AFRL-ML-WP-TP-2006-504

DEVELOPMENT OF LOW DENSITY CaMg-A1-BASED BULK METALLIC GLASSES (Preprint)

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OCTOBER 2006

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MATERIALS AND MANUFACTURING DIRECTORATE
AIR FORCE RESEARCH LABORATORY
AIR FORCE MATERIEL COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7750

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
October 2006	Journal Article Preprint	

4. TITLE AND SUBTITLE
DEVELOPMENT OF LOW DENSITY CaMg-A1-BASED BULK METALLIC GLASSES (Preprint)

5a. CONTRACT NUMBER
FA8650-04-D-5233

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
62102F

6. AUTHOR(S)
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5d. PROJECT NUMBER
2311

5e. TASK NUMBER
00

5f. WORK UNIT NUMBER
23110002

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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Air Force Research Laboratory, Air Force Materiel Command
Wright-Patterson AFB, OH 45433-7750

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Materials and Manufacturing Directorate
Air Force Research Laboratory
Air Force Materiel Command
Wright-Patterson AFB, OH 45433-7750

10. SPONSORING/MONITORING AGENCY ACRONYM(S)
AFRL-ML-WP

11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S)
AFRL-ML-WP-TP-2006-504

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES
Submitted for publication in the Journal of Alloys and Compounds, publisher: Elsevier. PAO Case Number: AFRL/WS 06-2304, 27 September 2006.

14. ABSTRACT
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15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT:	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON (Monitor)
a. REPORT	b. ABSTRACT	c. THIS PAGE			Daniel B. Miracle
Unclassified	Unclassified	Unclassified	SAR	22	19b. TELEPHONE NUMBER *(Include Area Code)* (937) 255-1305

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39-18

Development of Low Density Ca-Mg-Al- Based Bulk Metallic Glasses

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Abstract

Low density Ca-Mg-Al-based bulk metallic glasses containing additionally Cu and Zn, were produced by a copper mold casting method as wedge-shaped samples with thicknesses varying from 0.5 mm to 10 mm. The compositions of the alloys were selected using recently developed specific criteria for glass formation. A structural assessment using the efficient cluster packing model was also applied and showed a good ability to represent these glasses. Thermal properties of the new metallic glasses, such as the glass transition, crystallization and melting temperatures, as well as heats of crystallization and melting are reported. The critical cooling rate for amorphization and the fragility index are estimated for these alloys. The effect of the alloy composition on glass forming ability is discussed.

Introduction

Ca-Mg-based bulk metallic glasses are relatively new class of amorphous alloys, which attract interest of several research groups for their unique properties [1-10]. In particular, these metallic glasses have the lowest density (~2.0 g/cc) among all known amorphous metallic alloys. They also have low Young's modulus (~20-35 GPa) [11] comparable to the modulus of human bones, low glass transition temperature (T_g ~ 100-150°C) and a wide temperature range of super-cooled liquid ($\Delta T_{xg} = T_x - T_g$ ~30-70 °C). It is also noteworthy that these glassy alloys are based on two simple metals, Ca and Mg, which distinguishes them from all other transition-metal based bulk

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metallic glasses [12], and most of these Ca-Mg-based glasses were produced using specific topological and thermodynamic criteria for glass formation, which have recently been developed at the Air Force Research Laboratory [5,13-19]. By applying these new criteria to Ca-based alloy systems, favorable glass formation was predicted in the alloys described by formula:

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

where A=0.40-0.70; B=0-0.25; C=0-0.25; D=0-0.35; E=0-0.35; $B+C+D \geq 0.05$; $A+B+C+D+E=1$; and *Ln* represents a metal from the lanthanide group. A strong topological basis exists for the compositions represented in Equation (1) [13-18], which are also well described by a recently developed structural model for metallic glasses [19].

The main drawback of the Ca-based metallic alloys is their poor oxidation and corrosion resistance. Many Ca-based crystalline alloys are very reactive, even in pure water, and oxidize in air in a matter of days. Transition in the amorphous state considerably improves the oxidation and corrosion resistance of these alloys, although these properties also depend on the alloy constitution [20-22]. For example, recent studies of four Ca-Mg-Zn, Ca-Mg-Cu, Ca-Mg-Zn-Cu and Ca-Mg-Al-Zn-Cu metallic glasses have shown that the ternary Ca-Mg-Zn glass has the least oxidation and corrosion resistance. Substitution of Zn with Cu and/or Al improves these properties, and the alloy containing Al has the best oxidation and corrosion resistance [22]. Several Ca-Al-based bulk metallic glasses have recently been reported [7]; however, these glasses have not very good glass forming ability and the maximum diameter of fully amorphous rods made of these alloys by a water cooled copper mold casting method generally does not exceed 2 mm. Only two of the reported amorphous alloys, $Ca_{56.5}Mg_{10}Al_{28.5}Cu_5$ and $Ca_{56.5}Mg_{10}Al_{28.5}Cu_5$, had a higher maximum diameter of 3 mm [7].

