COMPARATIVE STUDY BETWEEN TWO DIE CAST METHODS OF PROCESSING BULK METALLIC GLASSES[1]

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Abstract

In this work, two copper mold casting techniques with similar cooling rates were compared: the process with suction casting and the process with centrifugal casting. The suction casting technique has an arc-melting fusion mechanism while the centrifugal casting has an induction heating mechanism. Three samples of three alloys from the Cu-Zr-Al system in a wedge shape were produced by each process. The main characteristics evaluated were the mold-filling ability, the average time per cycle, the oxygen contamination and the maximum thickness on which glassy phase was obtained. The Cu-Zr-Al system was chosen due to its high glass forming ability, which is extensively reported in the literature.The used alloys with nominal compositions were $Cu_{53,5}Zr_{42}Al_{4,5}$, $Cu_{48}Zr_{43}Al_{9}$, $Cu_{42}Zr_{44}Al_{14}$ and $Cu_{43,5}Zr_{43,5}Al_{13}$. The wedge shape was chosen because it allows evaluation of different thicknesses (hence cooling rates) at the same sample. Results revealed that the copper mold centrifugal casting had a higher contamination by oxygen, whilst the mold-filling ability was similar in both processes. Also, the average time per cycle was higher and the maximum thickness in which glassy phase could be obtained was lower, for the centrifugal casting. A brief analysis considering the oxygen contamination on these alloys is also presented here, revealing the extreme importance of the control of this parameter.

Key words: Amorphous phase; Metallic Glasses; Processing; Rapidly quenching.

ESTUDO COMPARATIVO DO PROCESSAMENTO DE LIGAS METÁLICAS VÍTREAS DE GRANDE VOLUME POR COQUILHAMENTO

Resumo

No presente trabalho foi realizado um estudo comparativo do processamento de ligas metálicas vítreas de grande volume por dois processos de fundição em coquilha: fusão por arco elétrico com vazamento por sucção e fusão por indução com vazamento por centrifugação. Foram avaliadas as características do processo e do produto, tais como o preenchimento do molde, a contaminação de oxigênio, o tempo médio por ciclo, sendo a principal característica a espessura máxima da amostra com estrutura vítrea formada. Foram utilizadas quatro composições do sistema Cu-Zr-Al: $Cu_{53,5}Zr_{42}Al_{4,5}$, $Cu_{48}Zr_{43}Al_{9}$, $Cu_{42}Zr_{44}Al_{14}$ e $Cu_{43,5}Zr_{43,5}Al_{13}$. As ligas foram preparadas a partir de elementos puros e processadas em coquilhas com geometria na forma de cunhas em tréplicas aplicando as duas rotas de fundição. Os resultados mostraram que a contaminação por oxigênio e o tempo médio por ciclo foram maiores no processo de vazamento por centrifugação, enquanto que a qualidade do preenchimento do molde foi similar nos dois processos. A espessura máxima da amostra com estrutura vítrea foi maior naquela processada por vazamento por sucção.

Palavras-chave: Metais amorfos; Metais vítreos; Processamento; Fundição em coquilha.

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1 INTRODUCTION

The processing of metallic glasses was restrained to thin layer samples, ribbon shaped, up to 1990 when the copper mold casting method started to be used(1). Although previously reported in the literature(2), this versatile method of producing bulk samples was not widely explored before. Since then, alloys of different systems were processed by the copper mold casting to acquire a glassy structure.

It is important to recall that the composition of the alloy and the cooling rate are both extremely important to determine its glass forming ability (GFA) under a specific processing technique. Some thick samples of over 1 cm were obtained by the copper mold casting process on Fe-based(3) or Ti-based(4)alloys and over 2 cm for other systems such as Zr(5) or Cu(6) and many others reported so far(7,8). This breakthrough in metallic glass processing gave, for the first time, the perspective of conforming items of dimensions up to a few centimeters. Items of this size greatly increased the application field of metallic glasses(9). Many fields have nowadays more sophisticated applications for bulk metallic glasses, such as the production of microgears(10) in the microengineering of motors and machines or in the biomedical applications for implants(11).

