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Mechanical Spectroscopy Study of the $Cu_{36}Zr_{59}Al_5$ and $Cu_{54}Zr_{40}Al_6$ Amorphous Alloys

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A mechanical spectroscopy study of Cu-Zr-Al bulk metallic glasses, was performed with two types of equipment: a Kê-type inverted torsion pendulum and an acoustic elastometer, working in the frequency ranges of Hz and kHz, respectively, with a heating rate of 1 K/min. The analysis of the anelastic relaxation shows similar spectra for both types of equipment resulting in internal friction patterns that vary with temperature and are not reproducible at each thermal cycle. The normalized of the square of the frequency changes from the first to later measurement cycles. These results indicate that the specimens of Cu-Zr-Al alloys were changing by mechanical relaxation, owing to the motion of atoms or clusters in the glassy state and possible "defects" produced during the processing of alloys.

Keywords: *bulk metallic glasses, amorphous alloys, glass transition temperature, mechanical spectroscopy, internal friction, anelastic relaxation*

1. Introduction

In recent years, the study of multicomponent glass-forming alloys has been of great scientific and technological interest for their unique properties, due to the lack of long-range regularity in their atomic structure and compositional homogeneity similar to the liquid state. These alloys show better mechanical properties, superior corrosion resistance and high yield stress and fracture toughness, compared to their crystalline counterparts[1-4].

Bulk metallic glasses produced by very rapid solidification, usually exhibit a non-equilibrium structure, so that heating the material to below its crystallization temperature leads to an atomic rearrangement to a more stable state. This phenomenon is known as structural relaxation, which is manifested by a continuous change in some physical properties[5]. The free volume model, initially proposed by Cohen and Turnbull[6] and later used by Spaepen[7] to describe the kinetics of annihilation of frozen-in free volume is the most commonly used to explain the relaxation process in metallic glasses. Other studies in metallic glasses has shown that interstitialcy theory of condensed matter (ITCM)[8,9] may be related that structural relaxation below glass transition temperature (T_g). This structural relaxation can be understood as a decrease of the concentration of interstitialcy-like defects frozen-in upon glass production in which the concentration depends on the quenching temperature[10,11].

In order to understand the behavior of structural relaxation in the metallic glasses, many methods of characterization have been used, such as differential scanning calorimetry, measurement of electrical resistivity, ultrasound and Brillouin scattering among others[12-15]. Thus, methods that involve internal friction measurements, whose magnitude is related to mechanical energy loss due to phase transformations or by interaction with defects in the material commonly used in crystalline alloys[16,17], can be of great interest in the study of the transition from the glassy to crystalline state in bulk metallic glasses[18].

Taking into account that the internal friction (IF) is a structure sensitive physical property, in the present study, Cu-Zr-Al bulk metallic glasses have been characterized by mechanical spectroscopy, by using two systems, working in the flexural and torsional mode, operating in frequency ranges of Hz and kHz, respectively.

2. Experimental Procedure

Bulk metallic glasses of nominal compositions $Cu_{36}Zr_{59}Al_5$ and $Cu_{54}Zr_{40}Al_6$ were chosen for study, by combining the criteria of the minimum topological instability and the average electronegativity ($\lambda_{min}\cdot\Delta\bar{e}$) in the Cu-Zr-Al system[19,20]. At first, crystalline buttons were obtained by fusion of high pure materials (Cu, Zr, Al) in arc-melting under ultrapure argon atmosphere and Ti-gettered. Next, the $Cu_{36}Zr_{59}Al_5$ sample was melted again in a furnace (Discovery Plasma: EDG) and the bulk metallic glasses were obtained by the push-pull skull casting technique. The $Cu_{54}Zr_{40}Al_6$ sample, provided by Institute of Materials Research at Tohoku University, was melted in a quartz nozzle with a high-frequency induction furnace and cast into a copper mold[21]. The amorphous nature of the samples was verified by X-ray diffraction (XRD), thermal properties of the alloys were characterized by differential

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scanning calorimetry (DSC) at a heating rate of 40 K/min and the anelastic behavior was characterized by mechanical spectroscopy, using two experimental apparatus: a Kê-type inverted torsion pendulum and an acoustic elastomer system, operating in the Hz and kHz bandwidths respectively.

