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Consolidation of the $Cu_{46}Zr_{42}Al_7Y_5$ Amorphous Ribbons and Powder Alloy by Hot Extrusion

***Ana Karla Melle*[a], *Mauricio Mhirdaui Peres*[b]*, *Claudemiro Bolfarini*[a],**
***Walter José Botta*[a], *Alberto Moreira Jorge Jr.*[a], *Claudio Shyinti Kiminami*[a]**

[a]*Science and Materials Engineering Post Graduation Program, Department of Materials Engineering, Federal University of São Carlos – UFSCar, Rod. Washington Luiz, Km 235, CEP 13565-905, São Carlos, SP, Brazil*
[b]*Federal University of Itajubá – UNIFEI, Rua São Paulo, 377, CEP 37500 903, Itabira, MG, Brazil*

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The amorphous $Cu_{46}Zr_{42}Al_7Y_5$ alloy presents large supercooled liquid region (ΔT_X = 100 K), with a viscosity of about 10^6 N.s/m^2 where the material can flow as a liquid, making it possible an easy deformation in this temperature region. The aim of this work was to analyze processing routes to produce bulks of metallic glasses. Two kinds of materials were used: amorphous powders and ribbons, both were consolidated by hot extrusion in temperatures inside the range between T_g and T_x, with a ram speed of 1 mm/min and extrusion ratio of 3 : 1. Analysis of X-Ray Diffratometry (XRD), Differential Scanning Calorimetry (DSC) and Scanning Electron Microscopy (SEM), revealed that the proposed consolidation routes were effective to produce large bulks of amorphous materials, even with the strong decreasing of ΔT_X observed after deformation by milling and during extrusion.

Keywords: *amorphous copper alloys, hot extrusion, metallic glass*

1. Introduction

Bulk metallic glasses (BMG) of copper based alloys show a scientific and engineering importance due to its higher strength and ductility[1-3]. Strength of 2265 MPa and ductility up to 18% are reported for this alloy at room temperature[4]. Among the binary copper alloys, the Cu-Zr system has the highest glass-forming ability (GFA), among which $Cu_{46}Zr_{54}$ has a critical casting thickness up to 2 mm[5-7]. The presence of aluminum, in the ternary $Cu_{50}Zr_{45}Al_5$alloy, increases the GFA and the critical casting thickness can be increased up to 3 mm. This alloy shows a large supercooled liquid region ($\Delta T_x = T_x - T_g$), ΔT_x = 72 K, and a high reduced glass transition temperature ($T_{rg} = T_g/T_l$), T_{rg} = 0,61[8]. Some quaternary Cu-based alloys, such as those belonging to the Cu-Zr-Al-(Nb, Y, Gd)[9,1,10] and to the Cu-Zr-Hf-Al[8] systems, presented a higher GFA. Cu-Zr-Al-Y system, have been shown unusual high GFA[1] $Cu_{46}Zr_{42}Al_7Y_5$ alloys have shown critical casting thickness up to 1 cm and a ΔT_x of around 100 K[1]. Large ΔT_x is an important feature because when metallic glasses are deformed inside this temperature region they exhibit homogeneous deformation with significant plasticity[11] without crystallization. Considering these aspects, large BMGs can be produced by consolidation from amorphous powders[12] or directly from amorphous ribbons. In this article, such kinds of materials were consolidated by extrusion; in temperatures inside the supercooled liquid region to compare their microstructural characteristics and thermal behaviors.

*e-mail: peresmm@yahoo.com.br

2. Experimental

Ingots of the $Cu_{46}Zr_{42}Al_7Y_5$ alloy were prepared by arc melting under a titanium-gettered high-purity argon atmosphere. The ingots were produced from high purity elements Cu (99.99+%), Zr (99.5%), Al (99.99+%) and Zr (99.9%) after ultrasonically cleaning and mixing. To ensure compositional homogeneity, the ingots were melted several times. The alloys were then remelted in a melt spinning equipment to produce ribbons. For the first route, the ribbons were ball milled with ball-to-powder ratio of 20 : 1, rotation speeds of 150 rpm (during 1 hour) and 250 rpm (in the subsequent 8 hours), resulting in amorphous powders with mean diameter of about d_{50} = 106 μm. For the second route, small chips of 3 mm length were cut from the ribbons. Cylindrical pre-forms of the powders and of the ribbon chips were obtained by cold pressing at room temperature with uniaxial pressure of 1 GPa and then hot extruded in temperatures between Tg and Tx (671, 683 and 688 K), ram speed of 1 mm/min and extrusion ratio of 3 : 1, producing samples with a diameter of 4.5 mm. The structural characterization was performed by X-ray diffraction (DRX) in a Siemens D5005 diffractometer with CuKα radiation, and scanning electron microscopy (SEM) in a FEI-XL 30 FEG. The glass transition (T_g) and crystallization (T_x) temperatures were determined by differential scanning Calorimetry and scanned using a Netzsch DSC 200F3 Maia at a rate of 0.33 K/s. The mechanical properties were analysed by using Vickers hardness test.

