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COMPOSITION RANGE AND GLASS FORMING ABILITY OF TERNARY Ca-Mg-Cu BULK METALLIC GLASSES (Preprint)

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Composition Range and Glass Forming Ability of Ternary Ca-Mg-Cu Bulk Metallic Glasses

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ABSTRACT

A number of ternary Ca-Mg-Cu amorphous alloys with compositions ranging from 40 to 70 at.% for Ca, 5 to 25 at. % for Mg and 10 to 35 at. % for Cu were produced by a copper mold casting method as wedge-shaped samples with the thickness varying from 0.5 mm to 10 mm. The maximum thickness at which an alloy remains fully amorphous, glass transition temperature, crystallization temperature, temperature interval of the super-cooled region, solidus and liquidus temperatures, as well as heats of crystallization and melting, are reported for these alloys. The effect of the alloy composition on glass forming ability is discussed. In the studied composition range, the $Ca_{50}Mg_{22.5}Cu_{27.5}$ alloy has the best glass forming ability, being fully amorphous after casting to the thicknesses of at least 10 mm.

Keywords: Casting; Ca-Mg-Cu alloys; bulk metallic glass; differential scanning calorimetry; X-ray diffraction; glass forming ability.

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INTRODUCTION

Ca-based bulk metallic glasses are a relatively new class of amorphous alloys which have unique properties such as low density (~ 2.0 g/cc or less), low Young's modulus (~17-20 GPa), low glass transition temperature (T_g ~ 80-150°C) and a wide temperature range of super-cooled liquid (ΔT_x = 30-80°C). With the exception of Mg-based alloys, this is the only known simple-metal based system in the group of bulk metallic glasses. The first Ca-based glassy alloys, $Ca_{57}Mg_{19}Cu_{24}$, $Ca_{60}Mg_{20}Ag_{20}$, and $Ca_{60}Mg_{20}Ag_{10}Cu_{10}$, were reported by Amiya and Inoue in 2002 [1,2]. Fully amorphous rods with a diameter of up to 4 mm in the case of the ternary alloys and up to 7 mm for the quaternary alloy were prepared by a copper mold casting method. To date, numerous Ca-based bulk-glass forming alloys have been reported in the literature that also include Ca-Mg-Zn [3-6], Ca-Mg-Al [3,7,8], Ca-Al-Cu [3,7,8], Ca-Al-Zn [8], Ca-Al-Ag [8], Ca-Mg-Zn-Cu [3,4], Ca-Y-Mg-Cu [3,7], Ca-Mg-Al-Zn [3,7], Ca-Mg-Al-Cu [7,8], Ca-Mg-Al-Ag-Cu [7], and others. The composition of all these alloys can be described by the formula [3]:

$$Ca_A(Y,Ln)_B(Mg,Sn)_C(Al,Ag,Ga,Zn)_D(Cu,Ni,Si)_E \quad (1)$$

where A = 0.40 to 0.70; B = 0 to 0.25; C = 0 to 0.25; D = 0 to 0.35; E = 0 to 0.35; B+C+D ≥ 0.05; A+B+C+D+E=1, and Ln represents lanthanide group elements. The composition range described by Equation (1) was identified using the specific criteria for selection of bulk glass forming alloy compositions, which have recently been identified [3,7,9].

Although the $Ca_{57}Mg_{19}Cu_{24}$ was the first bulk metallic glass produced in the Ca-Mg-Cu system [1], no extensive work has been conducted yet to identify other bulk glassy alloys with better glass forming ability in this system. In the present work, a systematic study of glass forming ability in the ternary Ca-Mg-Cu alloy system in the composition range from 40 to 70 at.% for Ca, 5 to 25 at % for Mg and 10 to 35 at % for Cu was conducted and a number of new bulk glassy alloys were produced. Thermal properties of the new amorphous alloys are reported and the glass forming abilities are correlated with the alloy composition.

EXPERIMENTAL

$Ca_XMg_YCu_Z$ alloys, where X = 40 to 70 at.%; Y = 5 to 30 at.%; and Z = 10 to 36 at.%, were prepared by induction melting of mixtures of pure elements (99.9%) in a water-cooled copper crucible in an argon atmosphere. Some of these alloys were also prepared by melting the elements in a closed-end quartz tube using a radiant furnace and argon atmosphere. Each of the

produced alloys was then induction re-melted in a quartz crucible with a 12.5 mm inner diameter and a 2-3 mm diameter hole in the bottom of the crucible and cast through this hole into a water-cooled copper mold to produce wedge-like samples. Wedge-shaped samples of two different dimensions were produced. One type of samples had 5 mm width, 30 mm height, and thickness varying from 0.5 mm at the base of the wedge to 3 mm at the top of the wedge. Another type of samples had 10 mm width, 50 mm height, and thickness varying from 2 mm at the base of the wedge to 10 mm at the top of the wedge. The time to fill the mold cavity was about 0.5 seconds for smaller samples and ~1.0-1.5 seconds for larger samples. The amorphous or crystalline structure of the cast alloys was identified by X-ray diffraction of powdered samples using Rigaku Rotaflex diffractometer, Cu K_α radiation, and by differential scanning calorimetry (DSC). Glass transition and crystallization temperatures, as well as heats of crystallization and melting, of the cast alloys were determined using a differential scanning calorimeter DSC Q1000 by TA Instruments Inc., (109 Lukens Drive, New Castle, DE 19720) at a heating rate of 40 K/min. The solidus and liquidus temperatures of the alloys were determined by DSC using heating and cooling cycles at 10°C/min. The weight of samples used for DCS was in the range of 6 to 15 mg.

