Structure and thermal stability of melt spun and mechanically alloyed Cu$_{47}$Ti$_{34}$Zr$_{11}$Ni$_8$ and Cu$_{47}$Ti$_{34}$Sn$_{11}$Ni$_8$ alloys

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Abstract. Two applied samples preparation techniques (rapid quenching from the melt and mechanical alloying) resulted in the formation of fully amorphous Cu$_{47}$Ti$_{34}$Zr$_{11}$Ni$_8$ and Cu$_{47}$Ti$_{34}$Sn$_{11}$Ni$_8$ alloys. However, a significant differences in thermal stability and crystallization behaviour have been found, depending not only on the alloy composition, but on the fabrication method as well. MA powders of both alloys studied revealed one dominating DSC exothermic effect. Zr-containing ribbon showed four exothermic effects, while Sn-containing one – only two overlapping peaks. In the case of ribbons it was found that replacing Zr by Sn did not influenced the crystallization temperature or supercooled liquid region, however, the activation energy of crystallization increased significantly, from 190 to 223 kJmol$^{-1}$. Opposite behaviour was observed for MA powders. Introducing Sn into the alloy instead of Zr resulted in a considerably increase of the crystallization temperature (from 783 to 826 K), simultaneously the activation energy for crystallization remained the same.

1. Introduction
Since 1988 it has been demonstrated that metallic glasses can be made in a bulk form by solidifying the melt at relatively low cooling rates. The first bulk metallic glasses (BMGs) were limited to La-, Zr- and Pd-based systems, showing high glass forming ability and allowing fabrication of the samples with diameters of several millimetres [1]. Over the past decade, BMGs have gained considerable attention due to their properties (high yield strength, hardness and elastic strain limit, relatively high fracture toughness, fatigue resistance and corrosion resistance) and potential as new structural materials [2-4]. Nowadays Cu based bulk metallic glasses are considered as potential engineering materials due to their good mechanical properties [5]. Various Cu based alloys have been reported to show the enhanced glass forming ability, enabling the preparation of bulk alloys by conventional casting methods [6]. Another possibility of fabrication of bulk amorphous alloys is consolidation of amorphous powders obtained by melt atomisation [7-8] or by mechanical alloying technique [9]. There are also reports on the influence of minor additions of Fe, Si, Pb and Sn on the glass forming ability and crystallization of Cu-Ti-Zr-Ni BMGs [10].

In the present work, the influence of chemical composition on the amorphization by mechanical alloying of Cu$_{47}$Ti$_{34}$Zr$_{11}$Ni$_8$ and Cu$_{47}$Ti$_{34}$Sn$_{11}$Ni$_8$ elemental powder mixtures was studied. The thermal stability and crystallization behaviour of the amorphous MA powders was determined and compared with rapidly quenched ribbons with the same chemical compositions.
2. Experimental
For mechanical alloying (MA) experiments, the elemental powders of Cu, Ti, Zr, Ni and Sn with a purity of at least 99.8% and particles size less than 50 µm were used. The powder mixtures of Cu$_{47}$Ti$_{34}$Zr$_{11}$Ni$_8$ and Cu$_{47}$Ti$_{34}$Sn$_{11}$Ni$_8$ (at.%) were subjected to mechanical alloying. Fritsch P5 planetary ball mill, equipped with hardened steel vials and balls (10 mm of diameter), was employed for milling with a rotational speed of 250 rpm. The mass of the milled powders was 10 g and ball-to-powder weight ratio was 10:1. The milling experiments and all powder handling were performed under protective atmosphere of argon. Small amounts of powders were withdrawn after selected milling times for structural examinations. Simultaneously, the master alloys with the same compositions (Cu$_{47}$Ti$_{34}$Zr$_{11}$Ni$_8$ and Cu$_{47}$Ti$_{34}$Sn$_{11}$Ni$_8$) were prepared by arc melting of pure elements. Then, the rapidly quenched ribbons (RQ) with thickness of about 70 µm and width of 4 mm were melt spun on a copper wheel.

The structure of the rapidly quenched ribbons and the powders at different stages of milling and after completion of the process was investigated by X-ray diffraction (XRD) method in a Philips PW 1840 diffractometer using CuK$_\alpha$ radiation. XRD was also employed for the determination of the phase composition of the alloys after their crystallization.

For thermal stability investigations, Perkin Elmer DSC7 differential scanning calorimeter was used. DSC measurements allowed thermal effects registration during heating the samples and determination of the characteristic temperatures (glass transition temperature $T_g$, crystallization temperature $T_x$, peak temperature $T_p$, supercooled liquid region $\Delta T_s$) and heats evolved $\Delta H$. The samples were heated within the temperature range from 323 to 1000 K, applying the heating rates from 5 to 80 K min$^{-1}$. From the DSC measurements the activation energy of crystallization $E_a$ of amorphous alloys was calculated by the Kissinger method.

Morphology and powder particles size after MA was studied by scanning electron microscopy, using a Hitachi S 3500N unit.

3. Results and discussion
The phase evolution that occurred in the powders after various times of milling was observed for the Cu$_{47}$Ti$_{34}$Zr$_{11}$Ni$_8$ powder mixture (Figure 1). From these results, it can be seen that during milling the diffraction peaks attributed to Cu, Ti, Zr and Ni disappear gradually with increasing processing time. The formation of the intermediate phases was not observed and the amorphous alloy is the final product (50 h of milling) of the MA process.

