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# Preparation of Cu-based bulk metallic glasses by suction casting

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## Abstract

A series of Cu-Hf-Ti alloys prepared by rapid solidification of the melt and by copper mould casting were studied in the present work. Alloy ingots were prepared by arc-melting mixtures of pure metals in an argon atmosphere. An indication of the cooling rate obtained was determined using an Al-4.5 wt%Cu alloy. Cooling rates varied from 540 K/s for the centre section of a 4 mm die to 885 K/s for the outside wall section of the 2 mm die. The glass-forming ability, structure and thermal stability of Cu-Hf-Ti glassy alloys were studied by X-ray diffraction (XRD), differential scanning calorimetry (DSC) and differential thermal analysis (DTA). Bulk glass formation was observed for the $Cu_{64}Hf_{36}$, $Cu_{55}Hf_{25}Ti_{20}$ and $Cu_{56}Hf_{25}Ti_{19}$ alloys, with critical diameters $d_c$ for a fully glassy structure of 1, 4 and 5 mm, respectively. The substitution of Hf by Ti increased the glass-forming ability (GFA) and the thermal stability.

*Keywords: Rapid solidification, X-ray diffraction, thermal analysis, bulk metallic glasses.*

## 1. Introduction

Bulk-metallic-glass "BMG" materials are a new class of structural material that exhibit non-typical properties as compared with other metal alloys [1]. As their name suggests, BMGs are "glassy" metallic alloys, which exhibit noncrystalline or amorphous structures. For this reason, BMGs are currently of significant interest in the field of condensed matter physics in an effort to bring a greater understanding to the nature of glass and the glass transition in metals, at present a largely unresolved problem [2,3]. Due to their inherent absence of slip planes, the materials exhibit very high yield strengths (1 to 5 GPa) and elastic limits (~ 2%) [4], as well as demonstrating good fatigue endurance limits [5]. Also, BMG composites with crystalline inclusions in a glassy matrix are showing promise in enhancing ductility of these materials while retaining their high strengths [6]. Furthermore, the materials can be cast into high-precision net shapes [7]. Due to their unique processing capabilities and high strengths, BMG materials are of great interest to the industrial community and are expected to be used extensively in the aerospace and transportation industries in the future. Arc melting/suction casting involves sucking a melt into a die by use of a pressure differential between the casting chamber and the melting chamber. The base of the die is connected to a vacuum source which, when released, causes a pressure differential, which forces the melt into the chamber. The vacuum results from either the opening of a solenoid valve, which connects the casting chamber to some pre-evacuated chamber, or by the use of a mechanical piston [8]. Suction casting is the process that was used in the production of Cu-Hf-based bulk metallic glasses in the present work. The process has similar advantages to high pressure die casting, with good thermal and physical contact giving high quench rates and large pressure differential giving low levels of casting defects.

## 2. Experimental procedure

A number of Cu-Hf and Cu-Hf-Ti alloy ingots were produced by arc-melting of Hf (crystal bar), Cu (sheet) and Ti (Rod) having purities 99.5 at.%, 99.99 at.% and 99.8 at.%, respectively. The alloy ingots were inverted on the hearth and re-melted several times, to ensure compositional homogeneity. The alloy compositions represent the nominal values but the weight losses in melting were negligible (< 0.1%). Cylindrical alloy rods, of length ~ 50 mm and having either stepped diameters from 5 to 1 mm or a single diameter of 5 mm, were produced by copper mould, suction casting within the argon arc furnace. The specially designed casting unit utilised an argon arc to melt an ingot sample placed on a hearth directly above a cylindrical cavity in a solid water-cooled copper block. A solenoid valve connected a vacuum pump to the base of the copper die which, when connected, resulted in the melt being forced into the die. Details of the unit are given in ref. [9]. An indication of the cooling rate achieved by this system for the stepped die was determined by casting Al-4.5 wt%Cu alloy samples and measuring their secondary dendrite arm spacings ($\lambda_2$). Rods were cast, sectioned, polished to reveal the cross section, etched (0.5 vol% HF in de-ionised water for 30 seconds), and examined using an optical microscope with digital image analysis capabilities. Comparison of the obtained secondary dendrite arm spacings with published data [10,11] (giving a graphical relationship between arm spacing and cooling rate or solidification time) was used to determine the cooling rate obtained. Additionally, ribbon samples of each alloy, with cross sections of 0.03 mm x 2.0 mm and 0.2 mm x 3.2 mm, were produced by chill-block melt spinning in a sealed argon atmosphere. Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA), both at a heating rate of 20 K/min (0.33 K/s), were used to determine thermal parameters over the relatively low temperature supercooled liquid region and the high temperature melting region, respectively. Zinc and gold were used for temperature calibration of the DSC and DTA, respectively. The inflection point of the endothermic transition to the supercooled liquid state was chosen as $T_g$, rather than the onset that is commonly taken. The crystallisation temperature, $T_x$, was taken as the onset of the exothermic crystallisation peak. The melting ($T_m$) was defined as the offset of the melting range and the liquidus ($T_l$) temperatures corresponding to the completion of the melting transformation were adjusted to allow for thermal lag, using a correction factor determined earlier by Donald and Davies [12]. The ratio, $T_{rg}$, the reduced glass transition temperature, was defined as $T_g/T_l$. X-ray diffraction was employed to detect the presence of crystalline phases.