The Cu-based bulk metallic glasses(BMG) are cheaper than most other systems . They have a large compressive strain that reaches up to 18% together with an high maximum compressive stress of over 2200 MPa(12). Allied to that, the GFA of the Cu-based BMG is high enough to allow samples over 1 cm thick to be produced(13). Those BMGs, when under load, unlike other alloys, suffer work-hardening and not work-softening(12), which is essential for structural applications. But its most impressive property is to exhibit ductility under tension at room temperature(14). Those characteristics make this alloy an important candidate for practical applications in structural areas as the micro engineering cited before.

The major problem concerning applying those bulk metallic glasses in industrial parts is the processing stage. The research made in the area used mostly high vacuum chambers with minimal oxygen and other atmosphere gases contamination during the process. This, and the use of high purity elements, creates an unfeasible practical situation, nearly impossible to reproduce in a major scale. This work aims to connect the acquired information obtained for those Cu-Zr-Al alloys with low vacuum processes with a cycle time of around 20 minutes to 1 hour and a half. The two studied processes were the copper mold suction casting with arc melting and copper mold centrifugal casting with inductive melting.

2 MATERIALS AND METHODS

Using topological instability and average electronegativity difference criteria(15), four compositions with high glass forming ability of the Cu-Zr-Al system in the Cu-rich region were chosen for this study. Those compositions were divided between the two tested copper mold casting processes: suction (CMSC) and centrifugal (CMCC). A schematic view of both processes as well as the copper mold used in both processes can be seen in Figure 1.

In the CMCC process, the smaller crucible was made of high-alumina recovered by yttrium oxide (for details, see de Oliveira, 2009(16)).In the CMSC process, the crucible was made of copper.

Three samples of three alloys were produced by each process, what means that two alloys were made by both processes. The studied nominal compositions were

$Cu_{53,5}Zr_{42}Al_{4,5}$(CMSC and CMCC), $Cu_{48}Zr_{43}Al_{9}$(CMSC and CMCC), $Cu_{42}Zr_{44}Al_{14}$(CMSC) and $Cu_{43,5}Zr_{43,5}Al_{13}$(CMCC). The used ingot for each process was previously prepared in a high vacuum and Ti-gettered arc-melter, using high purity Cu and Al (99,999%) and medium purity Zr (99,2%).

Both processes occurred under an argon atmosphere prepared with a previous vacuuming. A low vacuum system, utilizing an ordinary mechanical pump, was used in both cases. This diminishes considerably the processing time and cost associated with the high vacuum.