The acoustic elastometer system (Vibran Technologies, AE 102 model) operates in a frequency range of 20 Hz to 20 kHz, with a frequency resolution bether than 10^{-6} and strain amplitude of 10^{-7} and 10^{-5}, measuring the mechanical damping (internal friction) between 10^{-6} and 10^{-1}, with a temperature resolution better than 1% in the temperature range of 293 K to 873 K. A flexural vibration was applied to rectangular samples with dimensions of $20.00 \times 6.00 \times 0.70$ mm^3. The principle of detection used by this system is a capacitive sensor and the modulated frequency method, where the capacitance between the surface of the specimen and the excitation electrode is part of a high-frequency oscillator, whose frequency is therefore modulated by the vibration of the specimen. The internal friction is obtained from the decay of the free oscillations of the specimen.

Measurements in the Kê-type inverted torsion pendulum, which operates in the frequency range of 1 to 10 Hz, have both a frequency and an internal friction resolution around 10^{-6} and 10^{-4}, respectively. A torsional vibration is induced in rectangular test-peace of dimensions $32.00 \times 1.00 \times 1.00$ mm^3, by current pulses in two electromagnets that release energy in the material due to internal friction arising in the the piece and the system, which is measured from the decay in oscillation amplitude of the sample.

The Internal Friction (IF) was determined by the logarithmic free decay δ, of the envelope of the measured amplitude signal $Q^{-1} = \delta / \pi$. There are a relationship between the flexural and torsional vibrations $f^2 \propto E$ and $f^2 \propto G$, respectively. Here f is the oscillation frequency of the specimen, E is the Young modulus and G the shear modulus[16].

3. Results and Discussions

Figure 1 shows the DSC traces for the two alloys, obtained at a heating rate of 40 K/min. Both thermograms show a clear glass transition temperature (T_g) at 658 K and 730 K, followed by a strong exothermic reaction at 729 K and 807 K, for $Cu_{36}Zr_{59}Al_5$ and $Cu_{54}Zr_{40}Al_6$ respectively, which characterizes the onset of crystallization (T_x). The supercooled liquid temperature range, defined as $\Delta T_x = T_x - T_g$, which represent the thermal stability and usually is considered a good indicator of the glass-forming ability of an alloy[22], is 71 K and 77 K for the two alloys tested.

Figure 2 shows the XRD patterns corresponding to $Cu_{36}Zr_{59}Al_5$ and $Cu_{54}Zr_{40}Al_6$ bulk metallic glasses in the as cast condition, exibiting a broad diffuse halo characteristic of amorphous structure in both patterns. However, some superposed sharp peaks can be seen in the $Cu_{36}Zr_{59}Al_5$ patterns, corresponding to metastable or nanocrystalline phases in which it is possible to identify the Zr_4Cu_2O phase known as "big cube"[23], suggesting a heterogeneous microstructure, such as a composite with an amorphous matrix.

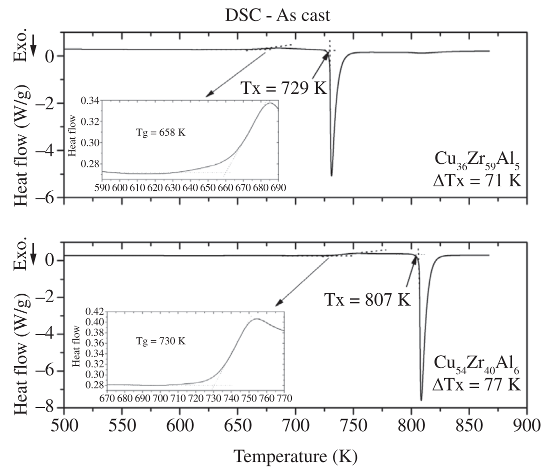

Figure 1. DSC thermograms of the alloys $Cu_{36}Zr_{59}Al_5$ and $Cu_{54}Zr_{40}Al_6$ alloys at a heating rate of 40 K.min^{-1}. The inset illustrates the definition of T_g.

