Investigation of new type Cu-Hf-Al bulk glassy alloys

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Abstract. In the last years new type Cu-Hf-Al ternary alloys were developed with high glass forming ability and ductility. The addition of Al to Cu-Hf alloys results in improvements in glass formation, thermal stability and mechanical properties of these alloys. We have investigated new Cu-based bulk amorphous alloys in Cu-Hf-Al ternary system. The alloys with Cu₄₉Hf₄₂Al₉, Cu₄₆Hf₄₅Al₉, Cu₅₀Hf₄₂.₅Al₇.₅ and Cu₅₀Hf₄₅Al₅ compositions were prepared by arc melting. The samples were made by centrifugal casting and were investigated by X-ray diffraction method. Thermodynamic properties were examined by differential scanning calorimetry and the structure of the crystallising phases by scanning electron microscopy. The determination of liquidus temperatures of alloys were measured by differential thermal analysis.

1. Introduction

The development of Cu-based bulk amorphous alloys has been very significant in the last some years. In case of the bulk amorphous materials, the most important factors of glass formation are the great number of component, the atomic size of the different elements and the composition [1,2]. However, nowadays the significance of another important factor is becoming more and more important – high stability supercooling region. The temperature interval of supercooling region (ΔTₓ) can be determined as the difference between the temperature of glass forming (T₉) and temperature of crystallization (Tₓ).

It is a generally true that the ability of glass forming increases by increasing the value of ΔTₓ[3]. Between 1988-1990, alloy-families having a high stability of supercooling region were found such as Mg, Ln, Zr-based alloys and in the last decade the group of alloys having such properties (i.e. the Ti, Zr, Ni, Hf, Co, Cu-based alloys belong to this group) increased. However, if the excellent strength properties are also important in addition to the supercooling region, it can be stated that only the Cu- and Ni-based alloy family has these properties. Considering the mechanical properties of Cu-based alloys it can be stated that their tensile strength can be even 2500-3000 MPa while the same of Zr-based alloys is only 1500-1900 MPa. In case of the Cu-based alloys, the excellent mechanical properties are accompanied by high ability of glass formation [4].

In 2003, Inoue et al. started to investigate the Cu-Hf-Al ternary alloys within the Cu-based alloy system [4]. Among others the Cu₅₀Hf₄₅Al₅ and Cu₅₀Hf₄₂.₅Al₇.₅ alloys were investigated by the authors. They have found that the critical size of the castable amorphous rods increases from 1.5 mm to 3 mm by adding Al to the Cu-Zr and Cu-Hf. [5]. The value of ΔTₓ of Cu-based alloys is usually 37-90K, but a value above 90K can frequently be experienced in the Cu-Hf-Al system, e.g. a value of 91K was measured in case of the Cu₅₀Hf₄₅Al₅ alloy and a value of above 100 K was obtained in the Cu-Hf-Al-
M (M=Ag, Pd) system [3]. In 2006– the Cu_{49}Hf_{42}Al_{9} alloy – was developed by Jia et al that show a critical value of 10 mm [6]. The new types of Cu-Hf-Al alloys are suitable for using as structural materials in the engineering industry and in the motor-car industry owing to their excellent mechanical properties, strength as well as corrosion- and wear resistance.

In the course of our research work, the amorphous formation and the thermal behaviour of wedge- and rod-shaped specimen were investigated within the Cu-Hf-Al alloy family. The wedge-shaped specimens were formed in such a way that the glass formation could be investigated at a continuously increasing cross section. The obtained results were compared with the results published earlier in the references.

2. Experimental
Four Cu-Hf-Al alloys with different compositions were investigated: the alloys Cu_{49}Hf_{42}Al_{9}, Cu_{46}Hf_{45}Al_{9}, Cu_{50}Hf_{42.5}Al_{7.5} and Cu_{50}Hf_{45}Al_{5}. The Cu-Hf-Al alloys were made from high purity (99.9%) Hf rod, Cu plate and Al plate by arc melting in a high purity Ti gettered Ar atmosphere. In order to obtain the homogenous state, the alloy was remelted four times then the master alloy was broken and remelted four times again. The oxygen content of master alloys were investigated by the ICP method and it was between 5-107 ppm.

