

## GLASS FORMING ABILITY OF BULK AND MECHANICALLY ALLOYED $\text{Zr}_{55}\text{Cu}_{19}\text{Ni}_8\text{Al}_8\text{Si}_5\text{Ti}_5$ AMORPHOUS ALLOYS

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Bulk liquid quenched and mechanically alloyed  $\text{Zr}_{55}\text{Cu}_{19}\text{Ni}_8\text{Al}_8\text{Si}_5\text{Ti}_5$  amorphous alloys have been prepared. These materials exhibit a wide supercooled liquid region and high glass forming ability. In both cases X-ray diffraction and thermal analysis were performed in order to verify the amorphous structure of the materials and determine their thermal properties. Glass transition ( $T_g$ ) and crystallization ( $T_x$ ) temperatures were measured and the Lu-Liu parameter  $\gamma$ , which estimates the glass forming ability for the two materials, was calculated. For the bulk amorphous sample we measured  $T_g = 363$  °C,  $T_x = 425$  °C, and  $\gamma = 0.344$ . The corresponding values for the ball milled material, are  $T_g = 336$  °C,  $T_x = 443$  °C, and  $\gamma = 0.367$ .

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### 1. Introduction

Since the first synthesis of amorphous metals [1] and alloys [2], a great variety of amorphous alloys have been prepared. All these alloys have to be treated by rapid solidification techniques with cooling rates well above  $10^5$  K/min, such as melt spinning, splat cooling, laser melting etc., in order to exhibit an amorphous phase. Also with high energy deformation processing via mechanical alloying, amorphous powders can be formed [3-5]. This results to limitations in the maximum sample thickness and geometry with most of the samples being in the form of amorphous powders or ribbons with 10-50  $\mu\text{m}$  thickness and 2-100 mm width. Since the late 80's a new generation of alloys shows amorphization at much lower cooling rates. Some of these alloys are Ln- [6], Zr- [7], Pd- [8] based alloys systems and show a wide supercooled liquid region and high glass forming ability. More important these alloys exhibit superplasticity with their liquid like behaviour, between the glass transition temperature  $T_g$  and the crystallization temperature  $T_x$ , which allows them to be molded in the desirable shapes.

The latter property and the excellent mechanical properties are of great importance since they may have high technological impacts in industry. In this paper we will discuss some thermal properties of Zr- based bulk amorphous alloys with the nominal composition  $\text{Zr}_{55}\text{Cu}_{19}\text{Ni}_8\text{Al}_8\text{Si}_5\text{Ti}_5$ , prepared by arc melting and mechanical alloying and we will also compare the two products.

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## 2. Experimental

Elemental powders of Cu (99.98 % <300 mesh), Ni (99.98 % <300 mesh), Zr (99.98 % <300 mesh), Si (99.999 % 325 mesh), Ti (99.5 % 325 mesh) and Al (99.98 % <300 mesh) were accurately weighted to give the desired compositions. Powders of 6 g were hand-mixed, then loaded into a high-energy ball milling apparatus (modified SPEX 8000) for processing using cylindrical hardened tool steel vials with 4 balls (6 mm in diameter) of tungsten carbide (with 6% - cobalt). The vial was sealed either with a VITON or Cu O-ring. In order to prevent oxidation of the powders, all ball milling processes were conducted in a glove box with vacuum gate (modified BRAUN MB 150-GI) under purified and controlled argon atmosphere ( $< 5$  ppm  $N_2$ ,  $O_2$  and  $H_2O$ ). For optimization of the MA process and for homogenization of the powders cluster, the vial was opened in the glove box periodically and cleaned to ensure thorough mixing of the components. After several hours of MA treatment we found a little contamination from iron, cobalt, tungsten, carbon (total <200 ppm) and oxygen (<100 vpm).

As regards the amorphization by rapid quenching, the alloys were prepared by mixing the elemental powders or small pieces of the above mentioned compositions and pressed into pellets (if it is necessary). The materials were first melted and in the sequel 2-3 times remelted in a conventional arc melting facility in purified argon atmosphere ( $\geq 99.999\%$ ). Prior to each melting the argon atmosphere was purified by melting of high purity Zr as oxygen and nitrogen getter material. In the final purified argon the total  $N_2$ ,  $O_2$  and  $H_2O$  impurities were  $< 1$  vpm. Inside the arc melting apparatus and under the same purification procedure bulk amorphous samples were prepared from the master alloy ingots, in a separate process by dropping the reliquefied alloy in a separate water cooled copper die. The produced samples had the form of polished rods with a diameter of 3 to 10 mm and a length of 15 to 25 mm, depending on the used dies.