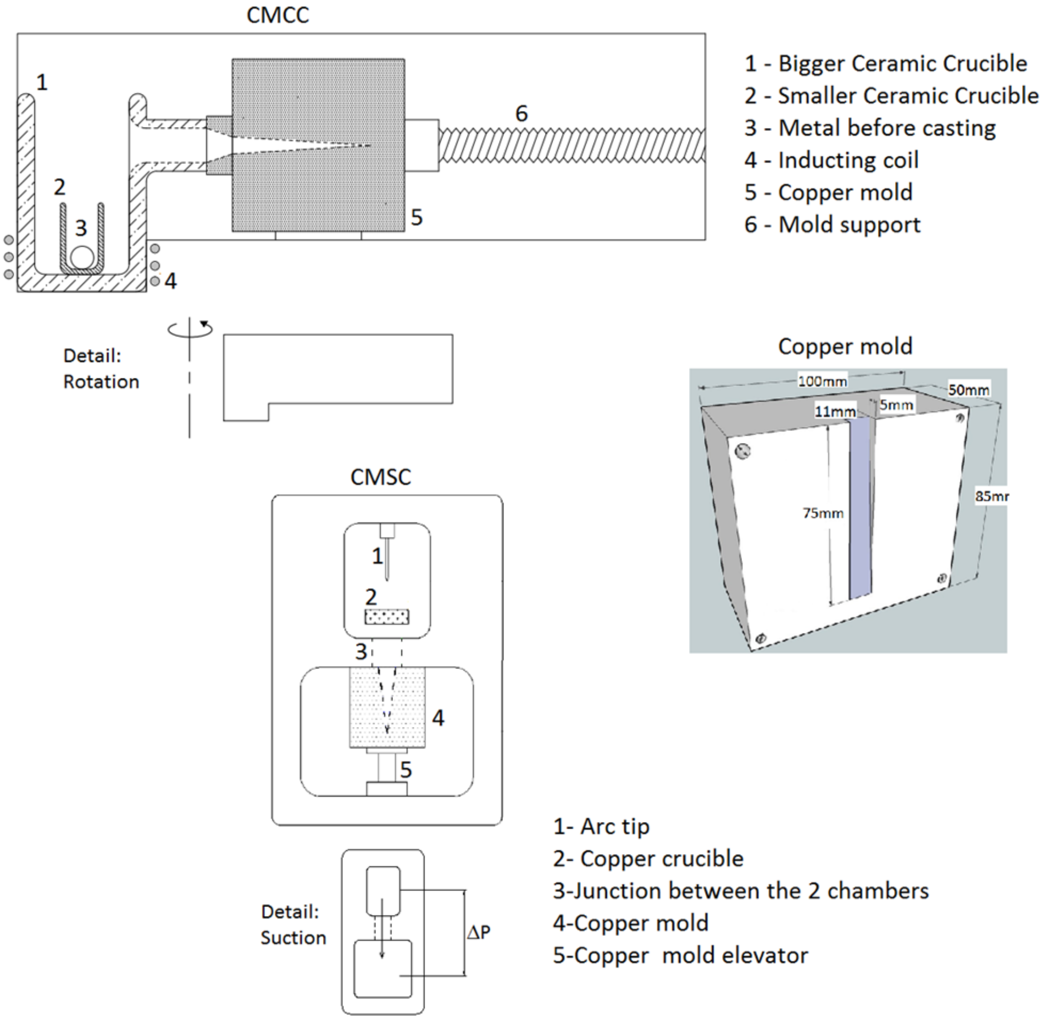

Figure 1. Schematic View of (a) CMCC (b) CMSC and (c) copper mold used in both processes.

The copper mold used for both processes was the same: a wedge-shaped mold with dimension varying from 0 to 10mm thickness, 11mm width and 75mm length. This mold was chosen once it can evaluate, in the same sample, different cooling rates characteristic to each thickness.

All samples were analyzed by scanning electron microscopy (SEM), differential scanning calorimetry (DSC) under a 40 K/min heating rate and by X-ray Diffraction (XRD), using Cu-Kα radiation. The samples for the XRD analysis consisted of cross sections in a range of thicknesses. The resulting small areas led to some interference but it was still possible to identify the diffraction peaks when they appeared. All the SEM images were taken using the backscattering electrons detector (BSE).

3 RESULTS AND DISCUSSION

The processing of the CMCC and CMSC wedge shaped samples took different times and required different amounts of materials. Although those parameters are directly related to the size of the used equipment, it is worth noting that the size of the chamber required to use the CMCC is necessarily higher, what leads to a higher raw materials cost (Argon) and time of processing once vacuuming the chamber takes more time. Furthermore, the amount of material that remains in the crucible is also higher in the CMCC process what requires more material to be spent in order to produce a sample. Those processing characteristics can be summed in Table 1, where the time per cycle and amount of required material is presented.

Table 1. Characteristics of the used processes

Process	Time per cycle	Amount of required material
CMSC	20 minutes	15 grams
CMCC	1 hour and 30 minutes	30 grams

Clearly the CMSC present some advantages. A minor time per cycle ensures higher productivity and the minor material loss diminishes the overall producing cost. Besides that, the CMCC process requires two ceramic crucibles. The first one is bigger, has almost no contact with the fused metal, and leads the melt to the copper mold when the centrifugal process starts. Into this crucible, goes the smaller one, which has an intense contact with the liquid metal during the fusion process. This smaller one cannot be reused and the bigger one cannot be utilized more than two cycles, contributing to an even higher production cost, since the copper crucible in the CMSC is fully reusable. Another problem associated with the ceramic crucible usage is the limit imposed to the heating rate once that it may break if the heating rate is too high, this results in a prolonged time in high temperatures, where oxidation is more accentuated.

