



## Air-oxidation of a Cu<sub>50</sub>Zr<sub>50</sub> binary amorphous ribbon at 350–425 °C

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### ABSTRACT

The oxidation behavior of a binary Cu<sub>50</sub>Zr<sub>50</sub> bulk amorphous ribbon (CZ2-AR) was studied over the temperature range of 350–425 °C in dry air. The oxidation kinetics of the CZ2-AR generally followed a parabolic-rate law, indicating that diffusion is the rate-controlling step during oxidation. The oxidation rates of the CZ2-AR were strongly temperature-dependent, with its scaling-rate constants ( $k_p$  values) increasing with temperature. Duplex scales formed on the CZ2-AR alloy were composed of an outer-layer of exclusive CuO and of a heterophasic inner-layer of CuO, monoclinic-ZrO<sub>2</sub> (m-ZrO<sub>2</sub>) and tetragonal-ZrO<sub>2</sub> (t-ZrO<sub>2</sub>). In addition, the CZ2-AR substrate started to form the crystalline Cu<sub>10</sub>Zr<sub>7</sub> phase beneath the scales during the oxidation at  $T \geq 375$  °C, indicative of the occurrence of the crystallization of the amorphous substrate.

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### 1. Introduction

Amorphous metals (AMs), containing thin glassy ribbons and thick bulk forms have been extensively studied during the past decades because of their unique properties, such as high mechanical strength and modulus, large supercooling-temperature range ( $\Delta T_x$ ), and excellent aqueous corrosion-resistance, as compared to commercial crystalline alloys [1–3]. Among those amorphous alloys developed, Zr-, Cu-, Cu–Zr-, and Zr–Cu-based systems were extensively fabricated to meet the industrial needs in combination with low material costs and excellent mechanical properties [4–6]. For example, the ternary Zr<sub>50</sub>Cu<sub>42</sub>Al<sub>8</sub> bulk-metallic glass (BMG) exhibited high fracture strength of 2 GPa and elastic modulus of 115 GPa [6]. This glassy alloy also possessed excellent room-temperature plasticity of ~20% under compression.

An important issue to be considered is that those amorphous alloys could suffer severe degradation when using in thermal-activated environments for practical applications. Therefore, a fully understand of their oxidation behavior is of essence to meet the industrial needs. In reviewing of literatures, a few studies on the oxidation behavior of multi-component Cu- and Cu–Zr-based BMGs were reported and summarized in many technical journals [7–11]. An example of our previous study [10] on the oxidation of a ternary Cu<sub>60</sub>Zr<sub>30</sub>Ti<sub>10</sub> BMG indicated that two different

modifications of t- and m-ZrO<sub>2</sub> formed after the oxidation, which was not verified in the oxidation of the Zr–Ni BMG [11].

Most recently, a series of binary Cu-based AMs or BMGs, such as Cu–Zr and Cu–Hf glassy alloys were successfully synthesized [12–14]. This development further provided a promising effort to synthesis relatively low-cost amorphous alloys for proper applications in industries. Nevertheless, the oxidation of those binary glass alloys has never been studied yet. Thus, the main goal of this study is to investigate the oxidation of a Cu<sub>50</sub>Zr<sub>50</sub> amorphous ribbon (CZ2-AR) and, in particular, to understand the roles of Cu and Zr on the scale constitution and phases.

### 2. Experimental

Seven amorphous strips of the CZ2-AR (about 60- $\mu$ m thick) were prepared by a single-roller melt-spinning technique, as described elsewhere [12]. The average composition of this glassy ribbon at five different regions analyzed by wavelength dispersive spectrometry (WDS) under an electron-probe microanalyzer (EPMA) gave 50.21% Cu and 49.79% Zr (in at.%). The rectangular samples (3 × 2 mm) were directly cut from the strips. All the samples were initially ground by #1000 SiC abrasive paper, polished down to a 0.3- $\mu$ m diamond paste, cleaned with acetone, and immediately dried before the tests.