Using a standard diffractometer (SEIFERT) with Ni-filtered Cu  $K\alpha$  radiation ( $\lambda = 0.154051$  nm) the nanostructurization and amorphization in both the above mentioned procedures was investigated by X-ray diffraction of bulk arc melted samples and mechanical alloyed powders. Thermal analysis measurements were carried out in a differential calorimeter (NETZSCH DTA 404S) with heating rates from 5 to 40 K/min and temperature from 300 to 1300 K).

## 3. Results

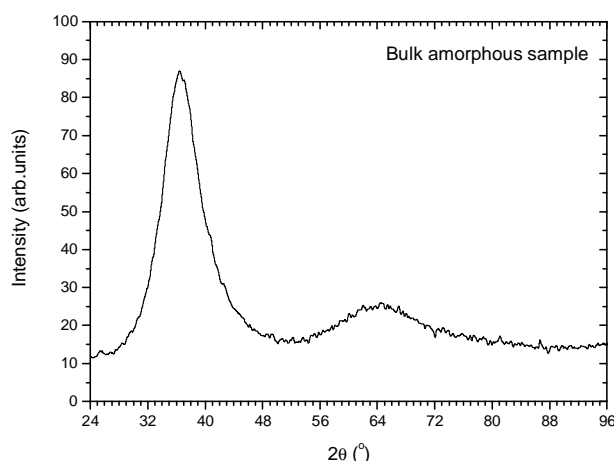


Fig. 1. X-rays diffractogram of the bulk amorphous alloy.

The bulk samples investigated have been produced and characterized in a previous work [9]. Fig. 1 shows the X-rays diffractogram of the bulk amorphous sample prepared by arc melting taken on the cross sectional surface of the produced rods with 5 mm diameter and 20 mm long. Two typical broad diffraction maxima can be observed and there is no trace of any crystalline phase. In Fig. 2 the DSC scans are shown for the same material and various heating rates. From this work we have

determined the glass transition temperature for this material to be  $T_g = 363^\circ\text{C}$ , the crystallization temperature  $T_x = 425^\circ\text{C}$  and the liquidus temperature  $T_l = 872^\circ\text{C}$ . This results to a supercooled liquid region of  $\Delta T_{\text{sg}} = 62^\circ\text{C}$ , and the glass forming ability which can be expressed as the Lu-Liu parameter [10]  $\gamma$  has a value of  $\gamma = 0.344$ .

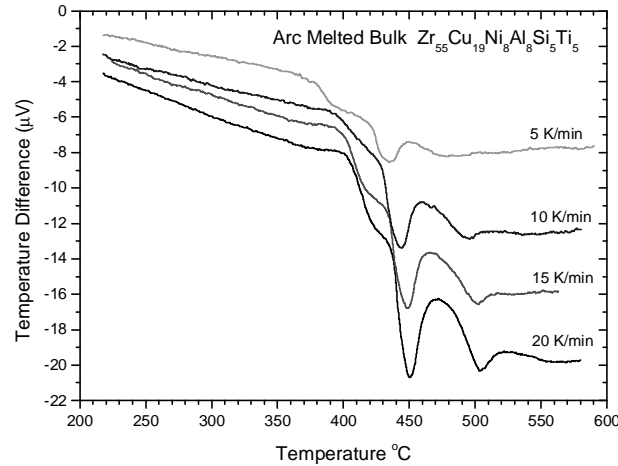


Fig. 2. DSC thermoscans of bulk amorphous  $\text{Zr}_{55}\text{Cu}_{19}\text{Ni}_8\text{Al}_8\text{Si}_5\text{Ti}_5$  samples.

Fig. 3 shows the X-rays diffractogram of  $\text{Zr}_{55}\text{Cu}_{19}\text{Ni}_8\text{Al}_8\text{Si}_5\text{Ti}_5$  powders after 3, 6, 9 and 12 h of mechanical alloying. After 3 h the alloy shows nanocrystalline phases, which are followed by a mixed state with both nanocrystalline and amorphous phases at 6 h. If the material is further processed, then at 12 h of mechanical alloying the crystalline peaks disappear and only two broad diffraction peaks are visible, indicating the complete amorphization of the  $\text{Zr}_{55}\text{Cu}_{19}\text{Ni}_8\text{Al}_8\text{Si}_5\text{Ti}_5$  powders.