The mold-filling ability of both processes was similar. Both were able to fill properly the wedge mold. Although the tip was not entirely homogeneous, the wedges presented a relatively smooth surface as illustrated in Figure 2.

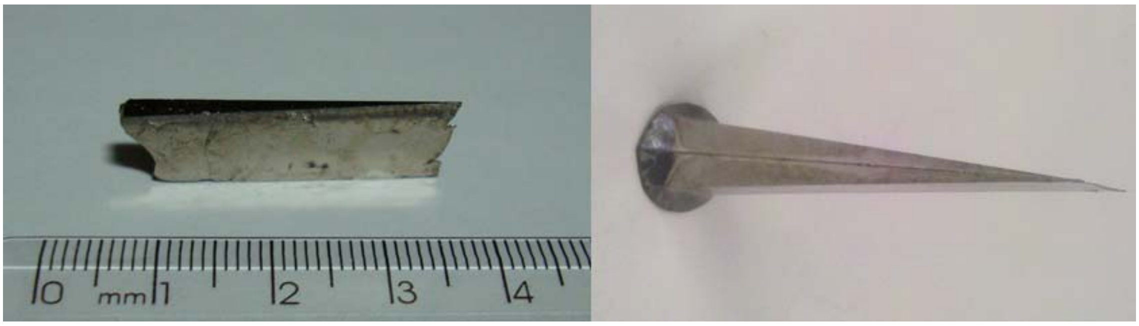

Figure 2. A transversally cut wedge-shaped sample obtained by the CMSC process (left) and an integral wedge-shaped sample obtained by the CMCC process (right).

Figure 2 also illustrates that the sample is broken in the thicker part. Most samples fractured in a certain position, always above the maximum glassy thickness.

The SEM results of the samples showed a different behavior than those reported in literature for similar compositions(13).

The maximum thickness in which a sample was still fully glassy among all samples of all compositions was around 2.5 mm, an order of magnitude below expected. On the other hand, alloys revealed distinct patterns of phase, which seems to be function of the sample composition and thickness. The Cu rich ($Cu_{53,5}Zr_{42}Al_{4,5}$) presented the highest maximum fully glassy thickness where no other phase could be seen. For higher thicknesses, dendritic phases appeared, and for even higher thicknesses, the matrix apparently was also crystalline. This behavior can be seen in Figure 3.

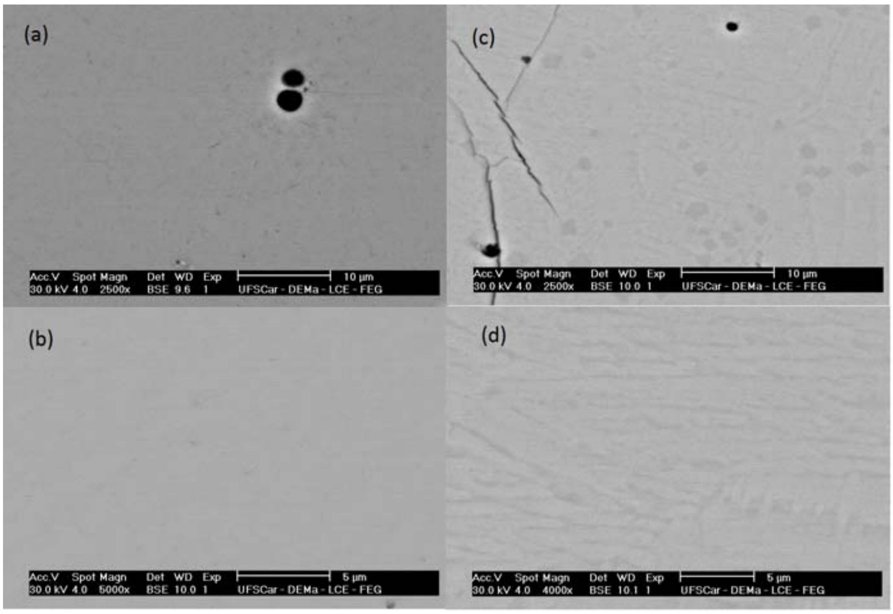

Figure 3. $Cu_{53,5}Zr_{42}Al_{4,5}$sample processed by the CMSC, with thicknesses: a) 1 mm, b) 2.75 mm and 3,2 mm for c and d.