The thermal stability of the CZ2-AR was examined by differential scanning calorimetry (DSC) at various heating rates of 10–100 °C/min. The oxidation tests were performed by a horizontal tube-furnace in dry air (>99.999 vol.% pure). The net flow rate of air was kept constant at 40 cm<sup>3</sup>/min, and the heating and cooling rates of the furnace were set at 10 °C/min throughout each experiment. The scale thickness was measured by the metallurgical analyses using scanning electron microscopy (SEM) under a backscattered electron-image (BEI) mode. At least 15 values of the scale thickness were taken at each temperature and individual exposure-time under the standard procedure of ASTM-G54 [15]. The characterization of the ribbons and oxide scales was analyzed by x-ray diffraction (XRD), SEM equipped with energy dispersive spectrometry (EDS), and EPMA equipped with WDS.

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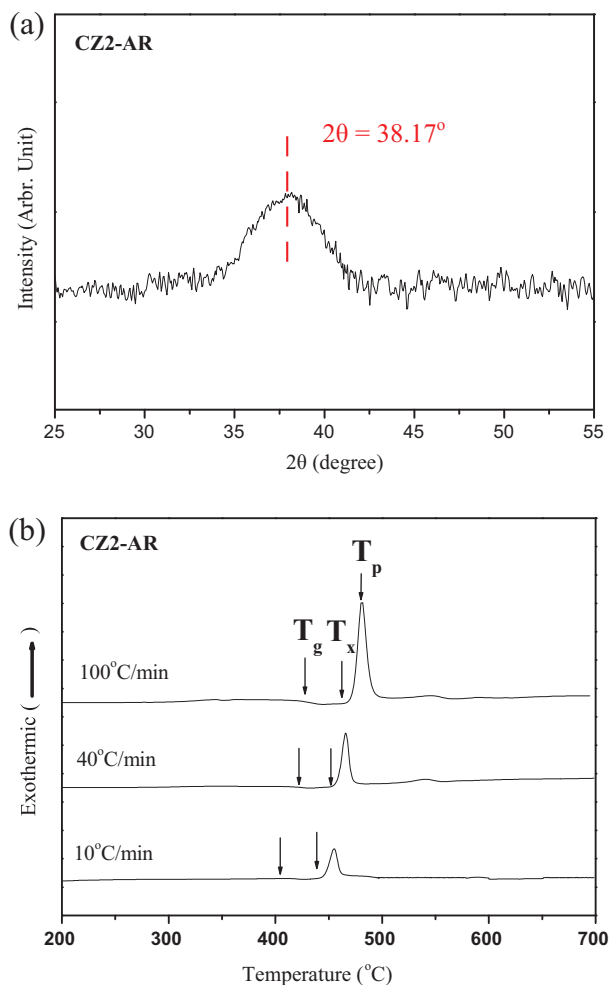
**Table 1**  
Thermal properties of the CZ2-AR at various heating rates.

Thermal properties Heating rate	$T_g$ (°C)	$T_x$ (°C)	$T_p$ (°C)	$\Delta T_x$ (°C)
10 °C/min	387.8	436.3	444.6	48.5
40 °C/min	411.7	458.6	466.0	46.9
100 °C/min	425.5	472.9	481.3	47.4