In the present work we report on several new Ca-Mg-Al-based amorphous alloys with better glass forming ability. The compositions of these alloys were selected using Equation (1) and recently developed specific criteria for glass formation. Thermal properties of the new metallic glasses, such as the glass transition, crystallization and melting temperatures, as well as heats of crystallization and melting are reported. The effect of the alloy constitution on glass forming ability and glass stability is discussed.

Experimental

Several Ca-Mg-Al-based alloys, which nominal composition is shown in Table 1, were prepared by induction melting of mixtures of pure elements (99.99% for Al and Cu, 99.9% for Mg and Zn,

and 99.5% for Ca) in a water-cooled copper crucible in an argon atmosphere. Each of the produced alloys was then induction re-melted in a quartz crucible with a 12.5 mm inner diameter and an ~2 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 of two different dimensions. One type of samples had 6.4 mm width, 35 mm height, and thickness varying from 0.5 mm at the base of the wedge to 3.5 mm at the top of the wedge. Another type of samples had 11 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 a Rigaku Rotaflex diffractometer, Cu K_α radiation, and a differential scanning calorimeter (DSC) Q1000, By TA Instruments, Inc. The glass transition, T_g, and crystallization, T_x, temperatures, the temperatures of start, T_m, and completion, T_l, of melting, and heats of crystallization, ΔH_x, of the cast alloys were determined using DSC scans at a heating rate of 40 K/min. The maximum thickness, τ_{max}, at which an alloy remained fully amorphous after the water-cooled copper mold casting, was determined using X-ray diffraction and DSC patterns of several samples extracted from different-thickness regions of the wedge specimens as a thickness above which ΔH_x starts to decrease from its maximum value and sharp peaks from crystalline phases appear on the X-ray diffraction patterns. This method is described elsewhere [8]. The weight of samples used for DCS was in the range of 6 to 15 mg.

Results

Ternary Alloys. The ternary alloys were produced with the concentrations of Ca varying from 50 to 75 at.% and the concentration of Al varying from 4 to 35 at.% (Table 1). The density of these alloys increases from 1.62 g/cc to 1.79 g/cc with a decrease in the concentration of Ca and an increase in the concentration of Al. Seven of nine produced ternary Ca-Mg-Al alloys have marginal glass forming ability, and the maximum amorphous thickness, τ_{max}, of these alloys after casting in a wedge cavity does not exceed 0.5 mm (see Table 1). Two other ternary alloys, $Ca_{65}Mg_{15}Al_{20}$ and $Ca_{70}Mg_{15}Al_{15}$, have better glass forming ability and show τ_{max} of 1.0 mm and 1.5 mm, respectively. Typical X-ray diffraction patterns and DSC heating curves for the ternary alloys in fully amorphous and partially amorphous conditions are shown in Figures 1(a) and 2(a-b), respectively. Three alloy groups with different crystallization kinetics can be recognized. The

first group consists of one glassy alloy, $Ca_{55}Mg_{15}Al_{30}$. A DSC pattern of this alloy shows two exothermic crystallization reactions near 283°C and 386°C and at least two endothermic reactions due to alloy melting, with the reaction peaks at 495°C and 540°C (see Figure 2). A shallow endothermic reaction is also recognized in the temperature range between 225°C and 282°C (ΔT_x = 57°C), which is due to transition of the glass into a super-cooled liquid state.

The second group consists of three alloys, $Ca_{62}Mg_9Al_{29}$, $Ca_{60}Mg_{15}Al_{25}$, and $Ca_{65}Mg_{15}Al_{20}$. For these alloys, only one sharp crystallization peak is observed, which shifts to a lower temperature range and becomes sharper and more intense with a decrease in the amount of Al. The super-cooled liquid range for this alloys is rather narrow (ΔT_x = 36°C, 26°C, and 20°C, respectively), and the melting temperature gradually decreases to an eutectic point at ~410-415°C (see Figure 2 and Table 1). During melting these alloys experience at least two phase transformations, which result in two sharp endothermic peaks.

In the third group, which consists of $Ca_{70}Mg_{15}Al_{15}$, $Ca_{70}Mg_{26}Al_4$, $Ca_{72.5}Mg_{12.5}Al_{15}$, and $Ca_{75}Mg_{15}Al_{10}$, several wide overlapped crystallization peaks are observed in the temperature range of 180°C to 280°C (see Figures 2a and 2b). Melting of these alloys starts at the same temperature of about 360°C and the enthalpy of the first melting peak is very low, about 8.3 J/g. The second melting peak is much more intense, $\Delta H_m \approx 125$ J/g, and it starts also at near the same temperature of ~414°C for these alloys. It is likely that the weak peak at 360°C is due to melting of a metastable eutectic and the sharp peak at ~414°C is due to melting of an equilibrium eutectic, which follows by a gradual melting of a primary phase with an increase in the temperature up to 480-510°C.