The Al rich ($Cu_{42}Zr_{44}Al_{14}$ and $Cu_{43,5}Zr_{43,5}Al_{13}$) alloys revealed the lowest maximum glassy thickness without dendritic shaped phases. The microstructure changed drastically from no visible phases to many small phases. This behavior can be seen in Figure 4.

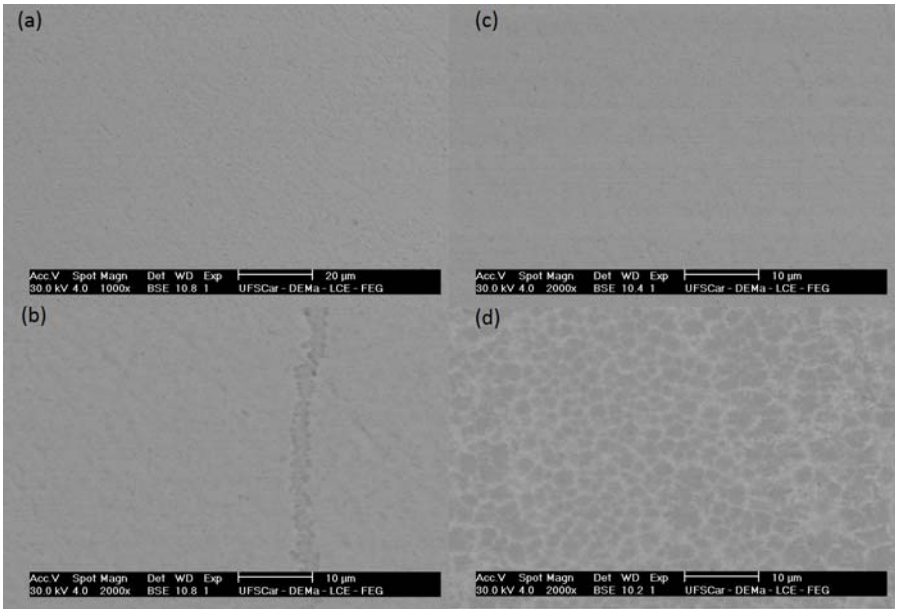

Figure 4. $Cu_{42}Zr_{44}Al_{14}$ sample processed by the CMSC, with thicknesses: a) 0.2 mm, b) 0.3 mm, c) 0.5 mm and d) 0.9 mm

The intermediate composition ($Cu_{48}Zr_{43}Al_9$) was the closest to the reported in literature(13),which has enough GFA to reach over 1 cm thick by copper mold casting processing. However, this composition was not the one with best glass forming ability analyzed in this study. The obtained samples of this alloy had a similar behavior to the Cu-rich alloys but they presented dendritic phases for almost all thicknesses, where the concentration grew along it. It is important to note that all the dendritic phase found had a maximum size about 15 microns for all analyzed thicknesses. This pattern can be seen in Figure 5.