3. Results and Discussion

Figure 1a shows the extruded sample of amorphous ribbon and the Figure 1b shows the extruded sample of amorphous powder, both at 688 K. In both cases rigid extruded samples were produced.

Figure 2 shows the XRD patterns of the ribbon, powder and extruded samples. All of them exhibit only characteristic amorphous peak without any detectable crystalline phases. This indicates that a single amorphous phase was kept after milling and after consolidation processes.

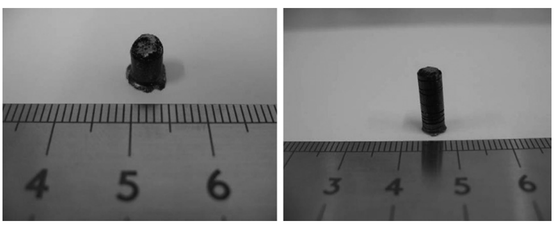

Figure 1. Extruded samples of $Cu_{46}Zr_{42}Al_7Y_5$ alloy using a) amorphous ribbons (T = 688 K) and b) amorphous powder (T = 688 K).

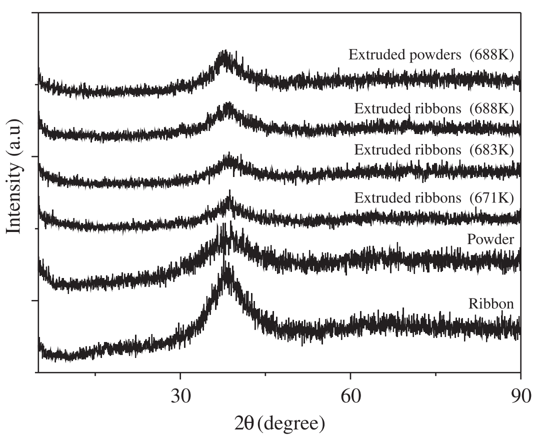

Figure 2. XRD patterns of ribbon, powder and extruded samples of $Cu_{46}Zr_{42}Al_7Y_5$.

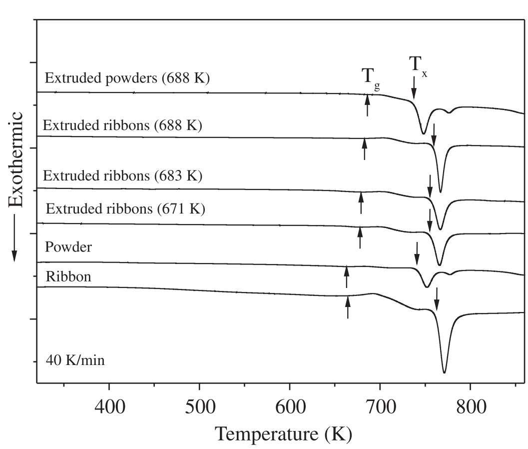

Figure 3. DSC curves of ribbon, powder and extruded samples of $Cu_{46}Zr_{42}Al_7Y_5$. The amount of 20 mg was used for each sample.

