-Zn bulk metallic glasses with strong glass-forming ability synthesized under air atmosphere

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Keywords: Ca-Mg-Zn, bulk metallic glass, air atmosphere, glass forming ability, new parameter σ

Abstract

The effect of alloy composition on the glass forming ability (GFA) of the Ca-rich Ca-Mg-Zn alloys has been investigated. In a wide composition range of 10 % - 30 % Zn and 5 % - 25 % Mg bulk metallic glass (BMG) samples with the diameter larger than 1 mm are fabricated by conventional copper mold casting method and injection casting method in air atmosphere. Among the alloys investigated, the $Ca_{65}Mg_{15}Zn_{20}$ alloy exhibits the highest GFA enabling to form BMG sample with the diameter of at least 15 mm. The σ parameter has better correlation with D_{max} in the Ca-Mg-Zn alloys than previously suggested parameters such as ΔT_x, T_{rg}, K and γ parameters.

1. Introduction

Most of the bulk metallic glasses (BMGs) reported so far are based on the multi-component system to improve the atomic packing density in the liquid state. However, recently, simple ternary alloys such as Mg-Cu-(Y, Gd), Cu-(Zr, Hf)-Ti, Cu-Zr-Al, Ni-Nb-(Sn, Ti, Ta) and Ca-Mg-(Cu, Ni, Ag, Zn) have been reported to have high glass forming ability (GFA) enough to form BMGs [1-5]. These simple ternary alloys can be more suitable for commercial use, and provide a good opportunity for the study of glass-forming mechanisms. Although most of the BMGs necessitate the fabrication under controlled inert atmosphere in an evacuated closed chamber, some ternary BMGs such as in Mg-Cu-Gd system can be fabricated by conventional Cu-mold casting method in air atmosphere [1]. Such a rapid and simple production technique will facilitate the wide-spread of BMGs in industrial products.

The Ca-rich Ca-Mg-Zn alloy system is expected to show high GFA due to: (1) large atomic size difference between the alloy elements (Ca: 1.97 Å; Mg: 1.60 Å; Zn: 1.38 Å); (2) large negative mixing enthalpy between the alloy elements (Ca-Mg: -20 J/mol; Ca-Zn: -72 J/mol; Mg-Zn: -13 J/mol); and (3) existence of a deep ternary eutectic reaction in the Ca-rich composition range [6]. It has been reported that BMG samples with the diameter larger than 6 mm in a wide composition of Ca-rich Ca-Mg-Zn alloys are fabricated by conventional copper mold casting method in air atmosphere [7]. The Ca-Mg-Zn alloy exhibits a significantly improved GFA when compared with Ca-Mg-M (M: Cu, Ni, Ag) alloys [4].

Prediction of GFA is important in developing new BMG forming systems. Although a great amount of research has been performed to find alloys with high GFA, only empirical rules have been suggested so far for the prediction of GFA. In the mean time, several parameters proposed for the estimation of GFA: ΔT_x (= T_x - T_g), T_{rg} (=T_g/T_l), K (=$[T_x - T_g]/[T_l - T_x]$) [8] and γ (= $[T_x]/[T_l+T_g]$) [9] where T_g, T_x and T_l are the glass transition temperature, crystallization onset temperature, and offset temperature of melting, respectively. In particular, for ternary alloy systems, we, recently, proposed a new parameter σ, defined as $\Delta T^* \times P'$ ($\Delta T^* = [T_m^{mix} - T_l]/[T_m^{mix}]$ [10], ,where $T_m^{mix} = \sum_i^n x_i \cdot T_m^i$, with x_i and T_m^i for the mole fraction and melting point, respectively, of the i-th component of an n-component alloy system and P'=

P/(C_B+C_C) [11], where C_i is the concentration of solute *i*, and P is shown in Eq.(1)), based on the consideration of atomic size mismatch criterion and deep eutectic alloy composition for GFA [12].

In this study, the effect of alloy composition on the GFA of the Ca-rich Ca-Mg-Zn alloys was investigated in a wide composition range of 5 - 35 at % Zn and 5 - 25 at% Mg. Firstly, cone-shaped ingots and rod samples were prepared by conventional Cu-mold casting method and injection casting method in air atmosphere to evaluate the GFA. Secondly, correlation between σ parameter and maximum diameter for amorphous phase formation (D_{max}) was investigated and was compared with those between ΔT_x, T_{rg}, K and γ parameters and D_{max}.