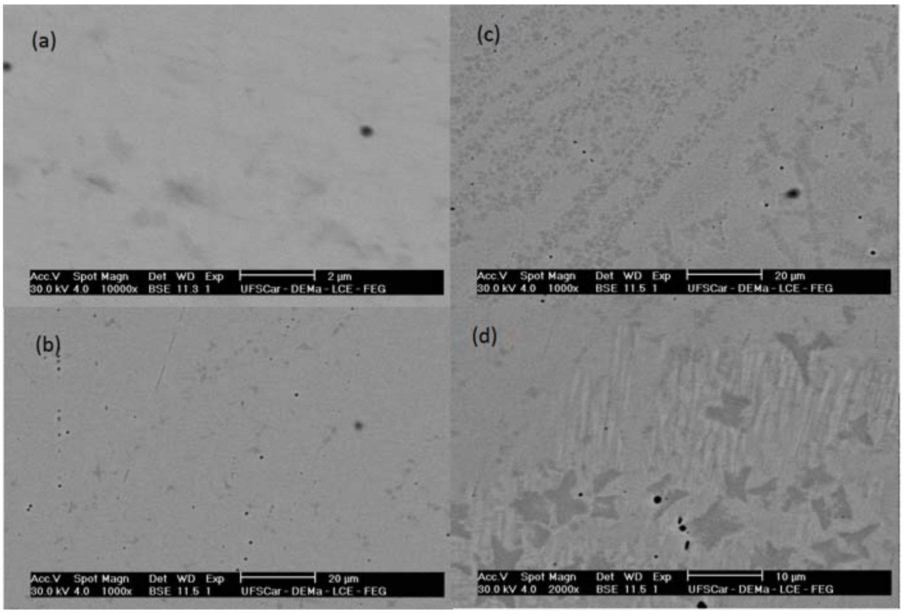

Figure 5. $Cu_{48}Zr_{43}Al_9$ sample processed by the CMSC. The thickness of each micrograph is a) 0,75 mm, b) 1,5 mm, c) 2,0 mm and d) 2,7 mm.

All the micrographs presented in Figures 3 to 5 were taken from samples processed by the CMSC technique. The reason is because all samples processed by the CMCC technique had the same behavior, but the all thicknesses where crystalline phases started to appear were lower. Therefore the maximum glass thickness obtained was lower for all CMCC samples.

XRD analysis were carried out in all samples for different thicknesses and the results confirmed what the SEM micrographs revealed: Cu-rich wedge samples and intermediate composition samples have 3 distinct regions: the first one (thinner) is composed by a fully glassy structure, the second one is composed by a crystalline phase inside of a remaining glassy matrix and the final one (thicker) is fully crystalline. The diffractograms in figure 6 reveals these 3 distinct regions.