Wedge- and rod samples were made by centrifugal casting in Ar atmosphere. The wedge-shaped sample has a length of 30 mm and a width of 20 mm, and its thickness continuously increases up to a value of 3.8 mm. The rod-shaped sample has a diameter of 3 mm and a length of 50 mm. 3 parallel wedge-shaped samples and 2 parallel rod-shaped samples were made from Cu_{49}Hf_{42}Al_{9} and Cu_{46}Hf_{45}Al_{9} alloys. One wedge-shaped sample and one rod-shaped sample were investigated of the Cu_{50}Hf_{42.5}Al_{7.5} and Cu_{50}Hf_{45}Al_{5} alloys. XRD measurements were performed in order to determine the amorphous state by using a Bruker D8 diffractometer equipped with a Monocap having a diameter of 1 mm. The samples were analyzed by Co Kα radiation. The diffractograms were evaluated by means of the BRUKER Diffrac Plus software. DSC measurements of amorphous sample were made different heating rates in Ar atmosphere by using the Netzsch 204 equipment. The T_g and T_x temperatures were determined from the DSC curves. DTA measurements were made for determining the liquidus temperature (T_l). The change of the mechanical properties was followed by hardness (HV). It was measured along the longitudinal axis as a function of distance in case of the wedges, and the measuring points were uniformly distributed on the cross section in case of the rods. Mituyoto MVK-H1 equipment was used for the measurements.

3. Results and discussion
The results obtained for four Cu-Hf-Al alloys are in Table 1.

Table 1.

| Alloys          | T_g (K) | T_x (K) | ΔT_x (K) | T_l (K) | T_{rg} | Amorphous thickness at wedge (mm) | Amorphous length of rod (from the bottom of mould) (mm) | HV (wedge) | HV (rod) |
|-----------------|---------|---------|----------|---------|--------|----------------------------------|------------------------------------------------------|------------|---------|
| Cu_{49}Hf_{42}Al_{9} | 780     | 847     | 67       | 1226    | 0.63   | 1.5-1.9; 3                       | 8                                                    | 630-670    | 534-575 |
| Cu_{46}Hf_{45}Al_{9} | 758     | 815     | 57       | 1225    | 0.61   | 0.5                              | -                                                   | 644-687    | -       |
| Cu_{50}Hf_{42.5}Al_{7.5} | 780     | 846     | 66       | 1218    | 0.64   | 1.2                              | 7                                                    | 570-667    | 511-552 |
| Cu_{50}Hf_{45}Al_{5}  | 774     | 858     | 84       | 1224    | 0.63   | 1.2                              | -                                                    | 623-664    | -       |

The investigations of the alloys at a heating rate of 20 K/min are shown in Fig. 1.
Temperature, °C
Heat flow, mW/mg

(1) Cu₄₉Hf₄₂Al₉
(2) Cu₄₆Hf₄₅Al₉
(3) Cu₅₀Hf₄₂.₅Al₇.₅
(4) Cu₅₀Hf₄₂.₅Al₇.₅

Figure 1. DSC curves of the investigated Cu-Hf-Al alloys
(heating rate is 20K/min)

The X-ray diffraction patterns were taken in the cross-section of rod samples and on the surface and cross-section of wedge-samples. The surface and cross-section of wedge-samples are amorphous in the same extent, the amorphous character appearing on the surface can be observed on the cross-section as well. Fig. 2 shows the X-ray diffraction patterns taken in the cross-section of wedges.

Figure 2. XRD patterns of wedges

An amorphous wedge having a thickness of 3 mm could be cast in case of the Cu₄₉Hf₄₂Al₉ alloy with highest Al content and we could reach a thickness higher than 1 mm only in this alloy for the other two wedges (1.2-1.5 mm). In case of the Cu₄₆Hf₄₅Al₉ alloy, an amorphous structure of a thickness of 0.4 mm could be developed only in one of the two wedge-samples, the other wedge had a crystalline structure. In case of the Cu₅₀Hf₄₂.₅Al₇.₅ and Cu₅₀Hf₄₂.₅Al₇.₅ alloys, merely 1 mm of the thickness of the individual experimental wedges became amorphous. In the rods, amorphous structure could be obtained only in case of the Cu₄₀Hf₄₂.₅Al₉ alloy. However, only two rods of the three samples became amorphous in case of this alloy.