RESULTS

Figure 1a illustrates typical DSC curves of a copper mold cast alloy $Ca_{53}Mg_{23}Cu_{24}$ of different thicknesses. An endothermic reaction corresponding to the glass transition into a super-cooled liquid condition and following exothermic reactions due to crystallization are characteristics of this alloy and indicate that the alloy contains an amorphous phase. At higher temperatures, an extensive endothermic reaction is seen due to melting. The heat of crystallization (ΔH_x) almost does not depend on the thickness of the cast specimen, τ, if the latter is below the critical value τ_{cr}; however, ΔH_x rapidly decreases at larger thicknesses, Figure 1b. The magnitude of the heat of crystallization is known to have maximum when the sample is fully amorphous, and it decreases when the volume fraction of the amorphous phase decreases [10]. Therefore, the maximum value of the heat of crystallization, which remains constant at the thicknesses below τ_{cr}, is an indication that at these thicknesses the alloy is fully amorphous, and at the thicknesses above τ_{cr} the alloy becomes partially amorphous. X-ray diffraction (XRD) analysis supports this conclusion. Indeed, the XRD patterns from the samples extracted from regions of the wedge cast specimen with the thicknesses below τ_{cr} show a single wide halo with the 2-Theta range of 30°-

35° from the amorphous phase only, while the XRD patterns taken from the specimen regions having the thickness larger than τ_{cr} show also sharp crystalline peaks from crystalline phases (Figure 2).

Figure 3 shows (a) DSC and (b) XRD patterns of the cast alloys $Ca_{58}Mg_{18}Cu_{24}$ and $Ca_{50}Mg_{25}Cu_{25}$. The patterns are taken from the regions of the critical thickness τ_{cr} (which is 6 mm for $Ca_{58}Mg_{18}Cu_{24}$ and 9 mm for $Ca_{50}Mg_{25}Cu_{25}$) and slightly above τ_{cr}. One can see that the intensities of the exothermic crystallization reactions on the DSC curves decrease and sharp crystalline peaks are formed on the XRD patterns for both alloys, when the thickness exceeds τ_{cr}. The values of τ_{cr} for different Ca-Mg-Cu alloys studied in the present work are given in Table 1. Characteristic temperatures, such as the glass transition, T_g, onset of crystallization, T_x, the temperatures of the start, T_m, and completion, T_l, of melting, as well as heats of crystallization, ΔH_x, and melting (fusion), ΔH_m, are also tabulated in Table 1 for these alloys. New compositions have been identified with very good glass forming abilities. For example, the alloy $Ca_{50}Mg_{22.5}Cu_{27.5}$ is fully amorphous at a thickness of at least 10 mm, the alloy $Ca_{50}Mg_{25}Cu_{25}$ is fully amorphous up to a thickness of 9 mm, the alloy $Ca_{50}Mg_{20}Cu_{30}$ has the critical thickness of 8 mm, and the alloys $Ca_{45}Mg_{25}Cu_{30}$ and $Ca_{58}Mg_{18}Cu_{24}$ are fully amorphous up to the critical thickness of 6 mm.

Figure 4 illustrates (a) DSC and (b) XRD patterns from the cast alloys $Ca_{70-X}Mg_{20}Cu_{10+X}$ of the critical thickness, where X = 0; 5; 10; 15; and 20. The glass transition and crystallization temperatures are seen to increase with an increase in X, which is an indication that the amorphous phase, once it is formed, is kinetically more stable in the alloys with the larger amount of Cu (at a constant Mg content, see also Table 1). On the other hand, the glass forming ability (GFA), or critical thickness, does not increase monotonically with an increase in the amount of Cu, but it has intermediate maxima for $Ca_{60}Mg_{20}Cu_{20}$ (τ_{cr} = 4 mm) and $Ca_{50}Mg_{20}Cu_{30}$ (τ_{cr} = 8 mm), see Figure 4a and Table 1. This result may indicate that there is no direct correlation between the GFA and the glass stability. Analysis of the X-ray diffraction patterns shows that the position of the amorphous halo maximum shifts to larger 2Θ (from 29.5° to 32.3°) and the halo becomes wider (i.e. the full-width-at-half-maximum [FWHM] increases from $\Delta 2\Theta$ = 3.99° to 9.06°) with an increase in Cu (from 10 to 30 at.%).

DISCUSSION

The results of the present work show that fully amorphous Ca-based ternary Ca-Mg-Cu alloys can be produced as plates with the thickness of 10 mm; which is much higher than a previously reported 4-mm maximum diameter rod of a fully amorphous ternary alloy $Ca_{57}Mg_{19}Cu_{24}$ [1]. The glass forming ability (GFA) of these ternary alloys is found to be very sensitive to the alloy composition. For example, the alloy $Ca_{50}Mg_{25}Cu_{25}$ has the maximum critical thickness of 9 mm; while the alloys $Ca_{50}Mg_{30}Cu_{20}$ and $Ca_{45}Mg_{30}Cu_{25}$, which compositions differ from the former alloy by only 5 at.%, have the critical thicknesses of 2 mm and 1 mm, respectively. Although the critical thickness depends on the casting conditions and it generally increases with increasing the cooling rate during solidification, in the case of the same casting procedure there is a direct relationship between the critical thickness and glass forming ability (GFA) [11], so that an alloy with larger τ_{cr} is a better glass former.