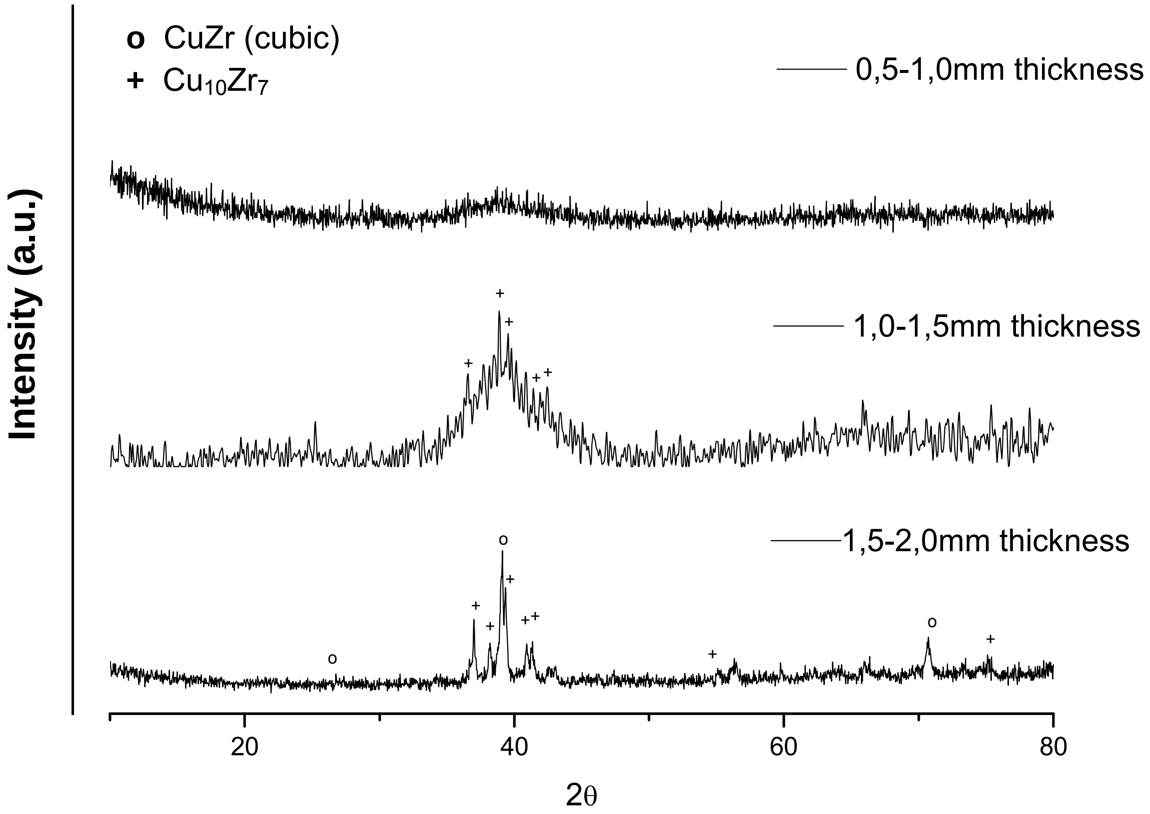

Figure 6. $Cu_{48}Zr_{43}Al_9$ sample processed via CMSC with the 3 well distinct regions.

The diffratograms revealed the presence of the $Cu_{10}Zr_7$ and CuZr phases, depending on the composition and on the thickness. Table 2 summarizes the results concerning maximum thicknesses with predominant glassy phase.

Table 2. Maximum glassy thickness obtained by each process

Alloy	Process	Maximum Glassy Thickness
$Cu_{53,5}Zr_{42}Al_{4,5}$	CMSC	2.5 mm
	CMCC	0.6 mm
$Cu_{48}Zr_{43}Al_9$	CMSC	1.5 mm
	CMCC	< 0.5 mm
$Cu_{42}Zr_{44}Al_{14}$	CMSC	0.5 mm
$Cu_{43,5}Zr_{43,5}Al_{13}$	CMCC	<0.5 mm

The thermal exchange conditions favors, if any, the cooling rate for the CMCC: the centrifugal force that acts to increase the contact of the melt to the mold wall during solidification is substantially bigger than the equivalent suction pressure that acts in the CMSC process. It cannot therefore explain why the results showed the CMSC process leading to thicker samples of metallic glass.

The oxygen contamination was then examined as an alternative explanation. Measurements were made in two samples processed by each technique and the results can be seen in Table 3.

Table 3. Oxygen contamination in the samples

Alloy	Process	Oxygen content (wt%)	Oxygen content (at%)
$Cu_{53,5}Zr_{42}Al_{4,5}$	CMSC	800 ppm	0.36
	CMCC	1600 pmm	0.72
$Cu_{48}Zr_{43}Al_9$	CMSC	600 ppm	0.27
$Cu_{43,5}Zr_{43,5}Al_{13}$	CMCC	1800 ppm	0.79

The results clearly show that besides minor differences in oxygen content between samples conformed by the same process, the oxygen contamination is intrinsically higher at the CMCC process. Therefore, the results revealed that the oxygen has a devastating effect on the GFA of Cu-based alloys of the Cu-Zr-Al system. Literature reports the effect of oxygen content in the crystallization resistance of Zr based alloys of the Cu-Zr-Al system(17,18) and also on the GFA leading to the creation of an oxygen induced *big cube*phase(15) or even the formation of quasicrystals containing oxygen that act as nucleating agents to the Zr_2Cu phase(18). But no references were found in the literature concerning Cu-based alloys in presence of oxygen discussing what phases are formed and what is the crystal nucleating mechanism. The only reference found citing oxygen values(12)report a contamination of 180 ppm what is considerably lower than the values found in this study. The levels of oxygen contamination found here can, in principle, be the reason of the difference between the maximum glassy thickness in this work is lower than those reported before(13).

The DSC scans revealed the typical transitions of glassy phases such as the crystallization temperature T_x and glass transition temperature Tg of the alloys for each process. It is reported(20) that higher oxygen contents in Zr based alloys leads to lower values of T_g. On this study, for the samples with high oxygen content (processed via CMCC), the Tg was not clear and the crystallization peak was diminished, as illustrated in Figure 7. This figure compares two samples processed via CMSC with another processes via CMCC at the same thickness of the sample.

