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Structural and thermal properties of Cu-Hf-Ti bulk amorphous alloys

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Abstract. Cu-Hf-Ti amorphous alloys are high strength and wear resistant materials. Master alloys of $Cu_{57.5}Hf_{27.5}Ti_{15}$ and $Cu_{57.5}Hf_{25}Ti_{17.5}$ ternary alloys have been prepared by arc melting, and wedge and rod shaped samples have been cast by centrifugal casting. Liquidus and solidus temperatures of the alloys were determined by DTA. The fully amorphous size was determined by X-ray diffraction. Thermodynamic properties of the amorphous alloys were studied by DSC measurements and Kissinger analyses were performed.

1. Introduction

In the course of study of the Cu-based amorphous alloys, the Cu-Hf-Ti alloy system began to be examined a decade ago. These alloys exhibit high strength and hardness, and in an amorphous state their strength exceeds 2 GPa. As in the case of other glass forming alloys, methods with that glass forming ability (GFA) was characterised were applied to the Cu-Hf-Ti alloys, too. According to these characterizations, an alloy is a good glass former if it displays a wide supercooled liquid region (ΔT_x) and the reduced glass transition temperature (T_{rg}) is equal to or higher than 0.6. The mentioned parameters were examined in many compositions of the alloy system and the following conclusions can be drawn:

- in the binary Cu-Hf system only ribbons can be produced with an amorphous structure [1-5];
- adding Ti to the binary system GFA of the ternary alloys became much better;
- study of the parameters provided contradictionary results concerning GFA, the widest ΔT_x, the highest T_{rg} and the produced amorphous rod with the larger diameter were found at different Ti content in one alloy series [2-5];
- as a result of casting rods with different diameters, the best glass forming alloys are obtained at 20-25 at% Ti in the range of 55-65 at% Cu, these results are reflected in T_{rg} values as well;
- in the composition area of Cu(57.5-62.5)-Hf(22.5-27.5)-Ti(12.5-17.5) (at%) the GFAs of the alloys are similar and their T_{rg} varies between 0.6-0.62 [5];

Except for the thermodynamical data of the alloys, however, there are no studies about the phases that solidify during equilibrium solidification, which may lead us closer to understanding the liquid and solid state behaviours. A few conceptions tried to describe the conditions in a liquid state saying that the enthalpy difference between the liquid and solid state influences GFA [4, 5]. Adding Ti to the

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binary Cu-Hf system improves the atomic arrangement and it enhances the stability of the liquid so the solidification of the phases is inhibited [2].

2. Experimental procedure

Alloys with two compositions were investigated in our work, $Cu_{57.5}Hf_{27.5}Ti_{15}$ (Alloy 1) and $Cu_{57.5}Hf_{25}Ti_{17.5}$ (Alloy 2). Master alloys were produced by arc melting high purity metals of Cu 99.9 mass%, Hf 99.7 mass% and Ti 99.8 mass% in Ar atmosphere. 3 pieces of each master alloy were prepared. Homogeneity of the samples was checked by a scanning electron microscope (SEM). Microstructure and the phases in a sample of the master alloys were examined by SEM-EDX. The other samples of each master alloy were cast into a wedge- and a rod-shaped Cu mould by centrifugal casting. The size of the wedge sample was 33mm (length) x 3.8 mm (the thickest part) x 20 mm wide. The diameter of the rods was 3 mm. Both the surface and the cross section of the wedge samples were examined by XRD with Co-Kα radiation, and high resolution SEM analyses were carried out on the cross sections of the wedge and rod samples. The amorphous part of the wedge samples was examined by a differential scanning calorimeter (DSC). Micro hardness was measured on the cross sections of the wedge and rod samples. Oxygen content of the master alloys and the samples after centrifugal casting was analysed by the ICP method.

3. Results and discussion

3.1 Master alloys

One piece of both master alloys was prepared for microstructural analyses. Fig. 1 only shows Alloy 2, since the microstructure of the two compositions were found to be the same. Two phases can be distinguished in the microstructure; fibers (light phase), and, between them, the dark grey phase can be seen. When the samples were broken, they broke along the fibres easily. Table 1 contains the amount of the elements in each phase in the case of both alloys.

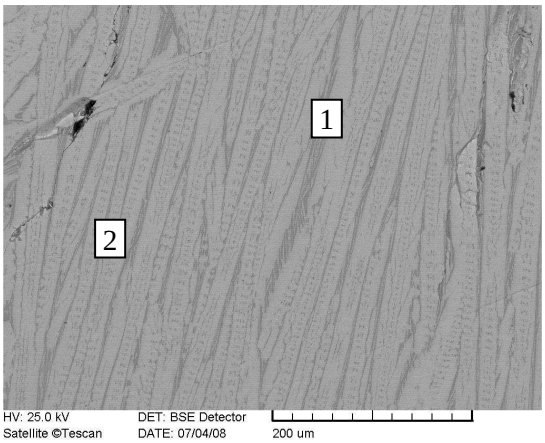


Figure 1. Microstructure of the master alloy of Alloy 2 by SEM. M = 500x

Table 1. Analysed composition of the phases of the master alloys by SEM-EDX in at %.