## 3. Results and Discussion

As mentioned above, the cooling rate obtained was determined using an Al-4.5 wt%Cu alloy. Cooling rate is a function of both the alloy composition and the casting parameters used; therefore, the values obtained give only an indication of the cooling rate attainable when casting BMG's. Cooling rates varied from 540 K/s for the centre section of a 4 mm die to 885 K/s for the outside wall section of the 2 mm die (see Table 1). The cooling rate of the 4 mm section is lower than the 2 mm, not only because of the larger diameter but also because of the proximity of this larger section die to the ingot melting zone on the top of the die when using a stepped mould. Suction cast rods were produced in diameters from 1 to 6 mm, they showed good metallic lustre and low incidence of fabrication defects.

The critical diameters, $d_c$, for all the binary Cu-Hf alloys are summarised in Table 2. In the Cu-Hf series of alloys studied in the present article, only $Cu_{65}Hf_{35}$ can be readily cast into 1 mm-thick fully amorphous form. Figure 1b, shows the $T_g$ and $T_x$ results plotted as functions of Cu content. Although no clear glass transition is observed for 70 at.%Cu, the alloys containing 50 at.% to 65 at.%Cu exhibit distinct glass transitions, followed by the glass transition region before crystallisation.

$T_g$ and $T_x$ increase with increasing Cu content from 35 at.% to 45 at.%, despite the fact that the Hf has a much higher cohesive energy than Cu. The substitution of Hf for Cu decreases the liquidus temperature, $T_l$ has minima of 1270 and 1263 K at 55 and 65 at.%Cu, respectively, in good agreement with the Cu-Hf equilibrium diagram [13] (Figure 1a). The values of the reduced glass temperature ($T_{rg} = T_g/T_l$) are plotted as a function of Cu content in Figure 3a.

$T_{rg}$ increases when increasing Cu content from 0.584 up to 0.617 for Cu = 50 and 65 at.%, respectively, then decreasing to the value 0.613 for Cu = 70 at.%. The data show that the observed glass formation is consistent with the trends in $T_{rg}$, since the $Cu_{65}Hf_{35}$ alloy composition had the largest $d_c$ of 1 mm and $T_{rg}$ of 0.617. The values of $T_l - T_g$, which is the magnitude of undercooling required to form an amorphous solid and avoid crystallisation are

**Table 1:** Cooling rates obtained for a stepped 4/3/2 mm diameter die cavity using Al-4.5 wt%Cu.

| | 4 mm | 3 mm | 2 mm |
|---|---|---|---|
| Maximum (K/s) | 620 | 885 | 885 |
| Minimum (K/s) | 540 | 770 | 770 |

**Table 2:** Critical glass forming diameter $d_c$ and thermal properties for the Cu-Hf and Cu-Hf-Ti alloys investigated.