The composition range for the prospective Ca-Mg-Cu bulk glass forming alloys was selected in the present work using Equation (1), and this range is shown in the currently available liquidus projection of the Ca-Mg-Cu system (Figure 5) as a trapezoid-like area surrounded by a dashed-line border. The compositions of 27 amorphous alloys studied in the current work are shown in this figure as solid circles. The selected (trapezoid) composition area contains, according to [12], a ternary eutectic reaction and two peritectic reactions. The eutectic ($\sim Ca_{67}Mg_{19}Cu_{14}$) and one peritectic ($\sim Ca_{63}Mg_{19.5}Cu_{17.5}$) compositions are located in the Ca-rich region of this selected area, and the alloys in this region have rather moderate GFA, showing the critical thickness, τ_{cr}, of 4 mm or less (see Table 1). This agrees with previous results of Amiya and Inoue [1] who reported that the alloy $Ca_{67}Mg_{19}Cu_{14}$ can be copper mold cast into a fully amorphous rod with a maximum diameter of 2 mm only. The GFA has a tendency to increase when the concentration of Ca decreases to about 50 at.% and the amount of Mg is within 19-25 at.% range (see Table 1 and Figure 5); so that the alloys located near the second peritectic (the composition of this peritectic, according to [12], is $\sim Ca_{46}Mg_{25}Cu_{29}$) are fully amorphous at τ_{cr} of 6 to 10 mm. Such behavior of the Ca-Mg-Cu glasses is different from the behavior of Ca-Mg-Zn glassy alloys that have the best GFA (and τ_{cr} of ~10 mm) at a near eutectic composition [5], and it also contradicts the experimental observation that the best glass forming alloys have near-eutectic compositions [11].

Thorough analysis of the melting behavior of the Ca-Mg-Cu alloys (see Table 1) and results reported by Myles [12] has led us to a conclusion that this apparent contradiction is due to an incorrect assessment of the Ca-Mg-Cu liquidus projection made by Myles. The diagram shown in Figure 5 was constructed in [12] based on the metallographic analysis of 15 different alloys only. The phase identification was partially supported by X-ray diffraction and electron-probe analysis; however, no DSC was conducted to identify the melting reactions and liquidus temperatures [12]. For example, according to this diagram, the alloys $Ca_{70}Mg_{20}Cu_{10}$ and $Ca_{70}Mg_{10}Cu_{20}$ should experience the eutectic reaction at ~67 at.% Ca and 19% Mg and T_m = 350 ± 5°C; however, according to our results (see Table 1) these alloys have the highest melting temperatures among the all studied alloys, T_m = 397°C and T_m = 386°C, respectively. The DSC analysis of 27 alloys conducted in the present work shows at least four characteristic temperatures for T_m (see Table 1). These are T_m = 397 °C for the alloy $Ca_{70}Mg_{10}Cu_{20}$; T_m = 386 °C for $Ca_{70}Mg_{20}Cu_{10}$, T_m = 363-364 °C for the alloys $Ca_{65}Mg_{20}Cu_{15}$ and $Ca_{65}Mg_{25}Cu_{10}$; T_m = 374-377 °C for the alloys $Ca_{40}Mg_{30}Cu_{30}$, $Ca_{40}Mg_{25}Cu_{35}$ and $Ca_{45}Mg_{19}Cu_{36}$; and T_m = ~352-357 °C for other 20 alloys. Table 1 also shows that two alloys, $Ca_{50}Mg_{25}Cu_{25}$ and $Ca_{53}Mg_{23}Cu_{24}$, have the lowest melting range, $\Delta T_m = T_l - T_m$, of ~28°C; which indicates the presence of an eutectic reaction at T_m = ~354°C, near a composition of ~51 at.% Ca and 24 at.% Mg. Our conclusion that the position of the eutectic shown in Figure 5 is incorrect is also supported by results of Amiya and Inoue [1], who reported T_m = ~370°C for the "eutectic" alloy $Ca_{67}Mg_{19}Cu_{14}$ and T_m = ~357°C for the alloy $Ca_{57}Mg_{19}Cu_{24}$. Detailed assessment of the liquidus projection is in progress in our group and the results will be published shortly [13].

According to the modified eutectic location, the best glass forming alloys, that have the maximum thicknesses in the range of 6 to 10 mm, have near eutectic compositions, which is in agreement with previous experimental observations (11). The worst glass forming alloys, that have the maximum thickness of ~0.5 mm, are located far from the eutectic and have a very high freezing range (such as $Ca_{65}Mg_5Cu_{30}$ and $Ca_{55}Mg_{10}Cu_{35}$, with ΔT_m = ~130°C and ~140°C, respectively); or high melting temperatures, indicating peritectic reactions (such as $Ca_{70}Mg_{20}Cu_{10}$ and $Ca_{70}Mg_{10}Cu_{20}$, which melting temperatures are about 35°C higher than the eutectic reaction). Both situations should favor crystallization during copper mold casting [5,11]

