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Strategy for preventing excessive wear rate at high loads in bulk metallic glass composites

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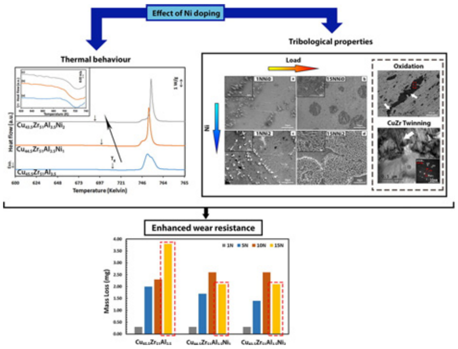
HIGHLIGHTS

- Small Ni addition decreases the glass transition temperature of the Cu-Zr-Al alloy.
- The mass loss during the wear test increases with increasing load from 1 to 10 N.
- The friction temperature can be close to the glass transition temperature.
- Partial crystallization and oxidation results in wear resistance increase.

GRAPHICAL ABSTRACT



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ABSTRACT

The effect of nickel additions to tune the wear performance of $Cu_{45.5}Zr_{51}Al_{3.5}$ at.% alloy has been studied to present a new strategy for preventing excessive wear rate at high loads in metallic glass composites. This strategy consists on proper selection of a doping element in controlled concentrations with the ability to decrease the glass transition temperature (T_g) of the alloy so that the friction temperature during sliding is close to the T_g. This enables the formation of crystalline phases and their subsequent oxidation (lubricating layer) on the contact surface during sliding thus enhancing the wear resistance. Proper doping can also contribute towards the wear resistance when the content of the doping element promotes the martensitic transformation. The results show that the main wear mechanism for the three studied alloys ($Cu_{45.5}Zr_{51}Al_{3.5}$, $Cu_{44.5}Zr_{51}Al_{3.5}Ni_1$ and $Cu_{43.5}Zr_{51}Al_{3.5}Ni_2$ at.%) is governed by delamination and the mass loss increases with increasing load from 1 to 10 N. However, for the maximum load of 15 N, the calculated friction temperature is close to T_g for the Ni-containing alloys and partial crystallization and oxidation take place resulting in a mass loss decrease from about 2.6 mg (at 10 N) to about 2.1 mg (at 15 N).

1. Introduction

Bulk metallic glasses (BMGs) are interesting materials due to their unique chemical and physical properties. Due to the combination of high hardness and high strength metallic glasses are expected to exhibit superior wear resistance and therefore they are promising materials for

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tribological applications. Higher values of the wear resistance were reported when BMGs are annealed [1] or when proper volume fractions of crystalline phases are embedded in the amorphous matrix (i.e., BMG composites) [2] for multiple alloy systems such as Fe-based [3], Zr-based [4] and Cu-based alloys [5]. The wear resistance can also be increased when a dissimilar/oxide layer is formed on the sliding interface of Ti-based [6], Zr-based BMGs [7] and on metal surfaces in general [8].

Previous studies suggest that during dry sliding, surface oxidation can occur when the contact temperature is near the glass transition temperature (T_g) [7] and above T_g [9] due to the high oxygen permeability of the oxide film formed in the supercooled liquid region where the viscosity drops. Additionally, the lack of long-range order inherent to amorphous materials can lead to microstructural changes during contact sliding, changing the wear performance of the material [6,10]. In this regard, contact temperature plays a central role in the wear performance of metallic glasses [6,11]. Insufficient temperature to promote crystallization can lead to super-plasticity and softening of the material, increasing the wear rate of the BMG [12] but when the temperature is high enough to result in microstructural changes, the wear rate decreases [13].

The wear rate not only depends on the volume fraction of crystalline phases embedded in the amorphous matrix [2] but also on their nature. Among these crystalline phases, shape memory phases are of interest since they exhibit stress induced martensitic transformation. Erosion resistance of martensite is superior to that of austenite [14], which can explain the interest in promoting the formation of martensite. An efficient method to do that is doping (i.e., microalloying) using elements such as Fe, Co and Ni because when added in the proper concentrations they can decrease the stress for transformation of CuZr austenite into CuZr martensite [15,16]. As a result, BMG composites with CuZr martensite phase embedded in the amorphous matrix are of interest to enhance the wear resistance.

The aim of this study is to propose a new strategy to decrease the wear rate of BMG composites at high loads based on controlled doping to promote partial surface crystallization and oxidation while at the same time promoting martensitic transformation of the crystalline phase. This strategy is expected to have important implication in the design of Micro-Electro-Mechanical Systems (MEMS) such as microgears and microbearings, where wear resistance enhancement is primordial to extend their service life [17,18]. We have shown that the friction temperature (ΔT_{max}) can be estimated from the equation given by Wu et al. [19] and that it gives sensible values to compare with the glass transition temperature of the doped alloy to be able to estimate whether the alloy will exhibit massive wear ($\Delta T_{max} << T_g$) or decreased wear ($\Delta T_{max} \geq T_g$).