At a constant Mg content, the glass transition, crystallization and melting temperatures for the ternary Ca-Mg-Al alloys have a tendency to decrease with a decrease in the amount of Al and an increase in the amount of Ca in the concentration range of Ca from 50% to 75% (see Table 1). For example, T_g decreases from ~240 °C to 130 °C and T_x decreases from ~280 °C to 150 °C in this composition range. There is, however, no correlation between the maximum amorphous thickness, τ_{max}, and the temperature range of the super-cooled liquid, $\Delta T_x = T_x - T_g$, which is used as a measure of glass stability, or other empirical glass forming ability parameters such as T_g/T_l or $T_x/(T_g+T_l)$. However, it can be noted from Table 1 that there is a tendency for τ_{max} to increase with a decrease in the melting range $\Delta T_m = T_l - T_m$.

Quaternary alloys. Two type quaternary alloys were produced, i.e. Ca-Mg-Al-Zn and Ca-Mg-Al-Cu (see Table 1). Typical X-ray diffraction patterns of one of these alloys, $Ca_{60}Mg_{15}Al_{10}Zn_{15}$, versus the alloy thickness are shown in Figure 1b. These patterns illustrate transition of the alloy from a fully amorphous to a partially crystalline state with an increase in the alloy thickness from 4 mm to 10 mm. The Zn containing glassy alloys contain 48 to 60 at.% Ca, 13 to 20 at.% Mg, 10 to 20 at.% Al, and 6 to 20 at.% Zn and their typical DSC curves are shown in Figure 3. The Cu-containing alloys have 50 or 60 at.% Ca, 9 to 22.5 at.% Mg, 5 to 11 at. % Al, and 10 to 22.5 at.% Cu and their DSC curves are given in Figure 4. The density of these alloys varies from 1.84 to 2.27 g/cc. The density increases with an increase in the amounts of Cu or Zn, and, in a smaller extent, Al and Mg. Ternary Ca-Mg-Zn and Ca-Mg-Cu bulk amorphous alloys recently reported elsewhere [8,23], which have a very good glass forming ability (τ_{max} = 10 mm), were used as a baseline to design these quaternary metallic glasses by partial substitution of the alloying elements (mainly Zn or Cu) with Al. The Al addition to these ternary alloys reduces the maximum amorphous thickness; however, it increases glass stability by increasing both T_g and T_x. (For the Ca-Mg-Zn and Ca-Mg-Cu alloys, T_g and T_x values change from 80 to 130°C and from 112°C to 170°C, respectively, depending on the alloy composition [8,23].)

The Cu containing alloys have the critical amorphous thickness within 1 to 3.5 mm range, while the Zn containing alloys have τ_{max} from 1 to 5 mm. When the specimen thickness τ exceeds τ_{max}, the volume fraction of the amorphous phase generally rapidly decreases to zero with a further increase in τ [8,23]. However, in two alloys, $Ca_{60}Mg_{15}Al_{10}Zn_{15}$ and $Ca_{60}Mg_{20}Al_{10}Zn_{10}$, the volume fraction of the amorphous phase, as estimated from the intensities of the X-ray diffraction peaks and the DSC exothermic peaks, remains above 80% in the specimens with thicknesses of up to 10 mm and 8 mm, respectively. In Ca-Mg-Al-Zn alloys, T_g varies from 130°C to 175°C, T_x varies from 176°C to 218°C and both T_g and T_x have a tendency to increase with an increase in the Al content. The Ca-Mg-Al-Cu alloys have smaller values of T_g (124°C to 143°C) and T_x (157°C to 183°C) and, therefore, lower glass stability than the Ca-Mg-Al-Zn alloys. The temperature range of a super-cooled liquid for these quaternary alloys is rather large. For example, in Zn-containing alloys it varies from ΔT_x = 36°C in $Ca_{55}Mg_{20}Al_{19}Zn_6$ to 71°C in $Ca_{60}Mg_{15}Al_{10}Zn_{15}$. In Cu-containing alloys, ΔT_x is between 30°C and 49°C.

Crystallization of these quaternary amorphous alloys is accompanied by a single or multiple exothermic reactions, depending on the alloy composition (see Figures 3 and 4). Melting of these

alloys occurs in a rather wide temperature range and is generally accompanied with several endothermic peaks. For example, the $Ca_{60}Mg_{20}Al_{10}Zn_{10}$ glass, which has the best glass forming ability (τ_{max} = 5 mm), has $\Delta T_l = T_l - T_m$ = 139°C, and the second best glass former, $Ca_{60}Mg_{15}Al_{10}Zn_{15}$, has ΔT_l = 80°C. It is well established for many glass forming systems, including Ca-Mg-Zn [8,24] and Ca-Mg-Cu [23], that the best glass forming alloys have a near-eutectic composition and slow crystallization kinetics. The fact that the majority of the developed Ca-Mg-Al-Zn and Ca-Mg-Al-Cu glassy alloys have a very wide melting range indicate that their compositions are far from the eutectic composition, and even better glass forming ability and larger maximum amorphous thicknesses are expected in optimized alloy compositions with a considerably reduced melting range.

