

## Manufacturing, Mechanical and Electrochemical Characterization of Zr-Based Amorphous Ribbons

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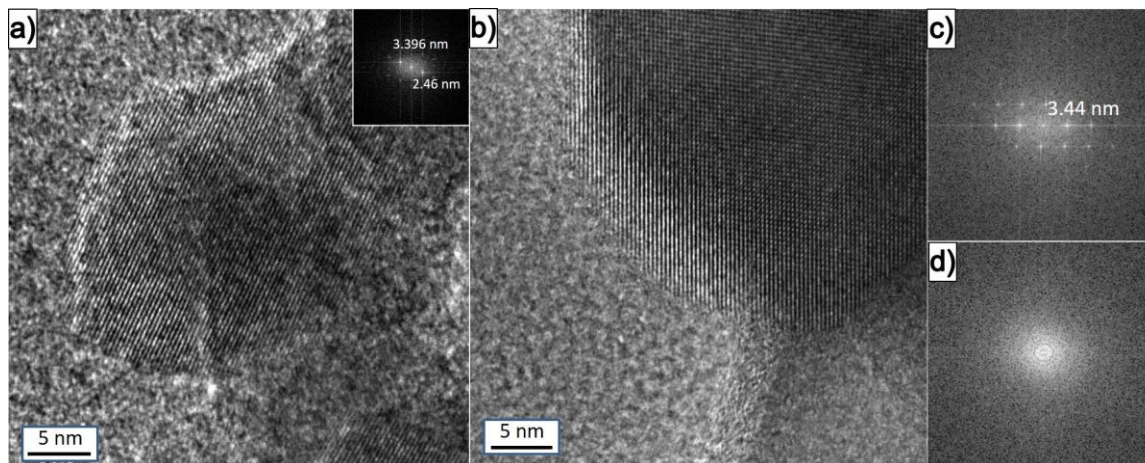
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Bulk metal glasses (BMG) have excellent properties such as high elasticity, mechanical strength, wear resistance and corrosion; due to its long-range order structure which does not contain defects such as dislocations and grain boundaries. Zr-based BMGs are among the most researched glass formation systems, because their Zr base element is highly biocompatible; these have a hardness approximately two or three times greater than that of conventional biomedical 316 L steel and that Ti alloys; as well as a high elastic limit. For these characteristics that are promising candidates for biomedical applications [1-4].

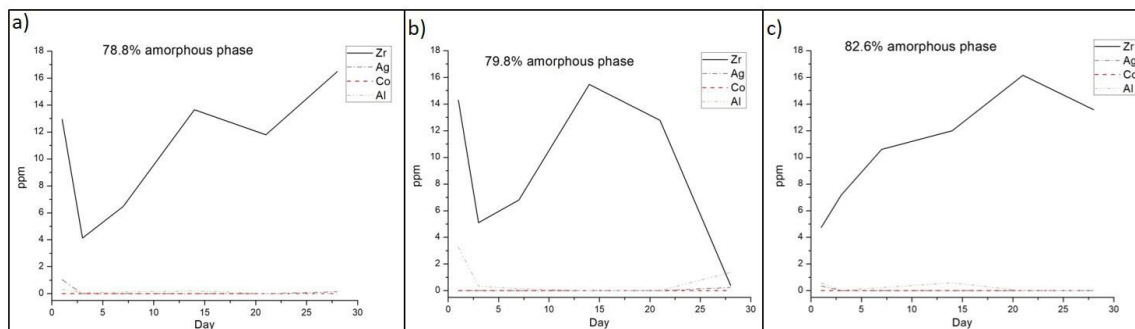
In this work three  $Zr_{58}Co_{21}Al_9Ag_{12}$  glassy alloys ribbons were obtained using a chill block melt spinner (CBMS) by varying the tangential speed of the cooling disk as well as the melting cast nozzle diameter, getting crystalline phase fractions for the 3 conditions close to 20%. The ribbons were characterized by TEM (Phillips Tecnai F20) to identify the phase structures. The surfaces of the tapes were observed in a scanning electron microscope (JEOL FEG-SEM 7600F). A simulated body fluid immersion test (SBF) with a pH of 7.4 was performed, in accordance with the ASTM-G31-72 standard to evaluate the inducing capacity of apatite. The phases after immersion were characterized by XRD (Bruker D8), identifying the presence of Ca and P, which could favor the precipitation of phosphates and accelerate the deposition process of apatite on the surface; carbonate-hydroxyapatite was found, which is the objective of the immersion test. The presence of some aluminum phosphates and oxides was also identified, that may come from the reaction between SBF with the ribbons, because the aluminum oxide suffers pitting in the presence of chlorides.

Figure 1a) shows a high resolution image of transmission electron microscopy (HRTEM) corresponding to the ribbon with 78.8% amorphous phase, for which the inter-planar distances corresponding to the planes (111) of  $ZrO_2$  and (312) of  $Al_2O_3$  of a crystalline domain are identified from the fast Fourier transform. Figure 1b) shows a HRTEM image of the ribbon with 82.6% amorphous phase with its respective FFT, where the presence of a crystalline zone and an amorphous zone indicated in c) and d) respectively is clearly observed; the interplanar distance corresponding to the planes (111) of  $ZrO_2$  is identified from the crystalline zone. The presence of  $ZrO_2$  and  $Al_2O_3$  is due to the content of highly oxylic elements Zr and Al in the  $Zr_{58}Co_{21}Al_9Ag_{12}$  alloy, which produce oxidation of the surface, forming these metal oxides. It has been reported that Zr-based BMGs have a passive layer of natural oxide ( $ZrO_2$ ), which is associated with good biocompatibility and corrosion resistance in the physiological environment [5-7]. Likewise, the presence of these metal oxides allows a much higher hardness than that of the Zr-based alloy, which contributes to their good wear resistance [8].

Figure 2 shows the graph corresponding to the measurement of the concentration of metal ions released for all three ribbons using a plasma atomic emission spectrometer (Agilent Technologies 4100 MP-AES), finding a high concentration of Zr (26,295 ppb) attributed to the effect of the chloride ions contained in the solution that are preferably absorbed by chemical and physical defects on the surface of the ribbons, leading to the selective dissolution of the amorphous phase, so it is important to consider; the concentration of Al and Ag is within the limits of toxicity and Co was null in all cases.



**Figure 1.** a) HRTEM image of a ribbon with a 78.8% amorphous phase of the Zr<sub>58</sub>Co<sub>21</sub>Al<sub>9</sub>Ag<sub>12</sub> alloy with insertion in the upper right corner of its fast Fourier transform indicating the interplanar distances of 3.396nm corresponding to the planes (111) of ZrO<sub>2</sub> and 2.46nm for (312) of Al<sub>2</sub>O<sub>3</sub>. Figure 1 b) HRTEM image of a ribbon with an 82.6% amorphous phase of Zr<sub>58</sub>Co<sub>21</sub>Al<sub>9</sub>Ag<sub>12</sub> alloy, c) fast Fourier transform indicating the interplanar distance corresponding to the planes (111) of ZrO<sub>2</sub> and d) fast Fourier transform of an amorphous zone.



**Figure 2.** Ion release graphs corresponding to ribbons with a) 78.8% amorphous phase, b) 79.8% amorphous phase and c) 82.6% amorphous phase.

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