European Journal of Engineering & Environmental Sciences

RESEARCH ARTICLE

Thermal Properties and Glass Forming Capability of Hf-Al-Ni and Hf-Al-Cu Melt Spun Ribbon.

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ABSTRACT

The glass formability of melt spun Hf-Al-Ni and Hf-Al-Cu systems has been studied and found to be similar to comparable Zr-based systems. Results for XRD, T_g, and ΔT_x are presented. A supercooled liquid region of 41K for $Hf_{54}Al_{17.5}Ni_{28.5}$ and 52K for $Hf_{45}Al_5Cu_{50}$ melt spun metallic glasses has been determined.

***Keywords:** Thermal Properties, Glass Forming Capability, Hf-Al-Ni and Hf-Al-Cu Melt Spun Ribbon*

Introduction

The use of zirconium as a base element in alloys of good glass formability with the additions of other metallic elements are well established. Systems presented as good glass formers at cooling rates less than 10^3K/s include Zr-Al-(Cu, Ni), Zr-Ti-Cu, Zr-Al-Ni-Cu, Zr-Ti-Be, and (Zr, Ti)-Al-Ni-Cu-(Pd, Be) [Johnson, 1994; Inoue, Shinohara, Yokoyama, & Masumoto, 1995]. Inoue et al (1995) has shown that ternary Zr-Al-(Cu, Ni) [Inoue, Kawase, Tsai, Zhang, Inoue & Masumoto, 1994] and quaternary Zr-Al-Ni-Cu [Shinohara, Yokoyama, Masumoto. Inoue & Zhang 1996] systems could produce bulk metallic glass (BMG) rods of diameter 30mm, while [A. Peker, W.L. Johnson] produced 40mm thick amorphous samples of alloys in the Zr-Ti-Ni-Cu-Be system having a supercooled liquid region-ΔT_x of up to 135K.

Chemically and physically, zirconium and hafnium are rather similar, having nearly identical atomic radii and the same number of oxidation states, therefore, one would expect that such glass-forming compositions would also form an amorphous phase if Hf was substituted for Zr.

There is limited published literature on Hf-based glass forming alloys. Earlier work examined melt spun Hf-(Ni, Co, Cu), Hf-Si-(Nb, V), and Hf-Co-Ni [Buschow 1984; Jansson & Nygren 1991]. Mechanical alloying has been used to form amorphous phases for Hf-(Ni, Cu, Ru) and $Hf_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ [Thompson, Politis, & Kim 1988; Damonte, Mendoza-Zélis & Eckert 2000]. [Zhang, Inoue & Masumoto 1994] found that $Hf_{65}Al_{10}Ni_{25}$ and $Hf_{65}Al_{10}Cu_{25}$ formed an amorphous phase with a ΔT_x of approximately 30K and 50K respectively. Preliminary work on Hf-Ni-Cu [Zhang et al] showed that amorphous phases could be formed with Ni and Cu over a wide compositional range of up to 70at% (the balance being Hf), with $Hf_{60}Ni_{20}Cu_{20}$ having a ΔT_x of 65K. Recently Inoue et al [Inoue, Zhang & Kurosaka 2001] has reported a critical diameter for glass formation of 4mm for $Cu_{60}Ti_{15}Hf_{25}$. However, no systematic detailed results on glass forming characteristics have been published for Hf-Al-Ni or Hf-Al-Cu ternary systems.

***Citation:** Figueroa, I. A. & Nnamchi, P. (2018). Thermal Properties and Glass Forming Capability of Hf-Al-Ni and Hf-Al-Cu Melt Spun Ribbon. *European Journal of Engineering and Environmental Sciences, 2(2), 1-9.*
***Accepted:** June 20, 2018; Published: June 30, 2018*

Experimental

Using elements of purity >99.9wt% (Hf) or >99.99wt% (Al, Ni, Cu) 10g ingots were produced by arc melting, followed by casting of ribbon with thickness 25-35μm and width 3mm using single wheel melt spinning under an argon atmosphere at a surface wheel speed of 49m/s.

A digital transducer was used to determine sample thickness (±1μm). A Philips XRD diffractometer with a CoKα source and a Dupont DSC unit were used for structural and thermal characterisation respectively. DSC analysis was carried out under argon atmosphere at 20 and 40K/min with an accuracy of ± 10K per data point.