Alloy 1	Point 1	Point 2	Nominal comp.
Cu	51.11	62.45	57.5
Hf	10.4	26.63	27.5
Ti	38.49	10.93	15
Alloy 2			
Cu	55.54	64.79	57.5
Hf	11.28	24.04	25
Ti	33.18	11.16	17.5

The light fibres solidify as the primary phase, their dendritic structure can be observed at higher magnification. It can be stated from the composition analyses that the phases are probably the same in both alloys. The dark grey phase becomes rich in Ti, while the Hf content is much lower than the nominal composition of the alloys. The light grey phase contains more Cu and less Ti than the average composition.

3.2 Wedge and rod samples

After centrifugal casting both the wedge and rod samples had a lustrous surface. The thinnest part of the wedge was very hard and tough to bend.

The surface and cross section of the wedge-shaped samples were examined by X-ray diffraction. Starting from the thinnest part of the wedge, measurements were carried out in several spots toward

the thickest part. In the cross sections measurements were performed in the middle of the length of the sample where the thickness is ~1.5 mm, at ~1 mm and at 2 mm thickness. Three wedges were cast in both compositions to justify the same results in each case, and all the wedges were examined in the above mentioned way. In Figure 2 diffraction patterns of Alloy 1 ($Cu_{57.5}Hf_{27.5}Ti_{15}$) can be seen. X-ray measurements reveal very similar results for both compositions. Namely, that either as a function of the length on the surface, or of thickness in the cross section, the amorphous part's thickness was not more than 1.5 mm. The structure is observed to be amorphous till a length of 18-20 mm from the thinnest edge of the wedge, but in the cross section only till a length of ~10 mm, which means about 1 mm in thickness. A very thin amorphous layer still covers the non-amorphous part in the case of the wedges.

The reflections of the crystalline phases cannot be clearly identified by XRD. Some of the reflections of the known binary equilibrium phase, Cu_8Hf_3 fit to the peaks in the patterns. Some reflections of a metastable phase are known from Louzguine's work [6], and some of the peaks of Cu-Hf-Ti 2 metastable phase match with our patterns.

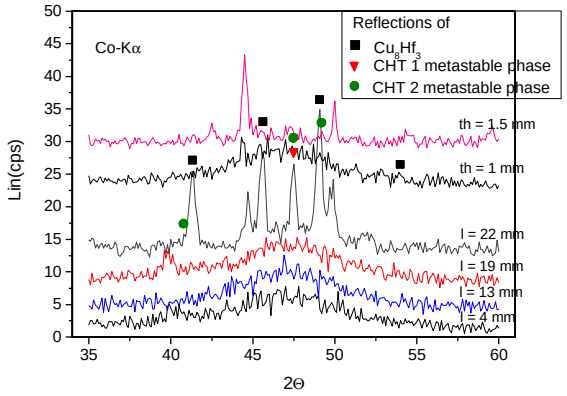


Fig. 2. XRD patterns of a wedge sample of Alloy1 recorded on the surface (l) and on the cross section (th). l = length, th = thickness

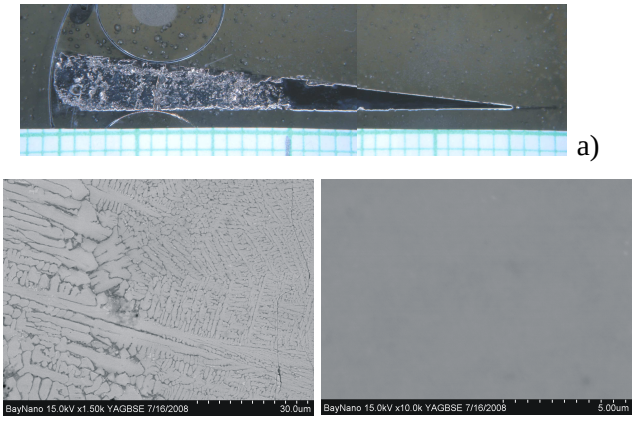
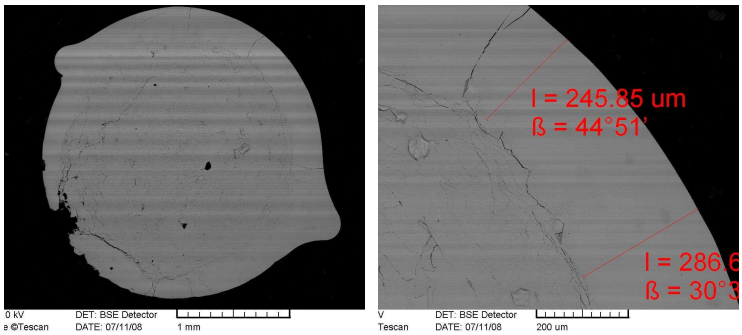


Fig. 3. a) Microstructure of a wedge sample (Alloy2) at M = 20x. SEM photographs of the wedge sample. 0 point is at the amorphous edge of the sample.