Quintenary Ca-Mg-Al-Zn-Cu alloys. The composition of five quintenary metallic glasses produced in this work is given in Table 1 and their DSC patterns are shown in Figure 5. A very good glass forming alloy, $Ca_{55}Mg_{18}Zn_{11}Cu_{16}$, which has been reported to have a maximum amorphous thickness τ_{max} >10 mm [10], was used as a starting point, and from 5 to 15 % Al, as well as up to 5% Ca, were added to this alloy to partially substitute Cu and Zn and reduce the density. Without Al, this alloy has T_g and T_x of 100°C and 166°C, respectively, and the density of 2.32 g/cc. Substitution of every 1 at.% of Cu and/or Zn with Al and Ca decreases the density of this alloy by ~1% and 1.5%, respectively. For example, the densities of $Ca_{55}Mg_{18}Al_{15}Zn_6Cu_6$ and $Ca_{60}Mg_{18}Al_{15}Zn_3Cu_4$ alloys are 1.99 g/cc and 1.84 g/cc, respectively (see Table 1). However, glass forming ability rapidly reduces with Al addition. For example, partial replacement of Cu in $Ca_{55}Mg_{18}Zn_{11}Cu_{16}$ with 5 at.% Al decreases the τ_{max} to 9 mm in a $Ca_{55}Mg_{18}Al_5Zn_{11}Cu_{11}$ alloy. A further increase in Al to 10 and 15 at.% decreases τ_{max} to 3 mm and 2.5 mm, respectively, in $Ca_{55}Mg_{18}Al_{10}Zn_{11}Cu_6$ and $Ca_{55}Mg_{18}Al_{15}Zn_6Cu_6$ alloys. At the same time, substitution of 5 at.% Al with Ca in the latter alloy leads to a $Ca_{60}Mg_{18}Al_{10}Zn_6Cu_6$ alloy with doubled glass forming ability (τ_{max} = 5 mm) and lower density of 1.94 g/cc (see Table 1). X-ray diffraction patterns of this alloy at different thicknesses are shown in Figure 1c. Only a diffuse amorphous halo is present at t up to 5mm; however, a number of peaks from crystalline phases are present on the X-ray diffraction pattern from a 7-mm thick region. Although it reduces the glass forming ability, addition of Al considerably improves the glass stability by increasing T_g and T_x (see Table 1 and Figure 5). For example, in the alloy $Ca_{55}Mg_{18}Al_{15}Zn_6Cu_6$ T_g and T_x are about 36°C and 11°C

higher than in $Ca_{55}Mg_{18}Zn_{11}Cu_{16}$. The temperature range of super-cooled liquid has a tendency to slightly decrease with an increase in Al and it is in the range of ΔT_x = 41 - 56°C.

Addition of Al changes the crystallization and melting patterns of the $Ca_{55}Mg_{18}Zn_{11}Cu_{16}$ glassy alloy (see Figure 6). Crystallization of the amorphous alloy without Al starts at ~166°C and produces a sharp exothermic peak with a maximum at ~171°C, which is followed by a smaller exothermic peak at ~210°C. Melting of this alloy occurs in a rather narrow temperature range by a single endothermic reaction, indicating that the alloy may have a near eutectic composition. When 5% Cu is substituted by Al ($Ca_{55}Mg_{18}Al_5Zn_{11}Cu_{11}$ alloy), both crystallization peaks become wider and their maxima occur at higher temperatures, 184°C and 235°C, respectively. Such behavior indicates that Al slows down the crystallization kinetics. Melting also occurs at higher temperatures and is accompanied by multiple endothermic reactions within about twice wider temperature range in the melting range.

The first crystallization reaction suppresses to a larger extend with further addition of Al up to 10 and 15 at.% in place of Cu and Zn ($Ca_{55}Mg_{18}Al_{10}Zn_{11}Cu_6$ and $Ca_{55}Mg_{18}Al_{15}Zn_6Cu_6$ glasses), while intensity of the second crystallization reaction almost does not change (see Figure 5). In addition, a third crystallization reaction occurs in these two alloys just prior melting and the melting temperature increases with an increase in Al content. The first melting reaction in the alloys with 10 and 15% Al starts rather slow; the reaction rate gradually increases to a maximum value and then abruptly decreases to almost zero. After that, a weak and shallow melting reaction is observed in a wide temperature range, probably due to gradual melting of a primary phase. Crystallization becomes even more complex in the $Ca_{60}Mg_{18}Al_{15}Zn_3Cu_4$ glass with an increased amount of Ca and at least 5 crystallization exothermic peak are recognized on a DSC pattern of this alloy. The melting range in the quintenary glasses is very wide, between 112°C for $Ca_{60}Mg_{18}Al_{15}Zn_3Cu_4$ and 221°C for $Ca_{55}Mg_{18}Al_{15}Zn_6Cu_6$. This provides an opportunity to design even better glass forming alloys in this system by modifying the composition and reducing the temperature interval for melting (solidification).