| Composition | $d_c$ mm | $T_g$ K(±4) | $T_x$ K(±4) | $T_m$ K(±10) | $T_l$ K(±10) | $T_{rg}$ ±0.01 | $T_l - T_g$ ±8 |
|---|---|---|---|---|---|---|---|
| $Cu_{50}Hf_{50}$ | 0.1 | 755 | 790 | 1256 | 1293 | 0.584 | 538 |
| $Cu_{55}Hf_{45}$ | 0.1 | 760 | 796 | 1253 | 1270 | 0.598 | 510 |
| $Cu_{60}Hf_{40}$ | 0.5 | 777 | 801 | 1243 | 1291 | 0.602 | 514 |
| $Cu_{65}Hf_{35}$ | 1 | 779 | 821 | 1246 | 1263 | 0.617 | 484 |
| $Cu_{70}Hf_{30}$ | 0.1 | 785 | 811 | 1243 | 1281 | 0.613 | 496 |
| $Cu_{55}Hf_{40}Ti_5$ | 0.5 | 751 | 798 | 1193 | 1269 | 0.592 | 518 |
| $Cu_{55}Hf_{35}Ti_{10}$ | 1 | 742 | 763 | 1183 | 1243 | 0.597 | 501 |
| $Cu_{55}Hf_{30}Ti_{15}$ | 2 | 736 | 756 | 1143 | 1213 | 0.607 | 477 |
| $Cu_{55}Hf_{26}Ti_{19}$ | 5 | 730 | 758 | 1146 | 1201 | 0.608 | 471 |
| $Cu_{55}Hf_{24}Ti_{21}$ | 4 | 721 | 748 | 1146 | 1189 | 0.606 | 468 |
| $Cu_{55}Hf_{22}Ti_{23}$ | 4 | 713 | 743 | 1137 | 1178 | 0.605 | 465 |
| $Cu_{55}Hf_{20}Ti_{25}$ | 3 | 715 | 733 | 1135 | 1168 | 0.612 | 453 |
| $Cu_{55}Hf_{15}Ti_{30}$ | 2 | 703 | 719 | 1138 | 1183 | 0.594 | 480 |
| $Cu_{55}Hf_{10}Ti_{35}$ | 0.5 | 684 | 705 | 1140 | 1198 | 0.571 | 514 |
| $Cu_{55}Hf_5Ti_{40}$ | 0.1 | 666 | 693 | 1143 | 1213 | 0.549 | 547 |

plotted in Figure 1c. The alloy $Cu_{65}Hf_{35}$ also had the lowest undercooling, 484 K, of all the binary system alloys.

Table 2 gives the critical rod diameters, $d_c$, the thermal properties, $T_g$, $T_x$, $T_l$, $T_l - T_g$ and the reduced glass temperature $T_{rg}$ (= $T_g/T_l$), for alloys in the series $Cu_{55}Hf_{45-x}Ti_x$ with $x$ in the range 5 to 40. The addition of Ti to the $Cu_{55}Hf_{45}$ binary alloy increased drastically the GFA observed experimentally in the bulk samples, the largest critical diameter $d_c$ for complete glass formation being 5 mm for the alloy $Cu_{55}Hf_{26}Ti_{19}$. Bulk rod samples showed a fully glassy structure up to 4 mm for $x = 21$ and $x = 23$, and up to 3 mm for $x = 25$. Increasing the Ti:Hf ratio resulted in rapid decreases in $T_g$ and $T_x$, as would be expected from the fact that the melting point and cohesive energy of Ti are substantially lower than for Hf (see Figure 2b). The solidus temperature ($T_m$) remains fairly constant in the range of $x = 15$ to 40, which suggests a common eutectic transformation over this range (Figure 2a). The liquidus temperature ($T_l$) for the ternary alloys is plotted against the solute content in Figure 2a. The liquidus temperature $T_l$ has its minimum value for the 25 at%Ti alloy, probably corresponding to a ternary eutectic, since only this composition has a single melting peak in the DTA trace or very close to the eutectic composition. The values of $T_{rg}$ are plotted against the Ti content $x$ in Figure 3b; the value peaks at $\sim x = 25$. The best four bulk glass forming alloys thus have compositions spanning the peak in $T_{rg}$. Thus, there is good correlation between the GFA and the measured $T_{rg}$. The usefulness of $T_{rg}$ as a figure of merit in predicting GFA for non-bulk glass forming metallic alloys is well established [6], For the present alloy system, the correlation between GFA and $T_{rg}$ is good, probably because the crystalline phases which are being suppressed by glass formation do not change over the composition range 5 to 40 at%Ti.

The values of the magnitude of undercooling required to form an amorphous solid, $T_l - T_g$, are plotted in Figure 2c. The alloy $Cu_{55}Hf_{20}Ti_{25}$ showed the smallest undercooling value of 453 K in both ternary and binary systems, probably because of its proximity to the eutectic zone. The magnitude of undercooling for the alloy with the largest $d_c$ was 471 K, which may suggest an off-eutectic composition, since this composition displays a pair of melting peaks in the DTA trace. The smaller the undercooling required, the lower the driving force for crystallization and the time permissible for any nucleants, both heterogeneous and homogenous, to grow and form crystals ($T_{rg}$ does not take into account nucleation growth kinetics or extrinsic factors such as heterogeneous nucleation). Therefore, the closer the freezing point of an alloy is to $T_g$, the better the GFA should be, i.e. this should be greater for a eutectic or near-eutectic alloy. Therefore, for an alloy to have any chance of forming an amorphous solid, it should have small $T_l - T_g$ values.