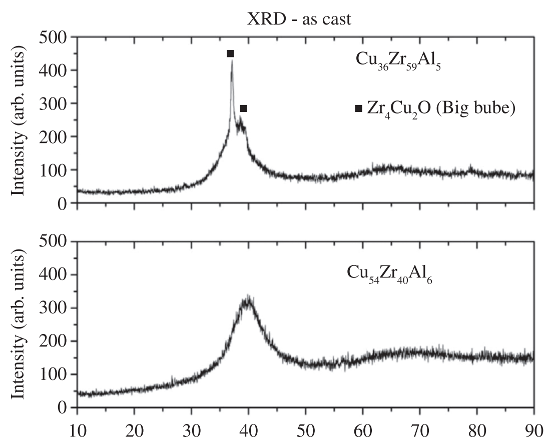

Figure 2. X-ray diffraction patterns for the composite $Cu_{36}Zr_{59}Al_5$ and amorphous $Cu_{54}Zr_{40}Al_6$ as cast.

Anelastic relaxation spectra, in which the square of the frequency (f^2), normalized at 305K, and internal friction (Q^{-1}) are plotted against temperature, for both alloys $Cu_{36}Zr_{59}Al_5$ and $Cu_{54}Zr_{40}Al_6$, are shown in Figures 3 and 4 for frequency ranges in kHz and Hz, respectively. In Figures 3a, b, the internal friction (Q^{-1}) was not repeatable among consecutive cycle of measurement, but decrease in each thermal cycle, as may be seen in the insets on figures, which may imply atomic rearrangement in the samples due to consecutive heating process. In Figure 4, the internal friction increases exponentially and the curve shifts to high temperatures, indicating a possible thermally activated relaxation process.

Figure 5 shows the temperature dependence of the normalized square of the frequency, for $Cu_{54}Zr_{40}Al_6$ comparing the spectra obtained in the two distinct apparatus, Kê-type inverted torsion pendulum operating in a Hz bandwidth and acoustic elastometer in a kHz frequency range. Qualitatively similar behavior is seen in the results

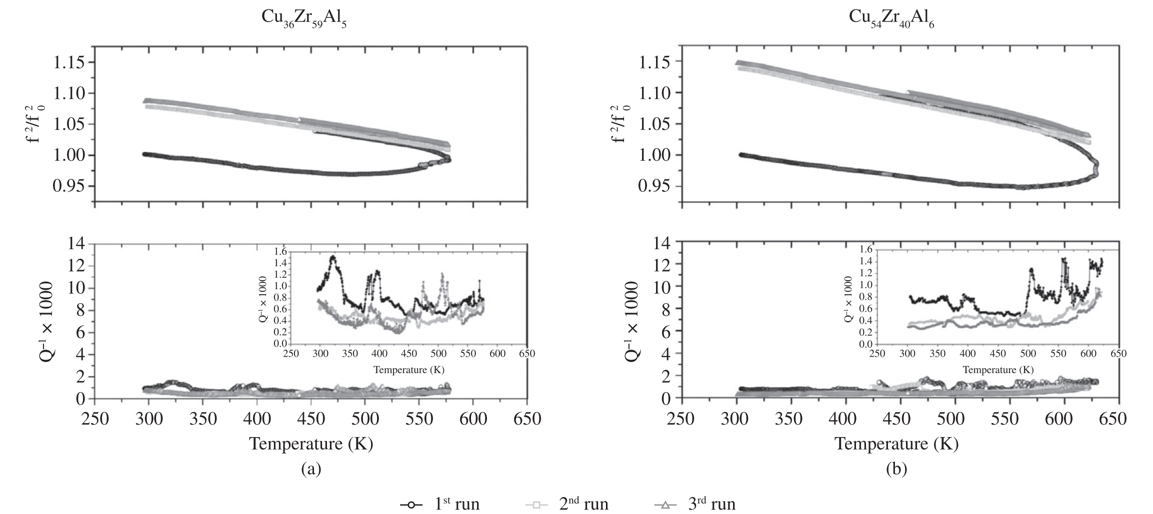

Figure 3. Anelastic relaxation spectra for alloys (a) $Cu_{36}Zr_{59}Al_5$ and (b) $Cu_{54}Zr_{40}Al_6$ obtained by acoustic elastometer (kHz bandwidth). The normalized square of the frequency and the internal friction as function are ploted against temperature.