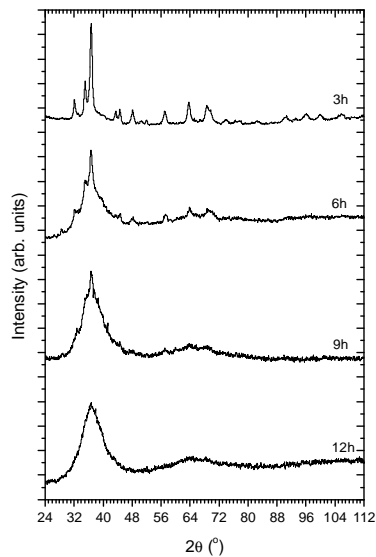


Fig. 3. X-rays diffractograms of the mechanical alloyed powders.

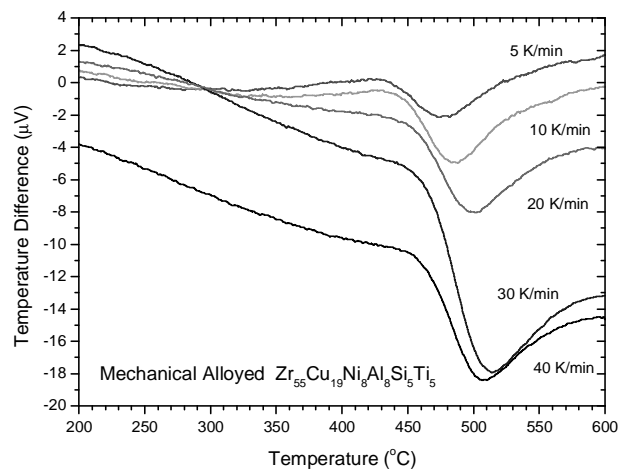


Fig. 4 DSC thermoscans of mechanically alloyed  $\text{Zr}_{55}\text{Cu}_{19}\text{Ni}_8\text{Al}_8\text{Si}_5\text{Ti}_5$  powders.

In Fig. 4 the DSC scans are shown, this time for the mechanical alloyed material. By extrapolating the measured temperatures to a heating rate of 0 K/min we can obtain the value of  $T_x = 443$  °C for the crystallization temperature. The glass transition temperature of this powdered amorphous alloy corresponds to  $T_g = 336$  °C, taken from the heating curves of 20 K/min, resulting to a  $\Delta T_{xg} = 107$  °C and a value for the Lu-Liu parameter of  $\gamma = 0.367$ .

#### 4. Discussion

As can be seen from data of previous work [11], the supercooled liquid range, between  $T_g$  and  $T_x$ , is significantly larger in the case of mechanical alloyed powders compared to the bulk samples. This can be confirmed also in the case of the material investigated in this work. The crystallization temperature for the mechanical alloyed material is significantly higher than that of the bulk. Moreover, the glass transition temperature differs greatly between the two materials, by being lower in the case of mechanical alloying. It is well known that large  $\Delta T_{xg}$  implies that the supercooled liquid can exist in a wide temperature range without crystallization and with high resistance to the nucleation and growth of crystalline phases. In our case, we measured  $\Delta T_{xg} = 107$  K for the mechanically alloyed material. This value, compared to other values of  $\Delta T_{xg}$  for bulk metallic glasses taken from [10] and mechanically alloyed amorphous materials [12], is one of the largest known. These facts lead directly to a large glass forming ability as can also be seen in the values of the Lu-Liu parameter  $\gamma$ , which in the case of mechanical alloyed powders are larger.

The differences in the thermal properties of the two types of alloys arise not only due to the synthesis process but also because of small contamination. In the case of mechanical alloying it is known that the sample can be contaminated with metallic and non-metallic impurities, coming from the vials, balls and atmosphere under which the sample is being processed. Our starting materials are highly sensitive to oxygen contamination during the milling process and especially the Zr powder, that also has the largest concentration in our samples. The end products of the ball milling process, however, contain a very low level of iron, cobalt, tungsten, carbon (total <200 ppm) and oxygen (<100 vpm) impurities and as was proven by the X-rays diffractogram, are completely amorphous within 12 h of processing. This milling time is very short and proves the effectiveness of the ball milling process.

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