Presentation and Discussion of Results

Figure 1 shows that an amorphous phase (within the XRD limits of detectable crystal size and volume percent) is formed over a wide compositional range for both Hf-Al-Ni and Hf-Al-Cu. Fully amorphous ribbon was formed between Hf 40 to 65at% for Hf-Al-Ni and from Hf 30 to 66at% for Hf-Al-Cu. In Hf-Al-Cu there are two regions of glass formation, possibly corresponding to eutectic or near eutectic compositions focused around Hf 35 to 45 at% and 50 to 66at% respectively. This is similar to the known regions of glass formation associated with Zr-based alloys, namely $Cu_{60}(Hf/Zr)_{40}$ and Zr_{60} (i.e. $Zr_{55}Al_{10}Ni_5Cu_{30}$ to $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$). Hf-Al-Cu diffraction patterns indicate the presence of Hf_2Cu in partly crystalline ribbons and of $Al_{1.65}Cu_{0.35}Hf$ in Al rich crystalline samples. Only one range of glass formation is seen in Hf-Al-Ni, indicating that Ni is best used as an additive rather than as a main base element in Zr- or Hf-based bulk glass forming compositions.

These results are similar to results presented by Inoue et al [1990] for Zr-Al-Ni and Zr-Al-Cu [Inoue, Kawase, Tsai, Zhang & Masumoto 1994] melt spun ribbon. The range for which glass formation is detected for Zr-based alloys is greater than that for the respective Hf-based ternary alloy. This shows that Hf has a similar but diminished glass forming ability as Zr.

Figures 2 and 3 present values obtained for ΔT_x (=T_x-T_g, where T_x and T_g are the temperatures of crystallisation and glass transition respectively) and T_g respectively. T_g is selected as the offset of the slope transition presented as I in Figure 4 (using this measure decreases the apparent magnitude of the supercooled liquid region). For Hf-Al-Ni, T_g ranges from 795K ($Hf_{64}Al_8Ni_{28}$) to 893K ($Hf_{50}Al_{30}Ni_{20}$), with ΔT_x at a maximum of 41K for $Hf_{54}Al_{17.5}Ni_{28.5}$. For Hf-Al-Cu, T_g varies from 801K ($Hf_{66}Al_8Cu_{26}$) to 831K ($Hf_{50}Al_{20}Cu_{30}$). In the two regions of glass formation for Hf-Al-Cu ΔT_x is 48K for $Hf_{60}Al_{10}Cu_{30}$ and 52K for $Hf_{45}Al_5Cu_{50}$. T_g for Zr-Al-Ni and Zr-Al-Cu is approximately 50K to 130K less than for the respective Hf-based alloys.

Figure 5 show results of Inoue et al [1990]; Inoue, Kawase, Tsai, Zhang & Masumoto 1994] for the respective Zr-based systems superimposed with results attained from this study for Hf-based systems (for the purpose of comparison here the onset of the glass transition is used as the measure of T_g, i.e. II in fig. 4). The regions of largest ΔT_x for Hf-Al-(Ni, Cu) systems are similar to those of the comparable Zr-Al-(Ni, Cu) systems. The location of the largest ΔT_x of ~70K and 69K for Zr-Al-Ni and Hf-Al-Ni respectively is Zr/Hf 55-65at% and Ni 20-30at%. For Zr-Al-Cu and Hf-Al-Cu the largest ΔT_x's are ~80K for both at Zr/Hf 60-70at% and Cu 25-35at% and ~60K and 100K at Zr/Hf 40-50at% and Cu 45-50at% respectively. Overall, the values of ΔT_x and the compositions with a fully amorphous phase are smaller for the Hf-based systems. The only compositions of Hf based alloys to show an enhanced ΔT_x are Hf 50-60at% Cu 45-55at% (although Hf 55-70at% still shows considerable potential for good glass formation).