Analysis of the effect of the alloy composition on the position and width of the X-ray amorphous halo may provide some information on the nearest interatomic spacing in the amorphous

structure [14]. The position of an X-ray halo maximum is known to be directly related with the average radius of the first coordination shell, R*, through the Bragg equation:

$$R^{\wedge} = \lambda/(2\sin\Theta^{\wedge}) \qquad (2)$$

where λ is the X-ray wave length (= 0.15418 nm for the Cu K_α radiation) and $2\Theta^{\wedge}$ is the scatter angle at the halo maximum. Figure 6 shows the intensity of the X-ray scattering versus $R = \lambda/(2\sin\Theta)$ for several amorphous alloys $Ca_{50+X}Mg_{20}Cu_{30-X}$, where 2Θ is the angle of deviation of the diffracted beam. It can be seen that the value of $R^{\wedge}$ corresponding to the position of the scatter intensity peak decreases from ~ 0.3028 nm to ~ 0.2771 nm when the amount of Cu increases from 10 at.% to 30 at.%. This decrease in the average nearest inter-atomic spacing can be explained by a smaller radius of the Cu atoms relative to the radii of Ca and Mg atoms, which should increase the fraction of Ca-Cu and Mg-Cu bonds. The calculated values for the fist coordination shell radius can be compared with the atomic and covalent radii of the elements (Table 2) and atomic and covalent bond distances between Ca-Ca, Ca-Mg, Ca-Cu, and Mg-Cu (Table 3). These comparisons show that the calculated radius values for the first coordination shell can only be obtained if covalent bonds between the elements dominate. An increasing fraction of covalent bonding is known to increase the glass forming ability [15], and this can be one of the reasons of very good glass forming ability of the Ca-based metallic glasses.

CONCLUSIONS

Twenty seven ternary Ca-Mg-Cu bulk metallic glasses were produced by a copper mold casting method and their thermal properties were determined. The critical thickness, τ_{cr}, at which the alloys are fully amorphous after casting is sensitive to the alloy composition and it has a maximum value of at least 10 mm for the alloy $Ca_{50}Mg_{22.5}Cu_{27.5}$. The alloy $Ca_{50}Mg_{25}Cu_{25}$ has τ_{cr} = 9 mm; the alloys $Ca_{50}Mg_{20}Cu_{30}$ and $Ca_{55}Mg_{25}Cu_{20}$ have τ_{cr} = 8 mm; $Ca_{53}Mg_{23}Cu_{24}$ has τ_{cr} = 7 mm; $Ca_{45}Mg_{25}Cu_{30}$, $Ca_{47.5}Mg_{22.5}Cu_{30}$, and $Ca_{58}Mg_{18}Cu_{24}$, have τ_{cr} = 6 mm; $Ca_{40}Mg_{25}Cu_{35}$, $Ca_{60}Mg_{20}Cu_{20}$, and $Ca_{65}Mg_{15}Cu_{20}$ have τ_{cr} = 4 mm; and other alloys have the critical thickness between 0.5 and 3.0 mm. The glass transition temperature for these alloys varies from 83°C to 133°C and the crystallization temperature varies from 112°C to 169°C. Though the glass transition and crystallization temperatures have the maximum values for the best glass forming alloys, no direct dependence of these temperatures on the glass forming ability (or critical thickness) was found for other alloys. Ca-Mg-Cu alloys with good glass forming ability have the

lowest melting temperature (T_m = 354-357°C) and a rather narrow melting range, indicating that these alloys have near-eutectic compositions. Estimations of the average inter-atomic spacing in the Ca-Mg-Cu metallic glasses from the position of the amorphous halo during X-ray scattering lead to a conclusion that covalent bonds dominate in these glasses.

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TABLES

"Composition Range and Glass Forming Ability of Ternary Ca-Mg-Cu Bulk Metallic Glasses," by Senkov and Scott

Table 1. Critical thickness, τ_{cr}, glass transition, T_g, crystallization, T_x, melting, T_m, and liquidus, T_l, temperatures and heats of crystallization, ΔH_x, and fusion, ΔH_m, for Ca-Mg-Zn metallic glasses.

Alloy	τ_{cr} (mm)	T_g (°C)	T_x (°C)	T_m (°C)	T_l (°C)	ΔH_x (J/g)	ΔH_m (J/g)
$Ca_{40}Mg_{30}Cu_{30}$	0.5	122	157	374	421	91	221
$Ca_{40}Mg_{25}Cu_{35}$	4.0	126	163	377	407	89	196
$Ca_{45}Mg_{30}Cu_{25}$	1.0	128	163	354	444	94	241
$Ca_{45}Mg_{25}Cu_{30}$	6.0	127	165	354	405	132	222
$Ca_{45}Mg_{19}Cu_{36}$	0.5	126	155	376	441	106	190
$Ca_{47.5}Mg_{22.5}Cu_{30}$	6	126	167	352	400	154	219
$Ca_{50}Mg_{30}Cu_{20}$	2.0	129	166	354	458	104	235
$Ca_{50}Mg_{25}Cu_{25}$	9.0	127	166	354	382	129	210
$Ca_{50}Mg_{22.5}Cu_{27.5}$	10.0	127	169	354	390	150	208
$Ca_{50}Mg_{20}Cu_{30}$	8.0	128	169	355	417	139	378
$Ca_{53}Mg_{23}Cu_{24}$	7.0	133	166	354	382	134	196
$Ca_{55}Mg_{25}Cu_{20}$	8.0	125	155	354	395	125	226
$Ca_{55}Mg_{20}Cu_{25}$	2.0	126	153	355	447	106	170
$Ca_{55}Mg_{15}Cu_{30}$	3.0	124	164	353	433	137	220
$Ca_{55}Mg_{10}Cu_{35}$	0.5	124	149	356	497	98	198
$Ca_{58}Mg_{18}Cu_{24}$	6.0	115	153	355	394	119	186
$Ca_{60}Mg_{25}Cu_{15}$	2.0	117	143	355	403	102	198
$Ca_{60}Mg_{20}Cu_{20}$	4.0	114	139	356	405	105	181
$Ca_{60}Mg_{15}Cu_{25}$	1.0	123	155	354	414	99	205
$Ca_{60}Mg_{13}Cu_{27}$	1.0	121	153	355	428	98	204
$Ca_{65}Mg_{25}Cu_{10}$	0.5	132	156	364	418	96	204
$Ca_{65}Mg_{20}Cu_{15}$	2.0	113	132	363	406	101	193
$Ca_{65}Mg_{15}Cu_{20}$	4.0	110	136	357	409	115	195
$Ca_{65}Mg_{10}Cu_{25}$	2.0	115	147	357	438	114	177
$Ca_{65}Mg_{5}Cu_{30}$	0.5	130	151	357	484	89	155
$Ca_{70}Mg_{20}Cu_{10}$	0.5	83	112	386	429	87	153
$Ca_{70}Mg_{10}Cu_{20}$	1.0	112	134	397	440	107	175