2. Experimental

High purity elements Ca (99.9%), Mg (99.9%) and Zn (99.9%) were alloyed in a graphite crucible in an Ar atmosphere using an induction furnace. After complete melting, the liquid alloy was poured into a copper mold in air atmosphere. The copper mold is cone-shaped with 45 mm in height, 15 mm in diameter at the top, and 6 mm in diameter at the bottom. From the ingots, injection cast samples with a diameter below 6 mm and rapidly solidified ribbon samples were fabricated for GFA evaluation and thermal analysis. Injection cast samples were prepared by re-melting the appropriate amount of the alloys in quartz tubes under a purified inert atmosphere followed by injecting through a nozzle into a Cu mold, having cylindrical cavities of varying diameters from 1 to 5 mm. Rapidly solidified ribbon samples were prepared by re-melting the appropriate amount of the alloys in quartz tubes followed by ejecting with an over-pressure of 50 KPa through a nozzle onto a Cu wheel rotating with a surface velocity of 40 m/s. The resulting ribbons have a thickness of about 45 μm and a width of about 2 mm.

For the structural and thermal analysis, thin slices were cut from the as-cast cone-shaped ingots and injection-cast rod. The surfaces of the thin slices were examined by X-ray diffraction (XRD, Rigaku CN2301), with a monochromatic Cu K_α radiation. The thermal analysis of the as-melt-spun ribbons was carried out by differential scanning calorimetry (DSC, Perkin Elmer DSC7), using a heating rate of 0.667 K/s.

3. Results and Discussion

3.1. Evaluation of GFA

Figure 1 shows composition ranges for BMG formation in Ca-rich Ca-Mg-Zn alloys investigated in the present study; ●, ●, ⊛, O and ◉ symbols represent the composition ranges for D_{max} of <1 mm, ≥1mm, ≥3mm, ≥7 and ≥10mm, respectively. The BMG formation shown in fig.1 was evaluated from the cone-shaped Cu-mold-cast ingots. However, the BMG formation for D_{max}<6mm was evaluated from the injection-cast ingots due to the size limit of cons-shaoed Cu-mold. The result in fig.1 showed that BMG samples with the diameter larger than 1 mm can be fabricated in a wide composition range of 10 - 30 at% Zn and 5 - 25 at% Mg by conventional copper mold casting in air atmosphere. Among the alloys investigated, the $Ca_{65}Mg_{15}Zn_{20}$ and $Ca_{60}Mg_{15}Zn_{25}$ alloy exhibited excellent GFA enabling to form BMG sample with the diameter larger than 10 mm. In particular, the $Ca_{65}Mg_{15}Zn_{20}$ alloy exhibits the highest GFA enabling to form BMG sample with the 15 mm diameter.

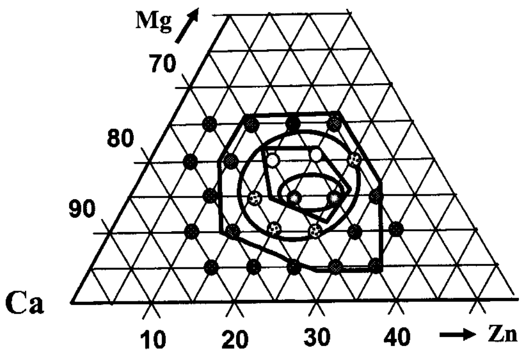

Fig 1. Map of composition ranges which can be form BMG samples in Ca-rich Ca-Mg-Zn alloys

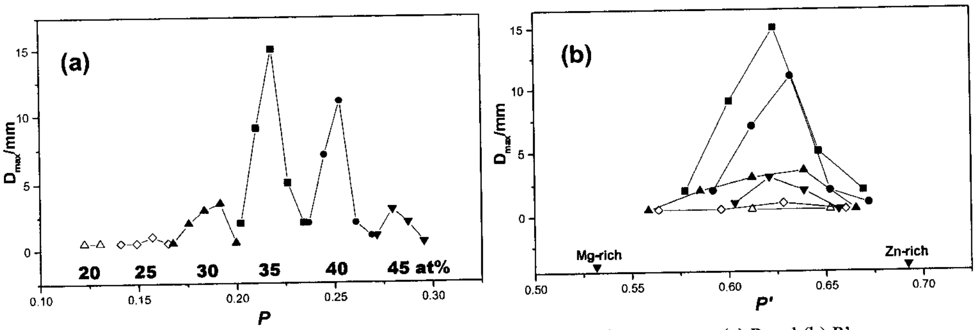

Fig. 2 A replot of D_{max} shown in Fig 1 as a function of the parameter (a) P and (b) P'.