No full explanation can be offered for the decrease in glass forming ability of Hf-Al-(Ni, Cu) compared with Zr-Al-(Ni, Cu). Several empirical and semi-empirical rules [Johnson. 1999; Davies & Luborsky, 1983; Inoue, Negishi, Kimura & Aoki 1997] which favour metallic glass formation can be considered:

1. multicomponent alloy systems consisting of more than three elements [Inoue, Zhang & Masumoto 1993],
2. significant difference of more than 13% in the atomic size ratios [Inoue et al 1993],
3. optimum negative heats of mixing among the constituent elements [Inoue et al 1993],
4. T_{rg}, ratio of T_g/T_l, (T_l being the liquidus temperature), with values greater than 0.6[Davies 1976; Turnbull & Fisher 1949],
5. large supercooled region (ΔT_x); this is not a measure of, but rather a reflection of the glass forming ability of an alloy [Molokanov, Mikhailova, Kliger & Petrzhik 1997],

6. the absence of contaminants acting as sites for heterogeneous nucleation [Drehmann, Greer, & Turnbull 1982; Kui, Greer & Turnbull, 1984],
7. superheating a glass-forming alloy well above its melting temperature can contribute to the formation of an amorphous phase [Ling, Ochin, Marmelin, Faudot & Bigot 1996].

Concerning rule 1 and 2, there is no significant difference in atomic size ratios of the constituent elements between the Zr- and Hf-based ternary systems. In relation to rule 3, the heats of mixing between Zr-Al, Zr-Ni, Zr-Cu are -44, -49, -23 kJ/mol [Boer, Boom, Mattens, Miedema & Niessen 1988] respectively, while for Hf the respective heats of mixing between Hf-Al, Hf-Ni, Hf-Cu are -39, -42, -17 kJ/mol [Ling, Ochin, Marmelin, Faudot & Bigot. 1996], indicating that an amorphous phase containing Zr would be more stable and likely to resist crystallisation in thicker sections (and at lower cooling rates) than the comparable Hf-based composition with the same Al, Ni, and/or Cu quantities. *As for rule 4, work concerning T_{rg} and the effects of T_l and T_m (solidus temperature) is on-going and will be presented in a future publication*. Regarding rule 5 ΔT_x can be used as an intrinsic variable reflecting the glass formability, This limited use is due to; a) at different heating rates applied during thermal analysis, T_x (path dependent) will vary more than T_g (material property, dependent on solidification profile), thus distorting the measure of ΔT_x, and (b); during solidification, the critical zone for vitrification will be the crystal-amorphous nose of the time-temperature transformation diagram and not T_g (where the viscosity will have reached a prohibitably high value, thus retarding rearrangement and crystallisation). Therefore, ΔT_x values presented for Hf-based ternary alloys (fig. 5), when compared with those for Zr-based ternary indicate that Hf has some potential, but less than Zr, as a basis for glass forming alloys.

The melting temperatures of Zr and Hf are 2125K and 2500K respectively. Thus, with regards to rules 6 and 7; within the operating temperature limits of a particular casting unit, there would be a greater possibility for impurity phases in Hf-based alloys of surviving a melting process than for Zr-based alloys. This could lead to a larger number of active heterogeneous nucleation sites because of the reduced magnitude of superheat given to the system (due to the reduced superheat a particular unit can impose on a higher melting point Hf containing phase when compared to the similar lower melting point Zr phase).

Conclusion

The glass formability of ternary Hf-Al-Ni and Hf-Al-Cu systems was presented. Results were compared with those previously published for Zr-Al-Ni and Zr-Al-Cu metallic glass forming systems.

Fully amorphous ribbon was formed for a content of Hf 40 to 65at%, Ni 10 to 35at% for Hf-Al-Ni and from Hf 30 to 66at%, Cu 20 to 60at% for Hf-Al-Cu. One centre for glass formation for Hf-Al-Ni was seen (fig. 1), approximately $Hf_{60}Al_{20}Ni_{20}$ (same as Zr-Al-Ni) and two main centres for Hf-Al-Cu, $Hf_{60}Al_{10}Cu_{30}$ and $Hf_{45}Al_5Cu_{50}$ (similar to Zr-Al-Cu). ΔT_x was seen to be at a maximum of 41K for $Hf_{54}Al_{17.5}Ni_{28.5}$, 48K for $Hf_{60}Al_{10}Cu_{30}$ and 52K for $Hf_{45}Al_5Cu_{50}$. Possible explanations for the difference in glass formability between Zr- and Hf-based systems in terms of reduced negative heats of mixing, vulnerability to heterogeneous nucleation, and reduced superheating have been proposed. Work concerning the T_{rg} ratio of these systems is currently under way and will be published in due course.