Conclusions

Several low density bulk metallic glasses were produced in Ca-Mg-Al, Ca-Mg-Al-Zn, Ca-Mg-Al-Cu and Ca-Mg-Al-Zn-Cu alloy systems. The maximum fully amorphous thickness of t_{max} = 9 mm was achieved in a $Ca_{55}Mg_{18}Al_5Zn_{11}Cu_{11}$ alloy. Two alloys, $Ca_{60}Mg_{20}Al_{10}Zn_{10}$ and

$Ca_{55}Mg_{18}Al_5Zn_{11}Cu_{11}$ have τ_{max} = 5 mm, eleven alloys have τ_{max} from 2 to 4 mm, and 5 alloys have τ_{max} of 1.0 to 1.5 mm. The compositions of these alloys provide efficiently packed cluster structure [Dan to describe]. An addition of Al usually reduces the glass forming ability, but it improves the glass stability by increasing T_g and T_x. The glassy alloys developed in this work have a wide temperature interval for solidification, which indicates that their compositions are rather far from eutectic points. It is therefore expected that even better glass former can be found in these alloy systems by modifying the compositions in order to reduce the solidification temperature range.

Acknowledgements

This work was conducted at the Air Force Research Laboratory, Materials and Manufacturing Directorate, under an on-site contract No. FA8650-04-D-5233.

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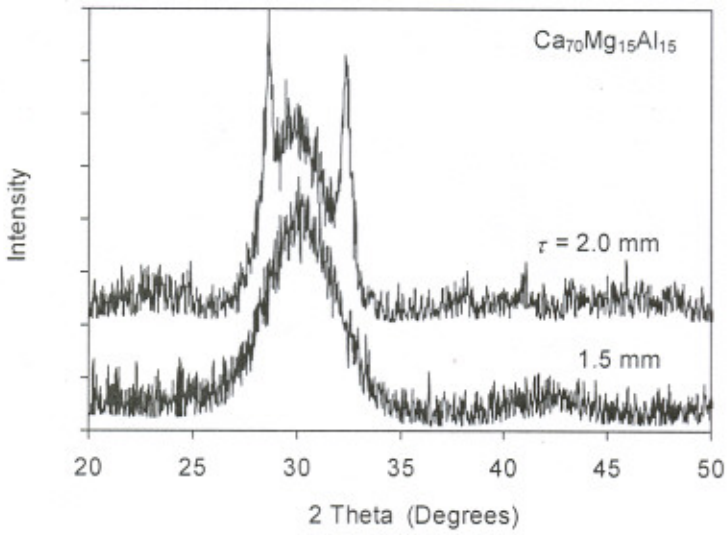
Table 1. Compositions (in at.%) of Ca-Mg-Al-based amorphous alloys and their glass transition, T_g, and crystallization, T_x, temperatures, the temperatures of start, T_m, and completion, T_l, of melting, and heats of crystallization, ΔH_x, and melting, ΔH_m, as well as the maximum thicknesses at which these alloys remain fully amorphous during copper mold casting.