Table 2. Atomic (r_A) and covalent (r_C) radii of Ca, Mg and Cu.

	r_A nm	r_C nm
Ca	0.197	0.174
Mg	0.160	0.136
Cu	0.128	0.117

Table 3. Atomic (R_A) and covalent (R_C) bond distances between the elements.

	R_A nm	R_C nm
Ca-Ca	0.394	0.348
Ca-Mg	0.357	0.310
Ca-Cu	0.325	0.291
Mg-Mg	0.320	0.272
Mg-Cu	0.288	0.253

FIGURE CAPTIONS

Figure 1. (a) DSC curves of a copper mold cast alloy Ca53Mg23Cu24 of different thicknesses. Locations of glass transition, T_g, and crystallization, T_x, temperatures, as well as the temperatures of the start, T_m, and completion, T_l, of melting, are indicated on one of the curves. An exothermic crystallization reaction with the heat of crystallization ΔH_x is also indicated as an area under the exothermic peaks and above the dashed baseline. Exothermic reactions are up and the heating rate is 40 K/min. (b) Dependences of the heat of crystallization and the volume percent of the amorphous phase on the sample thickness. The critical thickness (τ_{cr} = 7 mm) above which the alloy is partially amorphous after casting is shown.

Figure 2. X-ray diffraction patterns of samples extracted from regions of different thicknesses (shown in the figure) of a copper mold wedge cast alloy $Ca_{53}Mg_{23}Cu_{24}$.

Figure 3. (a) DSC and (b) X-ray patterns of samples extracted from the regions of different thicknesses (shown in the figures) of the copper mold wedge cast alloys $Ca_{58}Mg_{18}Cu_{24}$ and $Ca_{50}Mg_{25}Cu_{25}$.

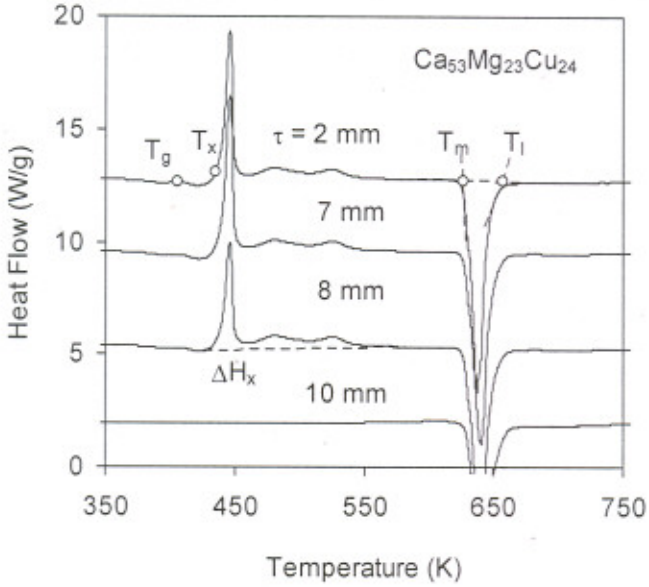
Figure 4. (a) DSC and (b) X-ray patterns of samples extracted from the regions of critical thicknesses [shown in the figure (a)] of the copper mold wedge cast alloys $Ca_{50+X}Mg_{20}Cu_{30-X}$, where X = 0, 5, 10, 15, and 20.

Figure 5. Liquidus projection of the Ca-Mg-Cu system, according to [12]. The location of the ternary eutectic ($L \leftrightarrows Ca+CaMg_2+Ca_2Cu$, 67 at. % Ca and 18 at.% Mg) is marked by open triangle and of the three peritectic reactions [(i) $L+CaCu_5 \leftrightarrows CaCu+Cu_2Mg$; (ii) $L+Cu_2Mg \leftrightarrows CaCu+CaMg_2$; (iii) $L+CaCu \leftrightarrows CaMg_2+Ca_2Cu$] are marked by an open circle. Compositions of 27 amorphous alloys studied in the current work are shown as solid circles. A trapezoid, with a dashed line border, represents a composition range for Ca-Mg-Cu bulk metallic glasses, according to equation (1).