Figure 3 shows typical crystallization DSC curves. Each of the traces exhibits endothermic event, characteristic of the glass transition, and a distinct undercooled liquid region, followed by one or two exothermic events, characteristic of crystallization processes. As also observed by other authors[13], the presence of two crystallization peaks for the powders indicates differences between the routes concerning the type and magnitude of the phases and/or the relative thermodynamic instabilities of the different phase and phase combinations due to the introduction of mechanical energy into the system, during the milling process. The exothermic peak seen before the glass transition is the result of annihilation of excess free volume. Hence, it is possible to estimate the relative changes (due either to heat treatments or to deformation) in the free volume by monitoring its intensity (or enthalpy). From Figure 3 it is also possible to observe that, even with deformation, the annihilation of free volume in all events involving powders was higher than for the ribbons. Really, the as-received ribbon had the highest excess of free volume. The free volume was also decreased after the ribbon extrusion. Probably this was due to the annealing produced or during the extrusion process or during the milling in the case of the powders. However, considering only the extrusion process, the reduction of free volume was more intense for the ribbons than for the powders that appeared to be kept constant.

Table 1 shows the obtained values for T_g, T_x and ΔT_x. As the expected, the results show a large supercooled liquid region for the ribbon (ΔT_x = 98 K) and for the powder (ΔT_x = 77 K), in agreement with the results reported by Xu[1]. By comparing the thermal behavior of the ribbon and the powder it is possible to observe that there is no significant difference between T_g's values (663 K for ribbon and 664 K for powder) and considerable differences between T_x's and, consequently, between ΔT_x's, with the smallest values presented for the extruded amorphous powder. Comparing powder and ribbon with extruded samples, it can be noted that the extrusion processes caused more significant variation in T_g values. For extruded samples using ribbons, T_g was increased in about 14 K and T_x was decreased in about 7 K, reducing ΔT_x from 98 K to 77 K. For sample obtained through powder consolidation, the T_g increasing was 23 K and the T_x decreasing was 4 K, decreasing ΔT_x in more than 27 K. This behavior can be

Table 1. The parameters of T_g, T_x, ΔT_x for ribbon, powder and extruded samples of $Cu_{46}Zr_{42}Al_7Y_5$.

$Cu_{46}Zr_{42}Al_7Y_5$	Extrusion temperature (K)	T_g (K)	T_x (K)	ΔT_x (K)
Ribbon	-	664	762	98
Powder	-	663	740	77
Extruded sample (ribbon)	671	678	755	77
Extruded sample (ribbon)	683	679	756	77
Extruded sample (ribbon)	688	683	759	76
Extruded sample (powder)	688	686	736	50