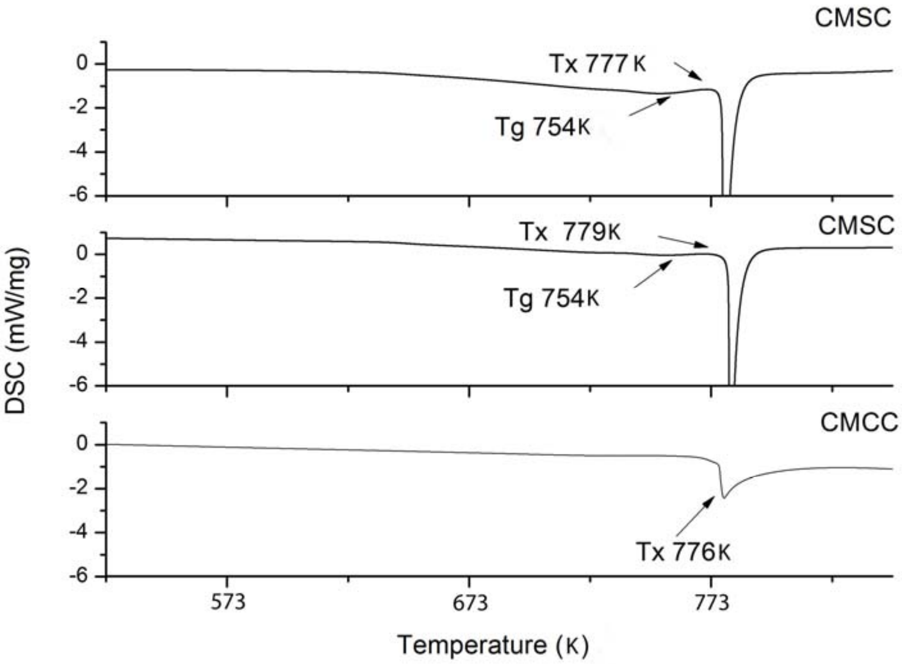

Figure 7. DSC analysis of samples of $Cu_{53,5}Zr_{42}Al_{4,5}$ alloy.

Table 4 compares the results between the T_x, T_g, T_m and T_l temperatures found for the four alloys analyzed. It is clear that the oxygen contamination altered completely their solidification behavior. The values for T_g and T_x are in the same range of those found in literature(13), but the value of $\Delta T_x = T_x - T_g$ is considerably lower. While the value found for the sample of over a centimeter thickness is of 80K, the value found in this study is just 40 K, what is consistent with the information that the oxygen reduces the supercooled region of metallic glasses of Cu-Zr-Al system(18). The T_l found for the $Cu_{48}Zr_{43}Al_9$ also matches the value found for a similar composition of 1.190 K(18).

Table 4. Important temperatures from DSC analysis

Alloy	Process	T_g (K)	T_x (K)	T_m(K)	T_l(K)
$Cu_{53,5}Zr_{42}Al_{4,5}$	CMSC	754	778	1142	1197
	CMCC	-	776		
$Cu_{48}Zr_{43}Al_9$	CMSC	720	760	1141	1198
	CMCC	-	759		
$Cu_{42}Zr_{44}Al_{14}$	CMSC	728	748	1136	1223
$Cu_{43,5}Zr_{43,5}Al_{13}$	CMCC	-	773	1138	1204

4 CONCLUSIONS

Both processing routes studied here, the copper mold suction casting (CMSC) and copper mold centrifugal casting (CMCC), were able to produce Cu-based BMG samples of different compositions, with glassy structures and dimensions up to 2.5 mm. The processing characteristics put the CMSC process in advantage for practical uses due to its operational conditions (less time per cycle, smaller time of fusion and smaller chamber volume). These conditions also contributed for a lower oxygen contamination.

The oxygen content in Cu-based alloys of the Cu-Zr-Al system has a devastating effect on the glass forming ability (GFA) and on the solidification behavior leading to the nucleation of primary phases during the solidification at lower cooling rates, mainly the cubic CuZr and the $Cu_{10}Zr_7$.

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