2. Experimental

Alloy ingots of nominal composition $Cu_{45.5}Zr_{51}Al_{3.5}$, $Cu_{44.5}Zr_{51}Al_{3.5}Ni_1$ and $Cu_{43.5}Zr_{51}Al_{3.5}Ni_2$ (at.%) were prepared from elements with purity higher than 99.9 at.%. The master alloys were remelted three times in a Ti-gettered high purity argon atmosphere to attain good chemical homogeneity. Rod samples of 2 mm in diameter were obtained from the master alloy by copper mould casting in an inert gas atmosphere. The structure of the as-cast samples was studied by X-ray diffraction (XRD) using a Bruker D8 diffractometer with monochromated Cu Kα_radiation (2θ range 20°–90°, step size = 0.03°). Thermal behaviour of the samples were studied using differential scanning calorimetry (DSC, SETARAM C131 EVO) at a constant heating rate of 20 K/min up to 773 K. The microstructure was investigated by scanning and transmission electron microscopy (SEM and TEM respectively). Dry sliding wear experiments were conducted using a pin-on-disc (DUCOM Micro POD) in dry conditions in air at room temperature following the ASTM-G99. The pins were made from BMG composite rods and the counterbody disc was En 31 steel hardened to 60 HRC and ground to 1.6 μm (Ra) surface roughness. Tests were performed at increasingly loads of 1, 5, 10 and 15 N at a sliding velocity of 0.5 m/s for a sliding distance of 1800 m. Mass loss was obtained by measuring the weight of the pins after and before the tests by using an analytical balance (Acculab Sartorius group, ±0.1 mg).

3. Results and discussion

3.1. Microstructure of the as-fabricated pins

Fig. 1 shows the XRD patterns for the three compositions selected in this study. For the $Cu_{45.5}Zr_{51}Al_{3.5}$ alloy (Fig. 1a), the scan shows the presence of peaks that could be associated with orthorhombic $Cu_{10}Zr_7$ (a = 0.9347 nm, b = 0.9347 nm, c = 1.2675 nm), orthorhombic Cu_8Zr_3 (a = 0.78686 nm, b = 0.81467 nm, c = 0.9977 nm), austenite B2 CuZr (a = 3.2562 nm, b = 3.2562 nm, c = 3.2562 nm), monoclinic martensite B19′ CuZr (a = 0.3237 nm, b = 0.4138 nm, c = 0.5449 nm) and tetragonal $CuZr_2$ (a = 0.3220 nm, b = 0.3220 nm, c = 1.1183 nm). These peaks are superimposed on a broad halo, suggesting the presence of an amorphous matrix. For the $Cu_{44.5}Zr_{51}Al_{3.5}Ni_1$ alloy (Fig. 1b), the scan is very similar but an additional small peak at 56.5° is observed, which could be attributed to CuZr martensite. For the alloy with 2 at.% Ni content (Fig. 1c), the main peak detected at 39.3°, corresponding to $Cu_{10}Zr_7$, Cu_8Zr_3 and $CuZr_2$, decreases in intensity while for the peak at 29.7°, attributed to Cu_8Zr_3, increases. These results suggest that there is no clear trend in the evolution of the glass forming ability (GFA) with the composition change.

The thermal behaviour of the three compositions was studied by running DSC scans at 20 K/min up to 765 K (Fig. 2). The glass transition temperature (T_g), crystallization onset temperature (T_x), super-cooled liquid region (ΔT) and crystallization enthalpy (H) have been measured and listed on Table 1. The T_g was evaluated from the tangent crosspoint while the crystallization enthalpy (ΔH) was obtained by integrating the area under the exothermic peak. For $Cu_{45.5}Zr_{51}Al_{3.5}$ alloy $T_g = 710.84$ K and H = 47.05 J/g while a small addition of Ni to 1 at.% lowers the T_g to 697.77 K and H to 49.08 J/g. Further addition of Ni to 2 at.% decreases the T_g to 685.39 K and the enthalpy decreases slightly to 42.54 J/g. The decrease of T_g would suggest that the amorphous structure becomes destabilized with increasing Ni content, which could be attributed to the positive heat of mixing with Cu (Ni-Cu: +4 kJ/mol). On the other hand, the heat of mixing of Cu-Zr is negative (−23 kJ/mol) [20] and therefore increasing Ni addition, which has unfavourable mixing relationships with Cu, would promote the formation of intermetallic Cu-Zr phases, which agrees with higher intensity of the XRD peak for Cu_8Zr_3 detected at about 30° (Fig. 1).

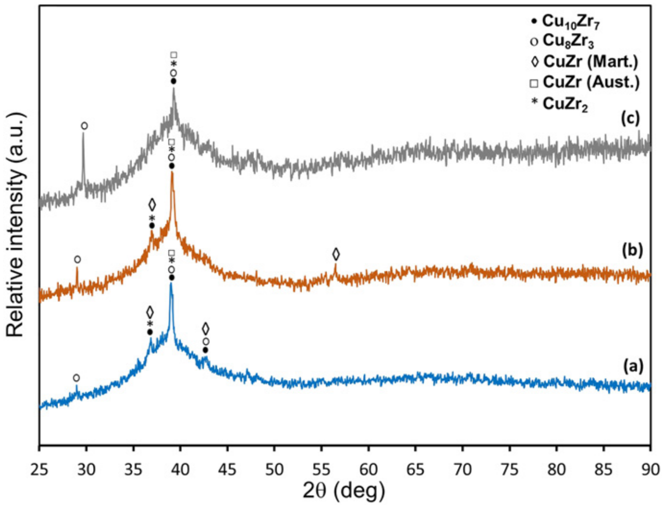

Fig. 1. XRD scans for (a) $Cu_{45.5}Zr_{51}Al_{3.5}$, (b) $Cu_{44.5}Zr_{51}Al_{3.5}Ni_1$ and (c) $Cu_{43.5}Zr_{51}Al_{3.5}Ni_2$ at.% alloys.