The XRD patterns of the final MA product and RQ ribbon for Cu$_{47}$Ti$_{34}$Zr$_{11}$Ni$_8$ composition are shown in Figure 2. Both patterns exhibit a diffused halo, typical for an amorphous phase.

A SEM micrograph of the amorphous Cu$_{47}$Ti$_{34}$Zr$_{11}$Ni$_8$ powders after 50 h of MA is presented in Figure 3. One can notice, that the powders reveal a spherical morphology and the average particle size is of the order of several tens of micrometers. Moreover, the particles do not exhibit a tendency to agglomeration.

The MA powders and RQ ribbons were subjected to DSC measurements. Figure 4 shows the DSC curves registered for the Cu$_{47}$Ti$_{34}$Zr$_{11}$Ni$_8$ amorphous powder and ribbon (heating rate 40 K min$^{-1}$) and the obtained data are collected in Table 1. A significant differences in thermal stability and crystallization behaviour between investigated samples were observed. The RQ ribbon reveals four exothermic events, while for the MA powders only two exothermic peaks were detected. The crystallization temperature $T_x$ (first crystallization peak) for the RQ ribbon is considerably lower than for the MA powders. Also the activation energy for crystallization calculated for the first crystallization peak is significantly lower for the RQ ribbon. The glass transition temperature $T_g$ is clearly visible at the DSC curve for the ribbon, while for the powder is not detected due to the fact that the amorphous powder was not obtained from the liquid state. It was also found that in the case of the powder the majority of the heat of crystallization was evolved during the first crystallization event (see Figure 4 – the numbers indicate the heat evolved in each exothermic event).
Figure 1. A sequence of the XRD patterns of Cu$_{47}$Ti$_{34}$Zr$_{11}$Ni$_8$ powder mixture subjected to MA for increasing milling time.

Figure 2. XRD patterns for rapidly quenched and mechanically alloyed (50 h) Cu$_{47}$Ti$_{34}$Zr$_{11}$Ni$_8$.

Figure 3. SEM micrograph of Cu$_{47}$Ti$_{34}$Zr$_{11}$Ni$_8$ powders after 50 h of MA.

Figure 4. DSC curves of Cu$_{47}$Ti$_{34}$Zr$_{11}$Ni$_8$ RQ ribbon and MA powder (heating rate 40 K min$^{-1}$).

Table 1. Thermal stability data obtained from DSC measurements of Cu$_{47}$Ti$_{34}$Zr$_{11}$Ni$_8$ alloys.

| type of sample | $T_s$ [K] | $T_{sl}$ [K] | $\Delta T = T_s - T_g$ [K] | $T_{pl}$ [K] | $\Delta H_1$ [J g$^{-1}$] | $E_{a1}$ [kJ mol$^{-1}$] |
|----------------|----------|-------------|--------------------------|-----------|----------------|------------------|
| ribbon         | 706      | 739         | 33                       | 749       | 34             | 190 ± 15         |
| powder         | -        | 783         | -                        | 796       | 58             | 252 ± 20         |

The XRD patterns of the final MA product (50 h) and RQ ribbon for Cu$_{47}$Ti$_{34}$Sn$_{11}$Ni$_8$ composition are shown in Figure 5. For this composition both patterns also exhibit a diffused halo, testifying an amorphous nature of the alloys.

However, the DSC measurements showed a considerably differences between these two amorphous alloys, as a consequence of various preparation techniques (Table 2, Figure 6). Replacing Zr by Sn resulted in dramatic changes in the crystallization behaviour of the ribbon – only two overlapping exothermic effects were observed instead of separated four events registered for Zr-containing alloy.

Table 2. Thermal stability data obtained from DSC measurements of Cu$_{47}$Ti$_{34}$Sn$_{11}$Ni$_8$ alloys.

| type of sample | $T_s$ [K] | $T_{sl}$ [K] | $\Delta T = T_s - T_g$ [K] | $T_{pl}$ [K] | $\Delta H_1$ [J g$^{-1}$] | $E_{a1}$ [kJ mol$^{-1}$] |
|----------------|----------|-------------|--------------------------|-----------|----------------|------------------|
| ribbon         | 714      | 745         | 31                       | 750       | 35             | 223 ± 12         |
| powder         | -        | 826         | -                        | 843       | 44             | 259 ± 13         |
In the case of MA powder these changes were not so dramatic – one dominating exothermic effect was observed, however, shifted to much higher temperature comparing to Zr-containing alloy. It is also worthy to notice that introducing Sn into the alloy instead of Zr resulted in a significant increase of the activation energy of crystallization of the ribbon, and simultaneously, this value remained practically unchanged for MA powders.

4. Conclusions
Rapid quenching from the melt and mechanical alloying techniques resulted in the formation of fully amorphous Cu_{47}Ti_{34}Zr_{11}Ni_{8} and Cu_{47}Ti_{34}Sn_{11}Ni_{8} alloys. The discovered differences in thermal stability and crystallization behaviour depended on the alloy composition and the fabrication method. MA powders of both alloys studied revealed one DSC exothermic effect, while the ribbons showed four or two exothermic effects, for Zr- and Sn-containing alloy, respectively. For MA powders introducing Sn into the alloy instead of Zr resulted in a considerably increase of the crystallization temperature, simultaneously the activation energy for crystallization remained the same. For the ribbons the influence of the replacing Zr by Sn was not so evident.

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