High resolution SEM analyses were carried out on the cross section of the wedge samples as well. After etching, a shiny, unique part could be distinguished from the part with crystalline structure. In the shiny part a plain grey matrix was observed. In some places however, very tiny white stars were noticed in the grey matrix. The SEM-EDX analyses showed that the stars have a higher Hf content than the matrix has. Toward the thicker part of the wedges some fine structure could be observed at ~1.3-1.5 mm thickness of the sample. The very fine structure then changed to dendritic structure and the coarsening of it can be observed, Fig. 3.

Since an amorphous structure could be observed at ~1 mm thickness in the wedge samples, good results were expected with rod samples of 3 mm in diameter. According to an earlier published paper [5], a rod of 6 mm in diameter was cast from Alloy 1 and another one of 3 or 4 mm in diameter from Alloy2. In our work, rods 3 mm in diameter were cast by centrifugal casting and then cut into several pieces to examine the cross sections. The rod samples were as shiny and lustrous as the wedge samples on the surface. SEM analysis revealed the microstructure in different cross sections, and an amorphous structure might have formed only in a very thin layer as a ring; the inner part, however, showed dendritic structure. Moreover, many holes and cracks can be seen in the samples (Fig. 4.).



a) b)

Fig. 4 SEM micrographs of a cross section of a rod of Alloy 2. a) M = 80x, b) M = 300x

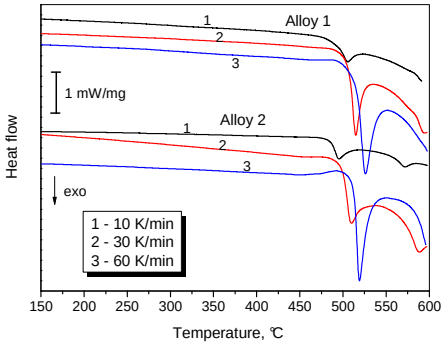


Fig. 5 DSC curves of Alloy 1 and Alloy 2 with different heating rates.

DSC measurements were performed from the thin part of the wedges. DSC curves verify that some part of the wedges had an amorphous phase, since glass transitions temperature can be seen on the curves that followed by the crystallization process in Figure 5. The determined T_g and T_x were nearly those that have been published for these alloys in other papers [2-4]. The activation energy of the crystallisation in the first DSC peak have been calculated 408 kJ/mol for Alloy 1 and 380 kJ/mol for Alloy 2. The difference between them is small. This may suggest that the crystallization of the amorphous phase occurs in the same way in case of these two compositions, namely by nucleation and diffusion controlled growth of the cubic Cu-Hf-Ti phase 1 as in $Cu_{60}Hf_{25}Ti_{15}$ [6].

4. Conclusions

Two compositions of Cu-Hf-Ti alloy system were prepared by arc melting and then wedge and rod samples were cast from both master alloys. The wedge-shaped samples contained an amorphous phase with a maximum thickness of 1.5 mm, verified by XRD and DSC measurements. In the case of rods (although rods 6 and 4 mm in diameter managed to be cast from the same alloys) only a thin amorphous ring surrounded the inner material, which solidified with dendritic structure. The cooling conditions in a wedge- and a rod-shaped Cu mould are different. A suitable cooling effect can evolve between two flats with relatively large surface, which are very close to each other. The heat extraction in the wedge is perpendicular to the sample surface, while in a rod-shaped mould it is radial. The cooling effect of the Cu mould and the air flowing around it is not sufficient to produce rods of 3 mm in diameter to be fully amorphous in cross section.

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References

[1] Duan G, Xu D and Johnson W L 2005 *Metallurgical and Materials Transactions A* **36A** 455-458
[2] Figueroa I A, Davies H A and Todd I 2007 *J. of Alloys and Compounds* **434-435** 164-166
[3] Inoue A, Zhang W, Zhang T and Kurosaka K 2001 *Acta Materiala* **49** 2645-2652
[4] Figueroa I A, Davies H A, Todd I, Verduzco J A and Hawksworth P 2007 *AZojomo* **3** 1-8
[5] Choi-Yim H and Conner R D 2008 *J. of Alloys and Compounds* **459** 160-162
[6] Louzguine D V and Inoue A 2002 *J. Mater. Res.* **17** No. 8 2112-2120