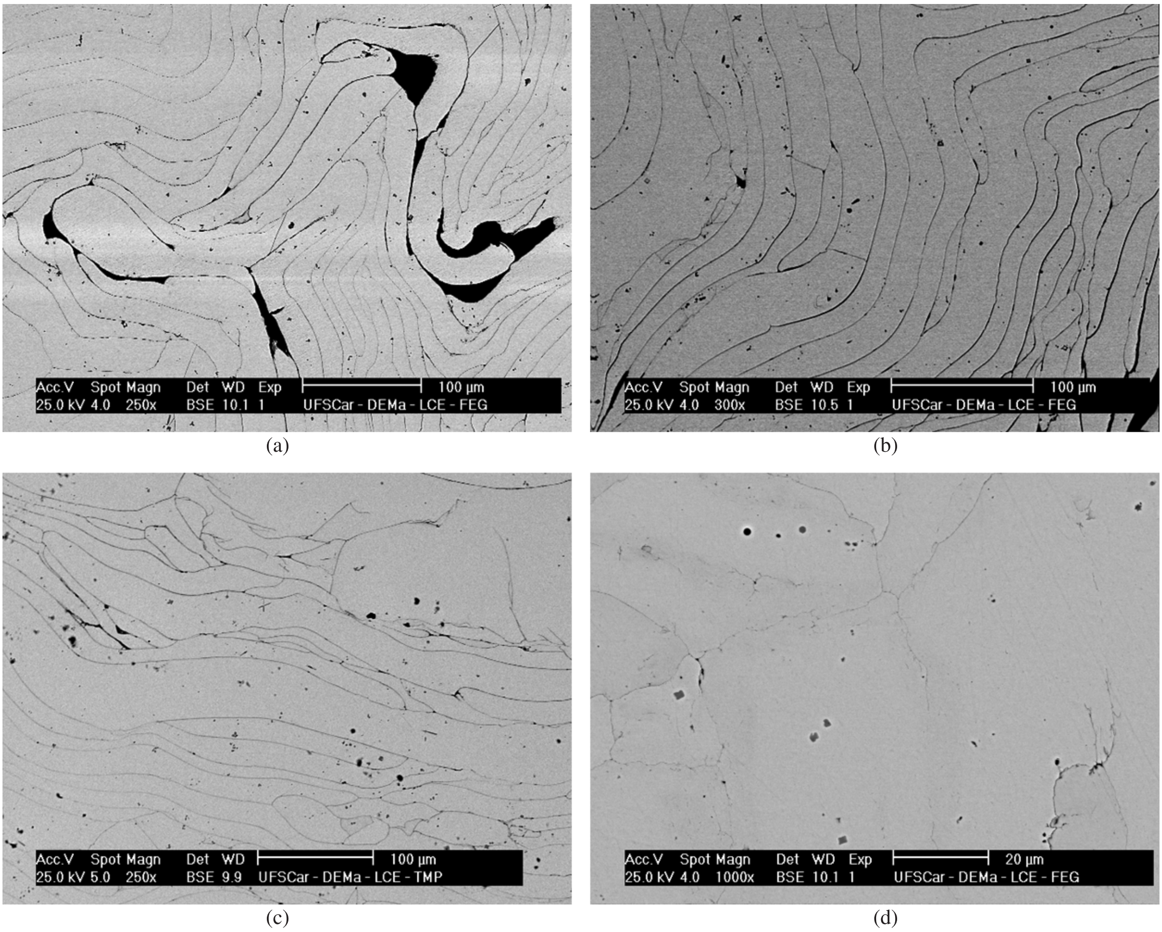

Figure 4. SEM images of extruded samples of $Cu_{46}Zr_{42}Al_7Y_5$, a) extruded ribbons (671 K), b) extruded ribbons (683 K), c) extruded ribbons (688 K), d) extruded powers (688 K).

explained by the evolution of the free volume during the processing routes. There are three processes that can change the local free volume concentration: diffusion, annihilation, and generation. The diffusion of free volume is analogous to the diffusion of vacancies in crystalline materials. The free volume is redistributed by diffusion until it is spatially uniform. In crystalline materials, vacancies can annihilate at certain locations, such as grain boundaries and dislocations, where the structural requirement of crystalline translational symmetry is relaxed. In metallic glasses, this requirement does not exist and free volume can annihilate at any position simply by the atomic rearrangement. The annihilation of free volume decreases the total free volume and the metallic glasses become denser after annihilation. As discussed before, after milling or after annealing during the extrusion process, there was a reduction of free volume, leading to more dense materials and so advancing the critical temperature of crystallization

Figure 4 shows SEM images of the extruded samples. In agreement with other authors[11], the consolidated amorphous powder and ribbons with large ΔT_x were deformed inside this temperature region exhibiting homogeneous deformation with significant plasticity. So is expected that can be produced by hot consolidation some fragmented materials with large BMGs, as the consolidation of amorphous powder[12]. By comparing powder and ribbon consolidation, it is possible to observe that the extruded ribbons were not fully consolidated (Figures 4a-c) and that its porosity decreased with the increasing of the temperature. Fully consolidation was achieved for the extruded powders (Figure 4d), probably due to the greater surface area, which produced more contact points between particles.

The results obtained from the hardness tests showed that it was obtained 623 HV for the extruded powders and 508 HV for the extruded ribbons at the same extrusion temperature that directly reflects the achieved porosity in such condition. Also, due to the highest amount of free volume in the ribbons, the reduction of hardness in such condition can suggest that nanovoids could be formed, due to the coalescence of the excess free volume during plastic deformation, and this could also be the reason for the observed lower hardness presented by the ribbons.

4. Conclusions

In summary, bulk metallic glasses of $Cu_{46}Zr_{42}Al_7Y_5$ were produced by extrusion process, using amorphous powder and ribbons. The more important results are:

- The extrusion parameters (temperature and ram speed) led to an adequate processing window, resulting in fully extruded amorphous samples;

- The milling method promoted strong decreasing of T_x probably due to the annealing produced during the milling process;
- The microstructure of extruded powders showed lower porosity with better bonding than the extruded ribbons; and
- The hardness value was higher for the ingots produced by the powder extrusion (623 HV) than for the ingots produced by the ribbons extrusion (508 HV) due to the higher porosity and to the generation of nanovoids produced by the coalescence of the excess free volume in the ribbons.

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