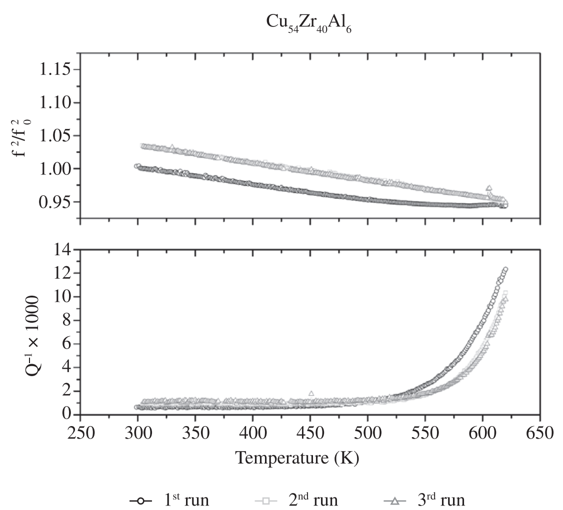

Figure 4. Anelastic relaxation spectra for $Cu_{54}Zr_{40}Al_6$ alloy obtained by Kê-type inverted torsion pendulum, showing the normalized square of the frequency and the internal friction plotted against temperature.

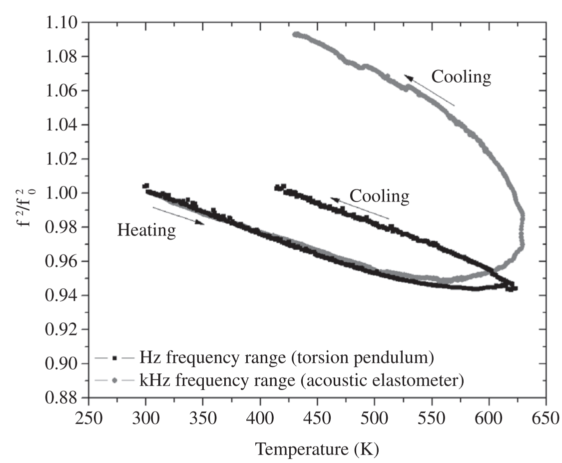

Figure 5. Temperature dependence of the square of the frequency, normalized at 305 K, for two apparatus: Kê-type inverted torsion pendulum (black) and acoustic elastometer (gray), showing the more sensitivity for second apparatus.

obtained by different equipment. The magnitude of the structural relaxation effect observed in the inverted torsion pendulum was less than that in the acoustic elastometer, owing to the fact that the pendulum results include the influence equipment, while the elastometer data are due only to the sample. This figure evidences the more higher sensitivity of the acoustic elastometer system.

The increasing values of the normalized of the square of the frequency in consecutive measurements and the non-reproducibility of the internal friction spectra are evidence that the specimen was changing in the different stages. These changes are possibly associated with mechanical relaxation due to the motion of atoms or clusters in the glassy state and consequently could be related to changes in free volume[24,25]. Nevertheless, other research[10,11] indicates that concentration of interstitial-like defects frozen-in during glass production can be decrease with heat treatment. In both cases the structural relaxation is related a more stable state at each thermal cycle.

In order to detect any kind of structural change in the alloys, new XRD measurements were performed. Figure 6 shows comparative XRD patterns for the alloys $Cu_{36}Zr_{59}Al_5$ and $Cu_{54}Zr_{40}Al_6$ alloys in the as-cast condition and after anelastic relaxation measurements. In the $Cu_{36}Zr_{59}Al_5$ sample, there is an increase in the number and intensity of peaks seen in the as-cast condition pattern and the formation of a new crystalline phase after the measurements, which shows that structural changes have occurred in the sample. The same behavior was not noted in the $Cu_{54}Zr_{40}Al_6$ composition, which remains amorphous after the anelastic relaxation measurements, despite the increment in frequency values observed during each thermal cycle.