Acknowledgements

This work has been financially supported by the Defence, Evaluation, and Research Agency (DERA), Farnborough, UK (DERA has split and is now known as Qinetiq, and The Defence Science and Technology Laboratory). Valuable technical support provided by Mr. Hawksworth is also acknowledged.

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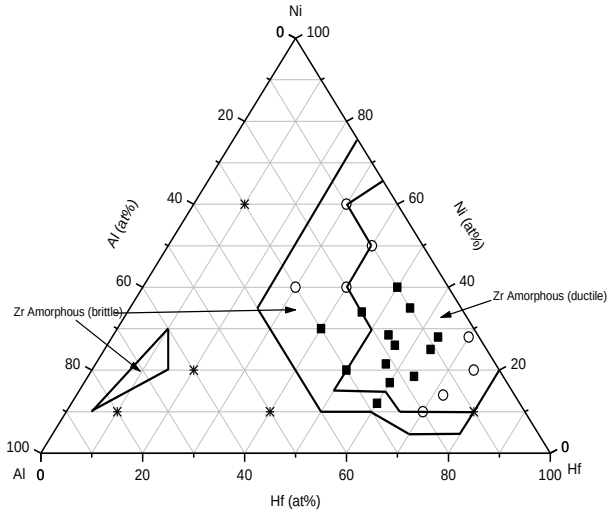
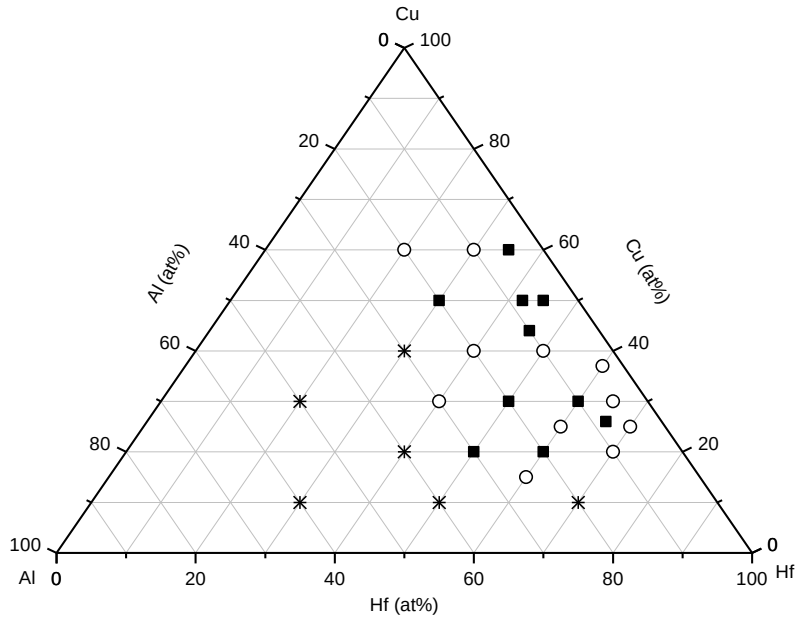
APPENDIX I



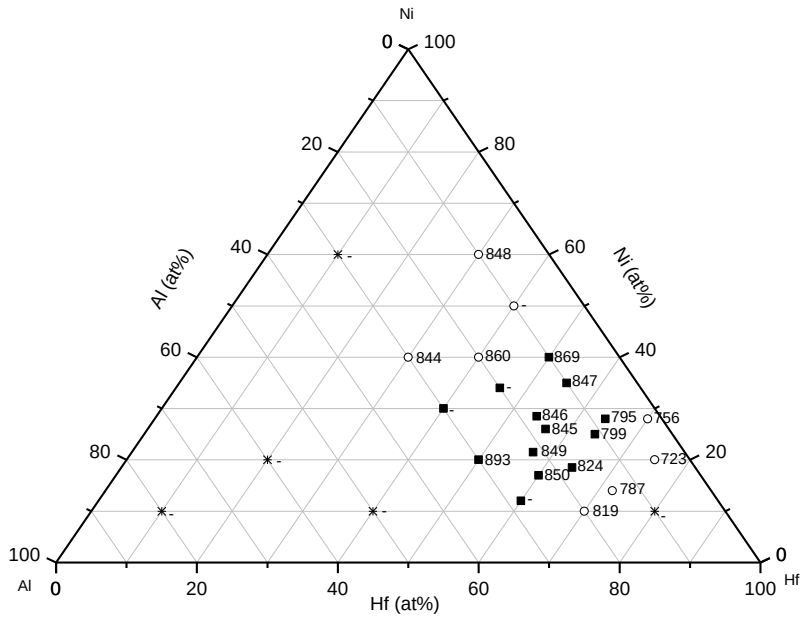
(a)