# 4. Conclusions

$Cu_{55-x}Hf_{45}$ and $Cu_{55}Hf_{45-x}Ti_x$ bulk metallic glasses were successfully prepared by water-cooled copper mould casting. Structural analysis indicated that the diameter of glassy phase had maximum values of 1 mm for the binary alloy $Cu_{65}Hf_{35}$ and 5 mm for the ternary $Cu_{55}Hf_{26}Ti_{19}$ alloy composition. The substitution of Hf in the $Cu_{55}Hf_{45}$ alloy

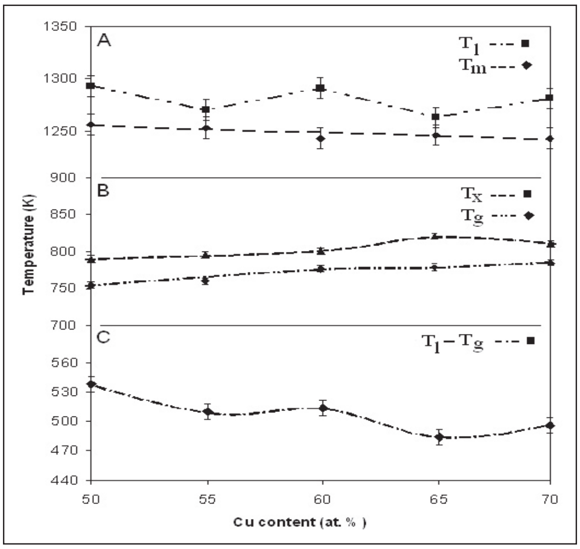


**Figure 1:** (a) Plot of $T_m$ and $T_l$, (b) $T_g$ and $T_x$ and (c) $T_l - T_g$ for the Cu-Hf alloys as a function of Cu content.

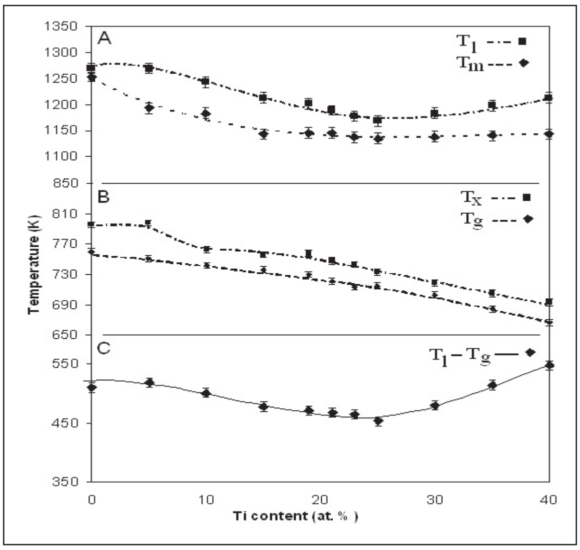


**Figure 2:** (a) Plot of $T_m$ and $T_l$, (b) $T_g$ and $T_x$ and (c) $T_l - T_g$ of the Cu-Hf-Ti alloys as a function of Ti content.

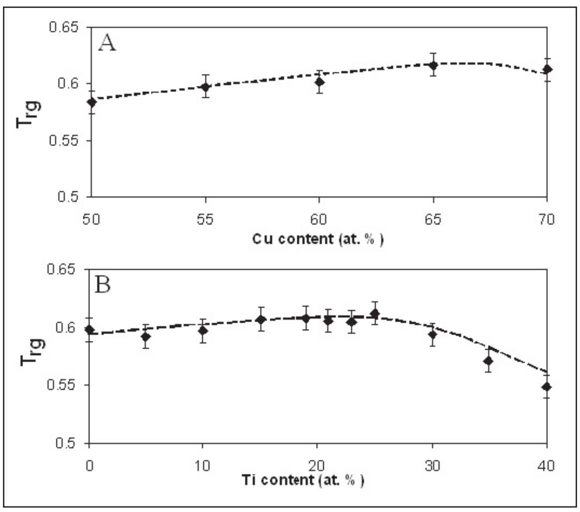


**Figure 3:** (a) Plot of $T_{rg}$ of $Cu_{100-x}Hf_x$ as a function of Cu content, (b) Plot of $T_{rg}$ of $Cu_{55}Hf_{45-x}Ti_x$ as a function of Ti content.

by Ti causes an increase in the glass-forming ability (GFA). As the Ti content increases, the glass transition temperature ($T_g$) decreases, while the crystallization temperature ($T_x$) shows a maximum at 5% Ti and then decreases. The liquidus temperature ($T_1$) has a minimum of 1168 K at 25% Ti, and hence, a maximum $T_g/T_1$ of 0.612 is obtained at 25% Ti with a $d_c$ = 3 mm. The alloy with the largest $d_c$ observed showed a $T_{rg}$ value of 0.608 and an undercooling of 471 K.

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