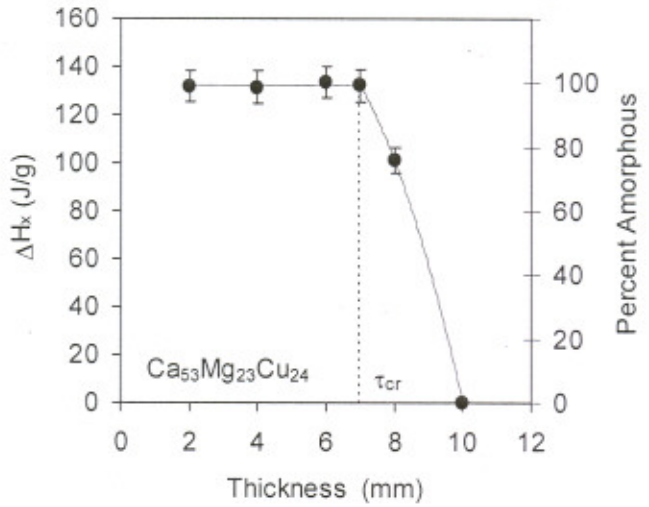
Figure 6. X-ray diffraction intensity vs. inter-atomic spacing in amorphous $Ca_{70-X}Mg_{20}Cu_{10+X}$ alloys (x = 0, 5, 10, 15, and 20).

REFERENCES

1. K. Amiya and A. Inoue, Mater. Trans. JIM, 43 (2002) 81.
2. K. Amiya and A. Inoue, Mater. Trans. JIM, 43 (2002) 2578.
3. O.N. Senkov, J.M. Scott, In: MRS Proceedings, Vol. 806 (Materials Research Society, Warrendale, PA, 2003), p. 145.
4. O.N. Senkov, J.M. Scott, Materials Letters, 58 (2004) 1375.
5. O.N. Senkov, J.M. Scott, J. Non-Cryst. Solids, (2005).
6. E.S. Park, W.T. Kim, D.H. Kim, Mater. Sci. Forum, 475-479 (2005) 3415.
7. O.N. Senkov, J.M. Scott, Scripta Materialia, 50 (2004) 449.
8. F.Q. Guo, S.J. Poon, G.J. Shiflet. Appl. Phys. Letters, 84 (2004) 37.
9. O.N. Senkov, D.B. Miracle, H.M. Mullens, J. Applied Physics, 97 (2005) 103502
10. T. Hatakeyama, Liu Zhenhai, Handbook of Thermal Analysis, (John Wiley & Sons, West Sussex, England 1998).
11. A. Inoue, Acta Mater. 48 (2000) 279.
12. K.M. Myles, J. Less-Common Metals, 20 (1970) 149-154.
13. O.N. Senkov and F. Meisenkothen, Ongoing work, 2005.
14. H. P. Klug and L.E. Alexander, X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials, John Wiley & Sons, NY, 1962.
15. R.W. Cahn, P. Haasen, E.J. Kramer, (eds), Materials Science and Technology, A Comprehensive Treatment. Vol. 9: Glasses and Amorphous Metals, VCH, NY, 1991.



(a)



(b)

Figure 1. (a) DSC curves of a copper mold cast alloy Ca53Mg23Cu24 of different thicknesses. Locations of glass transition, T_g, and crystallization, T_x, temperatures, as well as the temperatures of the start, T_m, and completion, T_l, of melting, are indicated on one of the curves. An exothermic crystallization reaction with the heat of crystallization ΔH_x is also indicated as an area under the exothermic peaks and above the dashed baseline. Exothermic reactions are up and the heating rate is 40 K/min. (b) Dependences of the heat of crystallization and the volume percent of the amorphous phase on the sample thickness. The critical thickness (τ_{cr} = 7 mm) above which the alloy is partially amorphous after casting is shown.