3.2. Correlation between σ parameter with GFA

Considering that dense atomic packing in the liquid stabilizes the liquid phase and that atomic size differences play an important role in increasing packing density, there may be an optimum ratio between solute contents. Then the effect of atomic size difference can be represented as follows[11]:

$$P = C_B\left|\frac{(v_B - v_A)}{v_A}\right| + C_C\left|\frac{(v_C - v_A)}{v_A}\right| \quad \text{--- (1)}$$

where C_i and v_i are the concentration of solute i and atomic volume, respectively. Figure 2(a) shows the plot of D_{max} as a function of P in the Ca-Mg-Zn alloys investigated in the present study. Each symbol in the figure represents a family with the same total amount of solute. For example, alloys with ■ symbol have a total solute content of 35 at%. Interestingly, each family curve shows a similar trend of D_{max} with P: i.e. initial increase, reaching a maximum and then decreasing with further increasing P. The peak position varies depending on the total solute content. With increasing solute content, the peak appears at higher P values. Therefore, we have normalized P by dividing by total content of solute elements. Figure 2(b) shows the replot of D_{max} as a function of the normalized atomic mismatch P'[11]:

$$P' = P/(C_B + C_C) \quad \text{--- (2)}$$

Each family of the alloys showed D_{max} at P' of ~ 0.625, indicating that the optimum ratio between Mg and Zn contents is ~ 1.39 for D_{max} in each family of alloys.

Considering higher GFA for deep eutectic alloys, ΔT^* parameter has been suggested for evaluation of GFA. It was found that most of the glass forming alloys such as Fe- and Ni-based metallic glasses had values of $\Delta T^* \geq 0.2$ [10]. Figure 3 shows the plot of D_{max} as a function of ΔT^* in the Ca-Mg-Zn alloys investigated in the present study. The ΔT^* values were over 0.22. As shown in the figure, the statistical correlation factor (R^2) for the plot is as high as 0.806, suggesting that there is a reasonably good correlation between ΔT^* and D_{max}.

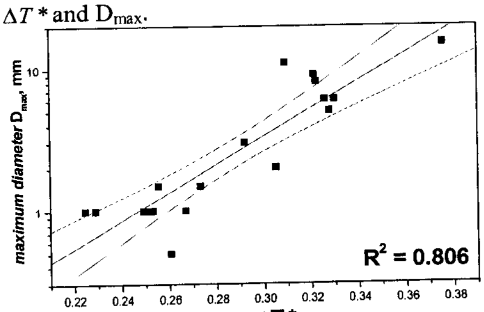

Fig. 3 A plot of Map of D_{max} as a function of ΔT^* in the Ca-Mg-Zn alloys investigated in the present study.

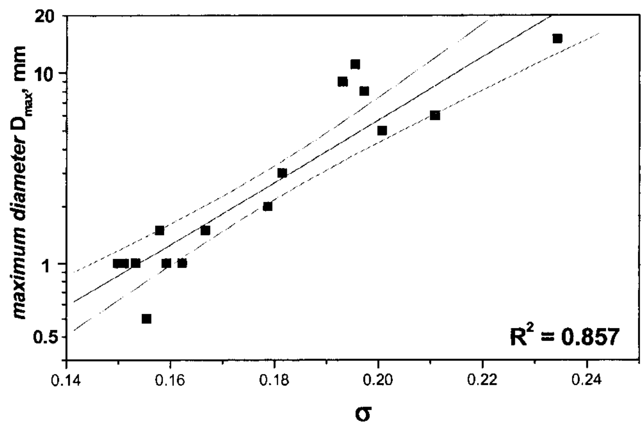

Fig. 4 DSC traces of rapidly solidified Ca-Mg-Zn alloy ribbons

Figure 4 shows a correlation between the σ parameter [12] and D_{max} in Ca-Mg-Zn alloys. The R^2 value for the plot is as high as 0.857, suggesting that there is a good correlation between D_{max} and σ parameter. The R^2 values for the plots between D_{max} and ΔT_x, T_{rg}, K and γ parameters were 0.358, 0.787, 0.607, and 0.774, respectively. Therefore the σ parameter exhibits a better correlation with GFA than the previously suggested parameters.

5. Summary

In a wide composition range of 10 - 30 at % Zn and 5 - 25 at % Mg BMG samples with the diameter larger than 1 mm are fabricated by conventional copper mold casting method under air atmosphere. Among the alloys investigated, the $Ca_{65}Mg_{15}Zn_{20}$ alloy exhibits the highest GFA enabling to form BMG sample with the diameter of at least 15 mm. The σ parameter has a better correlation with D_{max} in the Ca-Mg-Zn alloys than previously suggested parameters such as ΔT_x, T_{rg}, K and γ parameters, indicating that the σ parameter can be used more reliably for prediction of GFA in ternary alloy systems.

Acknowledgements

This work was supported by the Creative Research Initiatives of the Korean Ministry of Science and Technology.

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ISMANAM-2004
10.4028/www.scientific.net/JMNM.24-25

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