By using the wedge-sample, it was possible to compare the alloys by one casting. The amorphous character appears in the measurable thickness that qualifies the material. However, the thickness
obtained in the wedges cannot be rods. (It is the reason of the fact that a crystalline character is obtained in the rods in spite of the amorphous state of the wedge). From the point of view of cooling, the surface/volume ratio of wedges is lower than that of the rods. While the heat-extraction is radial in case of the rods, in wedges it is perpendicular to the normal of the surfaces, and the cooling effect of the sides can be neglected. The material solidifying at the thinner end of wedge touches the warmer material being in the vicinity of the thicker part. The warmer material may heat up the alloy in thinner part. In case of the rods, our sample perhaps will become entirely amorphous in the lower part of the mould during inflow while it will become amorphous only partially near the inlet. The mould can be warmer in case of rods and it decreases the intensity of cooling. The fact that the upper part of rods cools slower is confirmed by the results of the experiments considered unsuccessful by us. Less quantity of melt was cast into the same mould and it did not fill out the mould. A shorter cylindrical piece was formed from the material being at the bottom of mould and it became fully amorphous (Cu$_{49}$Hf$_{42}$Al$_9$ alloy). The rod is more important from practical point of view though differences can be experienced during the solidification of rods as well – as in case of the wedges – but these differences are of smaller extent.

By comparing the present results with the results published earlier [2] it can be stated that the results obtained in the course of investigation of Cu$_{45}$Hf$_{42.5}$Al$_{12.5}$ and Cu$_{50}$Hf$_{45}$Al$_5$ alloys correspond with the results obtained earlier. The high $\Delta T_c$ value and the high $T_g/T_f$ ratio combination in the case of amorphous development by Inoue et al. was met in our case. Concerning the results of Cu$_{48}$Hf$_{42}$Al$_9$ alloy, the thermal data published by Jia et al. correspond with the results obtained in the course of the measurement-series. Usually the crystallization develops a partially amorphous state at the investigated alloys; crystals develop from a part of the melt. The transition is continuous between the amorphous-crystalline regions. On the basis of the results of investigations, we would like to perform further measurements by investigating the Cu$_{49}$Hf$_{42}$Al$_9$ alloy of the Cu-Hf-Al alloy-family that has a higher Al-content. In the future, our purpose is to cast this alloy with a higher diameter and to investigate if an amorphous structure develops.

4. Summary
In case of the Cu$_{46}$Hf$_{42}$Al$_9$, Cu$_{48}$Hf$_{42}$Al$_9$, Cu$_{49}$Hf$_{42.5}$Al$_{12.5}$ and Cu$_{50}$Hf$_{45}$Al$_5$ alloys, our results concerning the thermal behaviour of amorphous bulk metallic glasses showed similar behaviour with the reference data. In case of the wedge-samples made of the Cu$_{48}$Hf$_{42}$Al$_9$, Cu$_{50}$Hf$_{42.5}$Al$_{12.5}$ and Cu$_{50}$Hf$_{45}$Al$_5$ alloys, an amorphous structure of a thickness of 1 mm – in some cases of 1.5 mm – developed, and in case of the Cu$_{48}$Hf$_{42}$Al$_9$ alloy, the amorphous state developed up to a thickness of 0.5 mm. An amorphous structure of the rods cast from the Cu$_{48}$Hf$_{42}$Al$_9$ alloy developed at a thickness of 3 mm, and no amorphous structure developed in the rod-samples made of Cu$_{50}$Hf$_{42.5}$Al$_{12.5}$ and Cu$_{50}$Hf$_{45}$Al$_5$, Cu$_{46}$Hf$_{42}$Al$_9$ alloys, the sample had a crystalline structure.

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6. References
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