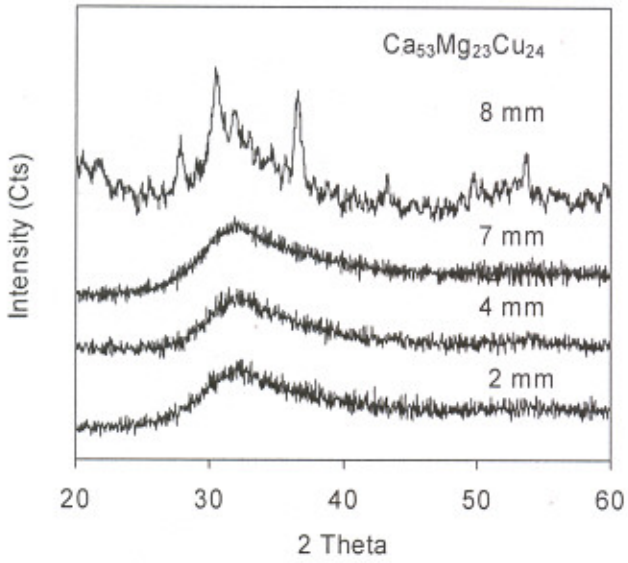
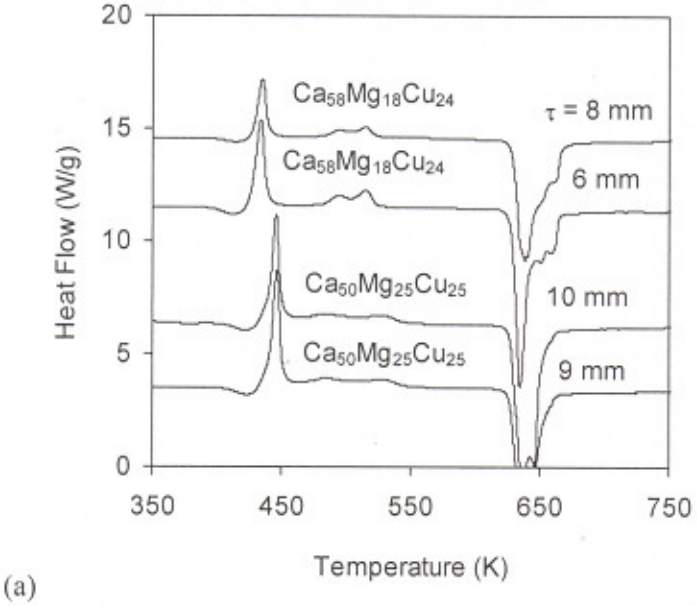
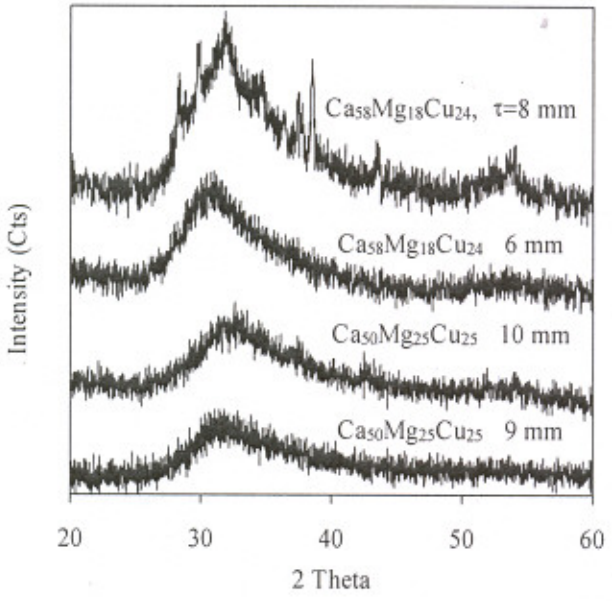


Figure 2. X-ray diffraction patterns of samples extracted from regions of different thicknesses (shown in the figure) of a copper mold wedge cast alloy $Ca_{53}Mg_{23}Cu_{24}$.

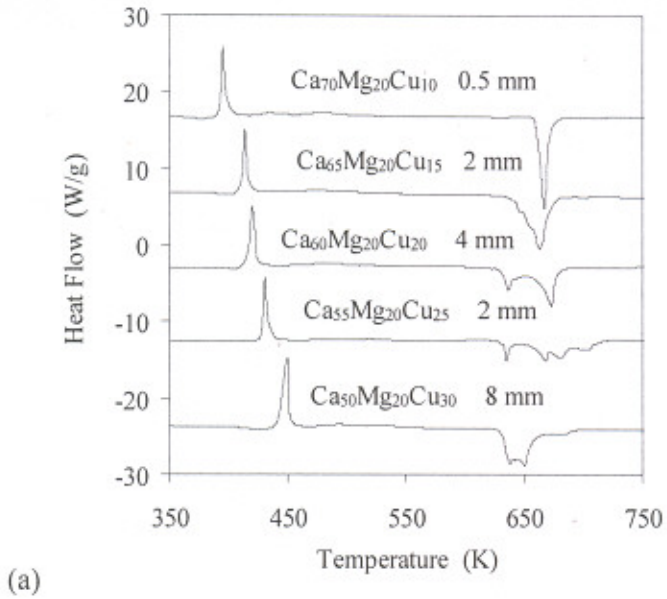


(a)

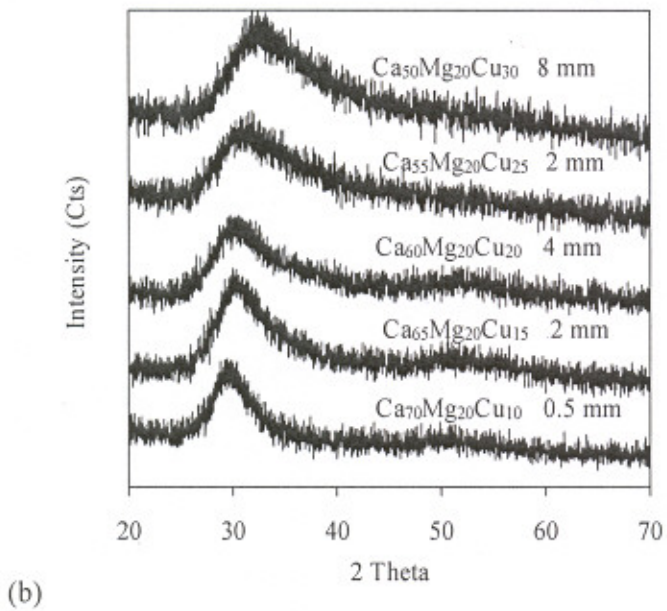


(b)

Figure 3. (a) DSC and (b) X-ray patterns of samples extracted from the regions of different thicknesses (shown in the figures) of the copper mold wedge cast alloys $Ca_{58}Mg_{18}Cu_{24}$ and $Ca_{50}Mg_{25}Cu_{25}$.