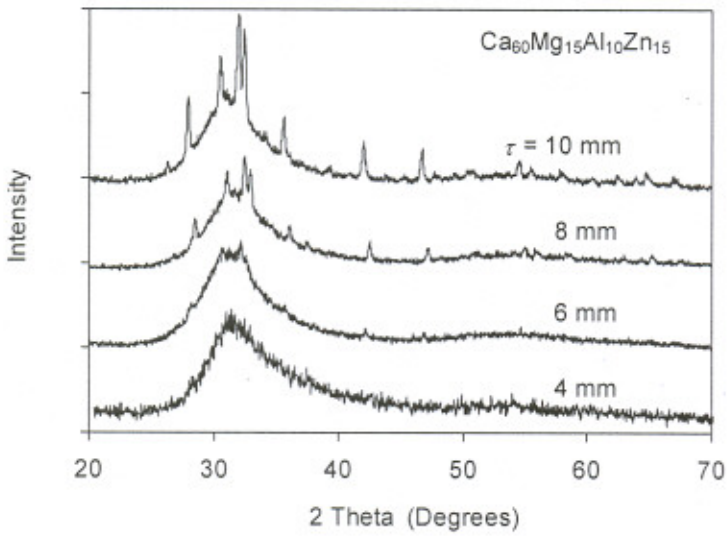
Composition (at.%)	ρ (g/cc)	τ_{max} (mm)	T_g (°C)	T_x (°C)	T_m (°C)	T_l (°C)	ΔH_x (J/g)	ΔH_m (J/g)
$Ca_{50}Mg_{15}Al_{35}$	1.79	<0.5	225	282	485	>600	96	>219
$Ca_{55}Mg_{15}Al_{30}$	1.75	0.5	240	276	473	>600	104	>275
$Ca_{60}Mg_{15}Al_{25}$	1.71	0.7	220	246	454	>600	153	>280
$Ca_{62}Mg_{9}Al_{29}$	1.73	0.5	234	254	475	600	124	309
$Ca_{65}Mg_{15}Al_{20}$	1.68	1.0	190	218	413	503	175	271
$Ca_{70}Mg_{15}Al_{15}$	1.65	1.5	147	187	414	498	146	213
$Ca_{70}Mg_{26}Al_{4}$	1.60	<0.5		225	358	540	-	207
$Ca_{72.5}Mg_{12.5}Al_{15}$	1.64	0.5	144	181	367	508	177	290
$Ca_{75}Mg_{15}Al_{10}$	1.62	0.5	130	152	367	471	113	214
$Ca_{48}Mg_{13}Al_{19}Zn_{20}$	2.26	0.5	163	214	375	540	70	114
$Ca_{55}Mg_{18}Al_{20}Zn_{7}$	1.88	1	174	218	352	549	76	189
$Ca_{55}Mg_{20}Al_{10}Zn_{15}$	2.03	3.5	130	196	358	500	76	179
$Ca_{55}Mg_{20}Al_{15}Zn_{10}$	1.93	2	148	204	334	533	91	262
$Ca_{55}Mg_{20}Al_{19}Zn_{6}$	1.85	1.5	175	211	358	472	92	223
$Ca_{60}Mg_{15}Al_{10}Zn_{15}$*	2.01	4	130	201	350	430	99	124
$Ca_{60}Mg_{18}Al_{15}Zn_{7}$	1.84	2.5	158	212	348	475	110	203
$Ca_{60}Mg_{20}Al_{10}Zn_{10}$♦	1.89	5	130	176	334	473	95	181
$Ca_{50}Mg_{20}Al_{10}Cu_{20}$	2.22	1	138	168	384	458	96	227
$Ca_{50}Mg_{22.5}Al_{5}Cu_{22.5}$	2.27	3.5	143	183	354	489	100	188
$Ca_{60}Mg_{9}Al_{11}Cu_{20}$	2.17	2	128	177	383	484	117	185
$Ca_{60}Mg_{15}Al_{10}Cu_{15}$	2.03	2	124	157	384	537	103	165
$Ca_{60}Mg_{20}Al_{10}Cu_{10}$	1.90	2	135	169	390	544	96	210
$Ca_{55}Mg_{18}Al_{5}Zn_{11}Cu_{11}$	2.22	9	119	175	331	513	114	192
$Ca_{55}Mg_{18}Al_{10}Zn_{11}Cu_{6}$	2.09	3	128	171	341	562	101	228
$Ca_{55}Mg_{18}Al_{15}Zn_{6}Cu_{6}$	1.99	2.5	136	177	360	581	95	293
$Ca_{60}Mg_{18}Al_{10}Zn_{6}Cu_{6}$	1.94	5	134	176	357	530	128	211
$Ca_{60}Mg_{18}Al_{15}Zn_{3}Cu_{4}$	1.84	2	144	195	370	503	123	193

* The alloy is more than 80% amorphous at the thickness of up to 10mm.

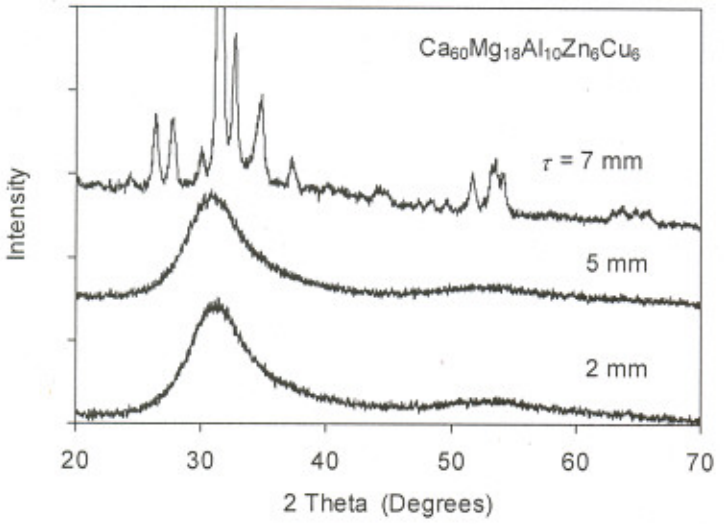
♦ The alloy is more than 80% amorphous at the thickness of up to 8 mm.