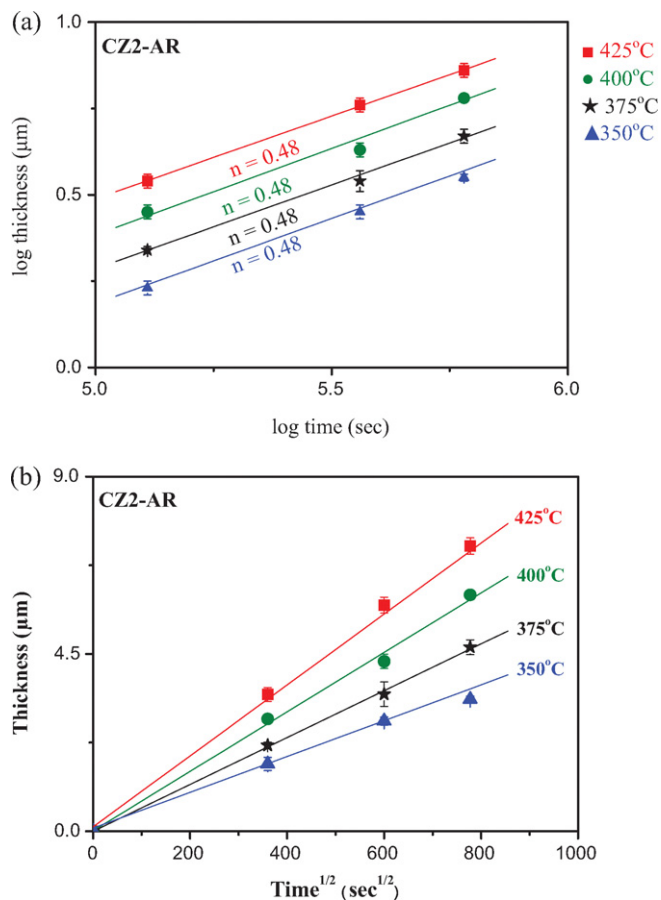
### 3. Results and discussion

#### 3.1. Substrate analyses

XRD spectra of the CZ2-AR, shown in Fig. 1a, revealed that this amorphous ribbon contained a wide-broadening peak at  $2\theta = 38.17^\circ$ , indicative of the amorphous nature for the as-cast substrate. DSC curves of the glassy ribbon at various heating rates are shown in Fig. 1b, and thermal properties of the corresponding glass transition temperature ( $T_g$ ), crystalline temperature ( $T_x$ ), and exothermic-peak temperature ( $T_p$ ) are summarized in Table 1. As shown in the table, all the  $T_g$ ,  $T_x$ , and  $T_p$  values steadily increased with increasing heating rate. The average supercooling-temperature range ( $\Delta T_x = T_x - T_g$ ) at various heating rates is around 47.6 °C. Thus, the temperature range of oxidation tests was set at 350–425 °C to cover the possible phase-transition regions.



**Fig. 1.** (a) XRD spectra of the as-cast CZ2-AR and (b) DSC curves of the CZ2-AR at various heating rates.



**Fig. 2.** (a) Double log-plots and (b) parabolic plots of the oxidation kinetics of the CZ2-AR over the temperature range of 350–425 °C.

#### 3.2. Oxidation kinetics

The double log-plots of the oxidation kinetics of the CZ2-AR over the temperature range of 350–425 °C are shown in Fig. 2a. As described previously [15], the oxidation kinetics can be described as an equation between the scale thickness ( $X$ ) and the exposure time ( $t$ ).

$$X = Kt^n + C \quad (1)$$

where the exponent ( $n$  value) was determined by the slope of the double log-plot of the scale thickness vs. time, and  $K$  and  $C$  are the rate constant and integration constant, respectively. As shown in this figure, a value of  $n = 0.48$  (close to 0.5) was obtained for the CZ2-AR, indicating that the parabolic-rate law was obeyed, and diffusion was the rate-controlling step during oxidation.

Oxidation kinetics curves of the CZ2-AR at 350–425 °C, in terms of the scale thickness vs. square-root of time, are further shown in Fig. 2b. In general, the scaling-rate constants ( $k_s$  values) gradually increased with increasing temperature, and all the  $k_s$  values over the temperature range of interest are summarized in Table 2. For comparative purposes, the  $k_s$  values of pure Cu and Zr obtained previously at 400 and 425 °C [10,16] are also reported in the same table. As clearly shown in Table 2, the  $k_s$  values of the CZ2-AR at 400 and 425 °C is much lower than those that of pure Cu, but slightly higher than those of pure Zr. The observed discrepancy of various  $k_s$  values deserved further discussion for the scale constitution and phases of the amorphous ribbon, as described below.

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