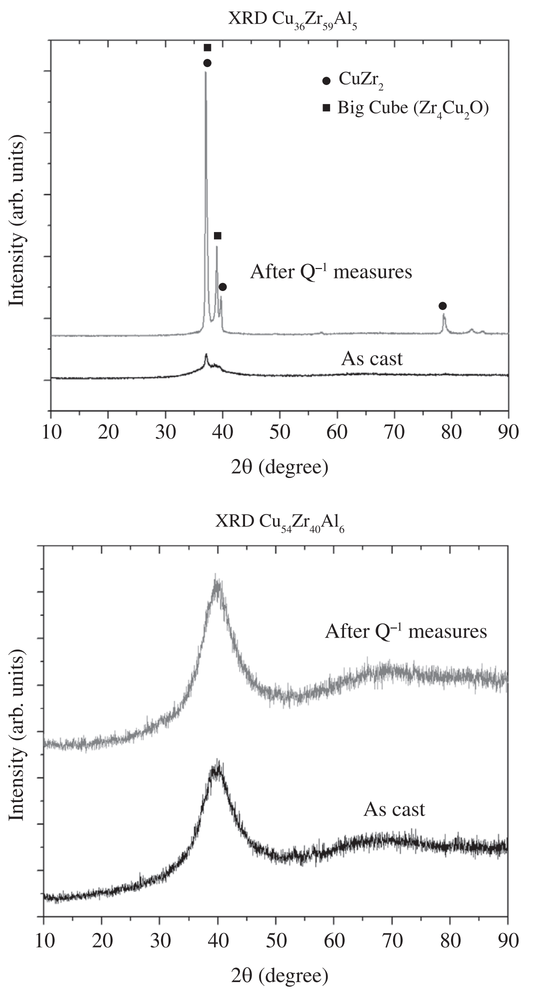

Figure 6. Comparative X-ray diffraction patterns for alloys $Cu_{36}Zr_{59}Al_5$ and $Cu_{54}Zr_{40}Al_6$ in the as-cast condition and after anelastic relaxation measurements.

This variation in the frequency values may be related to the presence of free volume and "defects" as well as to the appearence of crystalline phases. Since both samples show similar thermal stability but the $Cu_{36}Zr_{59}Al_5$ alloy, after heat cycles, shows a volumetric fraction of crystalline phases ($CuZr_2$ and Zr_4Cu_2O) and thus only a small amount of free volume undergoes a weaker relaxation process. However, the $Cu_{54}Zr_{40}Al_6$ alloy, which has a completely amorphous structure, shows a large free volume that migrating to a more relaxed state, though not enough to allow the formation of a crystalline state. Thus, the change is more evident in the first heating cycle, demonstrating that the technique of mechanical spectroscopy represents a powerful tool in the study of dynamic processes and phase transitions in amorphous alloys.

4. Conclusions

Two bulk metallic glasses with nominal compositions of $Cu_{36}Zr_{59}Al_5$ and $Cu_{54}Zr_{40}Al_6$ have been studied by mechanical spectroscopy, which showed behavior that changed with thermal cycles; in the $Cu_{36}Zr_{59}A_{15}$ specimen the presence of crystalline phase reflected in the anelastic relaxation spectra. The structural relaxation in this sample is smaller than that in $Cu_{54}Zr_{40}Al_6$, which has a completely amorphous structure, even after the cycles of internal friction measurements; therefore, the greater amount of free volume and possible "defects" in the latter leads to a more evident structural relaxation process. The relaxation process observed is also influenced by the slow heating rate during the measurement of Q^{-1}, which favors atomic mobility, leading the material to a fast relaxation process even though the maximum temperature reached during the measurement is around 100 K below the glass transition temperature.

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