$Ca_{70}Mg_{15}Al_{15}$
τ = 2.0 mm
1.5 mm
Intensity
20
25
30
35
40
45
50
2 Theta (Degrees)

(a)

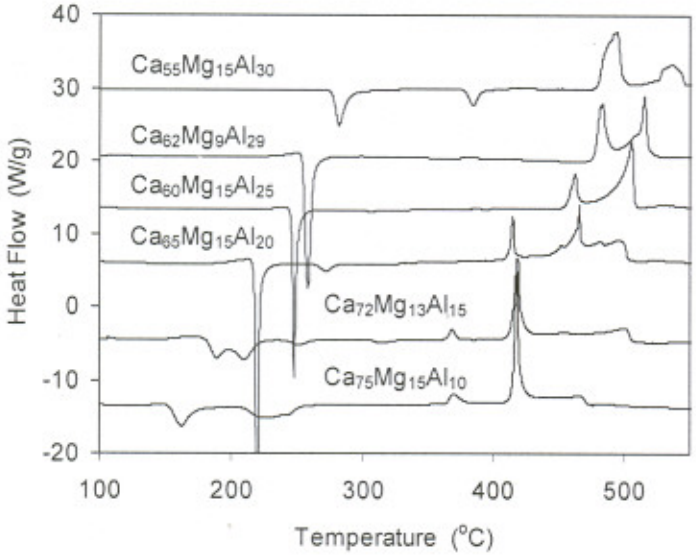

$Ca_{60}Mg_{15}Al_{10}Zn_{15}$
τ = 10 mm
8 mm
6 mm
4 mm
Intensity
20
30
40
50
60
70
2 Theta (Degrees)

(b)

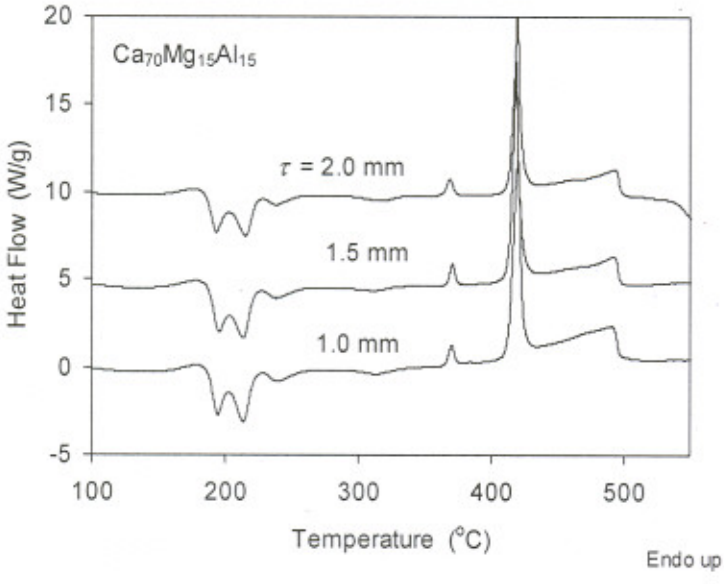


(c)

Figure 1. Typical X-ray diffraction patterns of amorphous and semiamorphous samples extracted from the regions of different thicknesses (shown in the figures) of the copper mold wedge cast alloys (a) $Ca_{70}Mg_{15}Al_{15}$, (b) $Ca_{60}Mg_{15}Al_{10}Zn_{15}$ and (c) $Ca_{60}Mg_{18}Al_{10}Zn_6Cu_6$.



(a)



(b)

Figure 2. DSC patterns of amorphous samples extracted from (a) the regions of the maximum amorphous thicknesses of different Ca-Mg Al- alloys (their compositions are shown in the figure) and (b) the regions of different thicknesses of a $Ca_{70}Mg_{15}Al_{15}$. The wedge-like alloys were prepared by casting in a water-cooled copper mold. The DSC patterns were obtained during continuous heating at a heating rate of 40°C/min and endothermic reactions are directed up.