(a)



(b)

Figure 4. (a) DSC and (b) X-ray patterns of samples extracted from the regions of critical thicknesses [shown in the figures] of the copper mold wedge cast alloys $Ca_{50+X}Mg_{20}Cu_{30-X}$, where X = 0, 5, 10, 15, and 20.

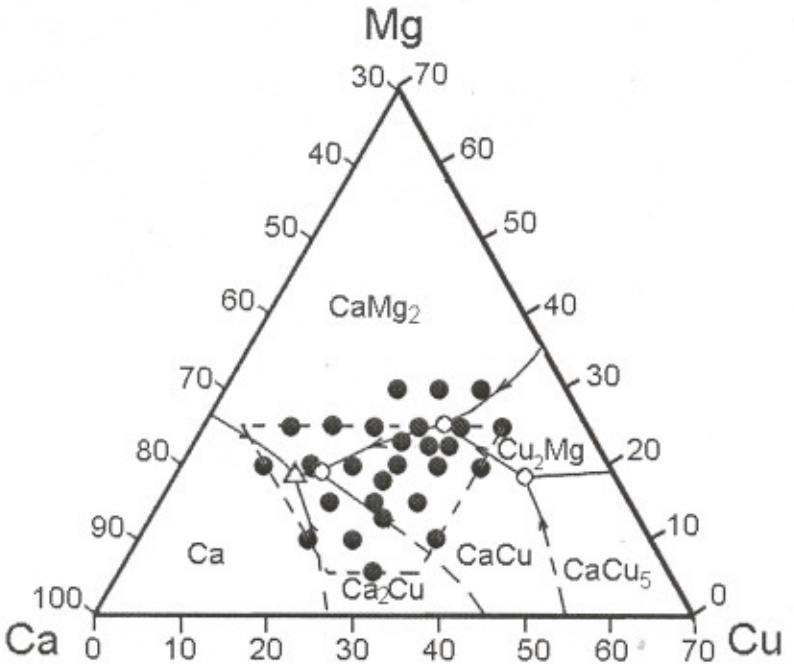


Figure 5. Liquidus projection of the Ca-Mg-Cu system, according to [12]. The location of the ternary eutectic ($L \leftrightarrows Ca+CaMg_2+Ca_2Cu$, 67 at. % Ca and 18 at.% Mg) is marked by open triangle and of the three peritectic reactions [(i) $L+CaCu_5 \leftrightarrows CaCu+Cu_2Mg$; (ii) $L+Cu_2Mg \leftrightarrows CaCu+CaMg_2$; (iii) $L+CaCu \leftrightarrows CaMg_2+Ca_2Cu$] are marked by open circles. Compositions of 27 amorphous alloys studied in the current work are shown as solid circles. A trapezoid, with a dashed line border, represents a composition range for Ca-Mg-Cu bulk metallic glasses, according to equation (1).

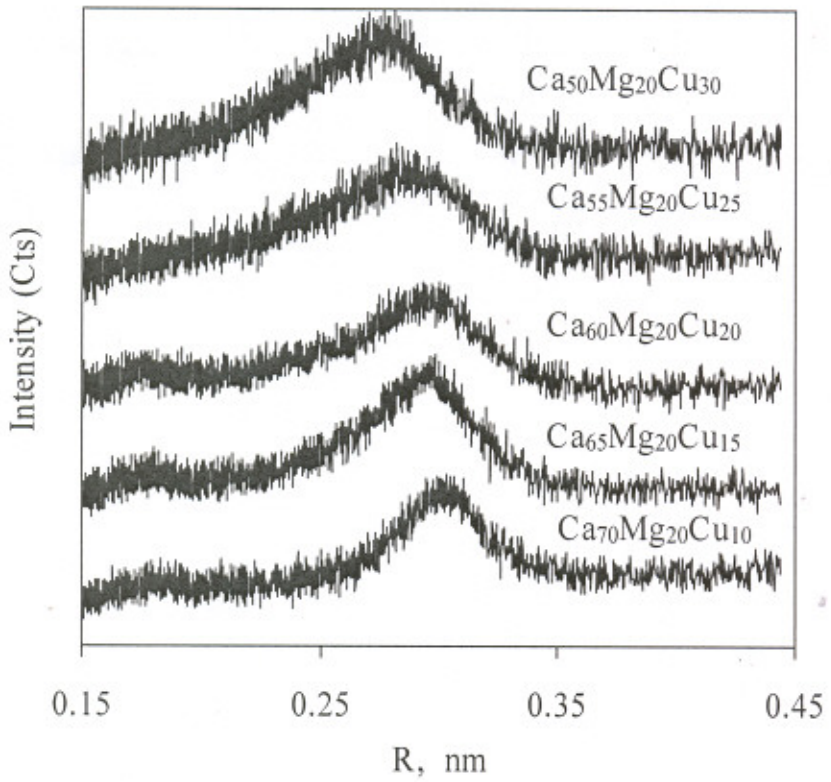


Figure 6. X-ray diffraction intensity vs. inter-atomic spacing in amorphous $Ca_{70-X}Mg_{20}Cu_{10+X}$ alloys (x = 0, 5, 10, 15, and 20).