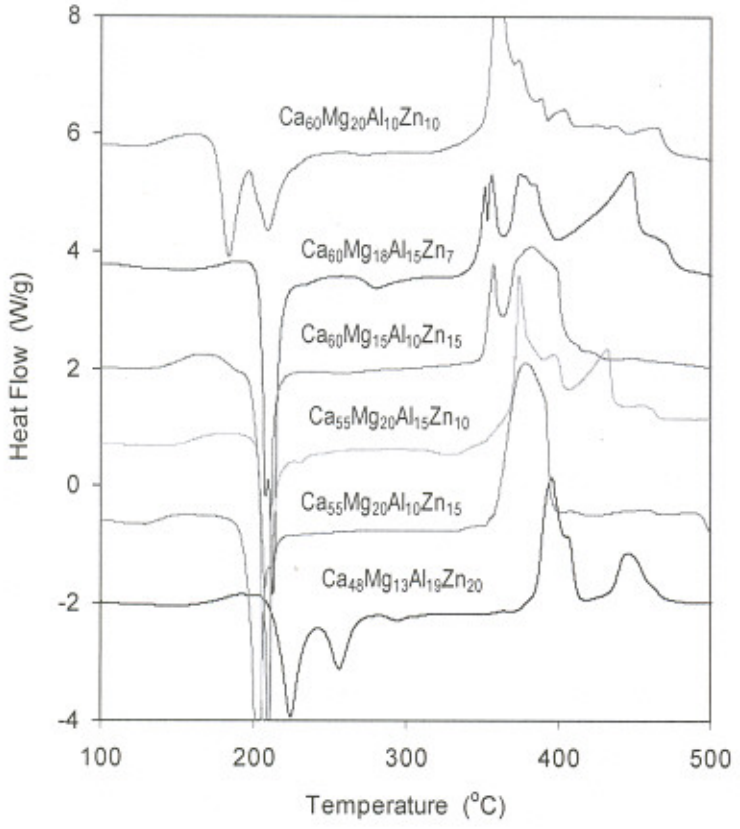


Figure 3. DSC patterns of amorphous samples extracted from the regions of maximum amorphous thicknesses of the copper mold wedge cast Ca-Mg Al-Zn alloys. The alloy compositions are shown in the figure and their glass transition, crystallization and melting temperatures, as well as maximum amorphous thicknesses, are given in Table 1. The DSC patterns were obtained during continuous heating at a heating rate of 40°C/min and endothermic reactions are directed up.

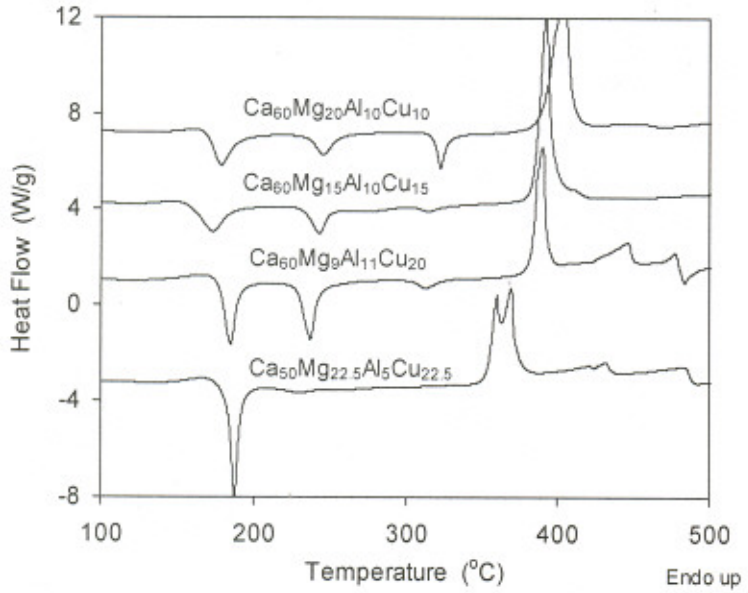


Figure 4. DSC patterns of amorphous samples extracted from the regions of maximum amorphous thicknesses of the copper mold wedge cast Ca-Mg Al-Cu alloys. The alloy compositions are shown in the figure and their glass transition, crystallization and melting temperatures, as well as maximum amorphous thicknesses, are given in Table 1. The DSC patterns were obtained during continuous heating at a heating rate of 40°C/min and endothermic reactions are directed up.

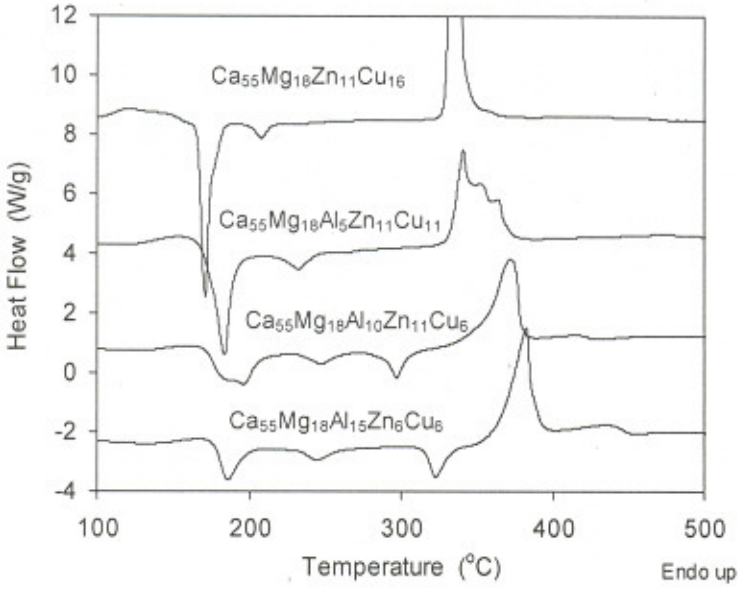


Figure 5. DSC patterns of amorphous samples extracted from the regions of maximum amorphous thicknesses, τ_{max}, of the copper mold wedge cast Ca-Mg Al-Zn-Cu alloys. The alloy compositions are shown in the figure and their glass transition, crystallization and melting temperatures are given in Table 1. A DSC pattern from a base-line $Ca_{55}Mg_{18}Zn_{11}Cu_{16}$ glassy alloy with τ_{max} = 10 mm is also shown. The DSC patterns were obtained during continuous heating at a heating rate of 40°C/min and endothermic reactions are directed up.