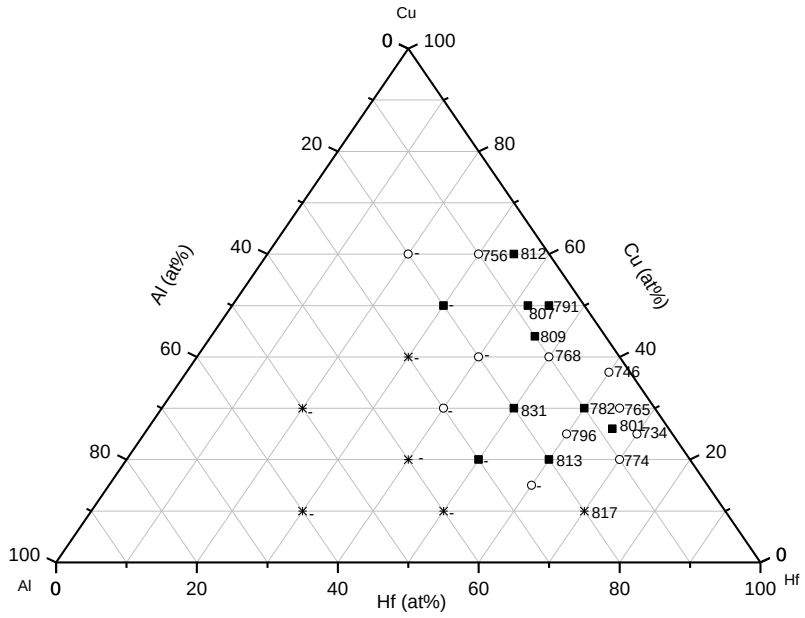
(b)

Figure 1: XRD results for melt spun ribbon; a) Hf-Al-Ni superimposed with results for Zr-Al-Ni (boundary line) [6], b) Hf-Al-Cu. Key: ■ = amorphous ○ = amorphous & crystalline, ⁎ = crystalline.

APPENDIX II



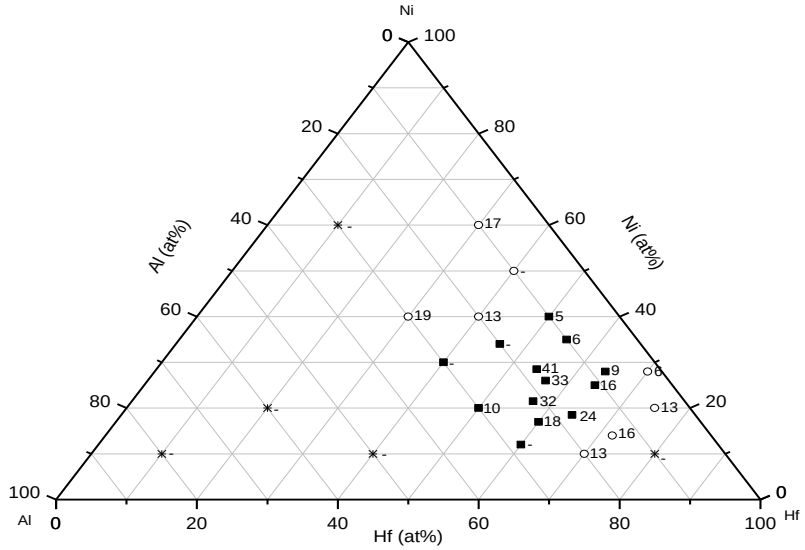
(a)



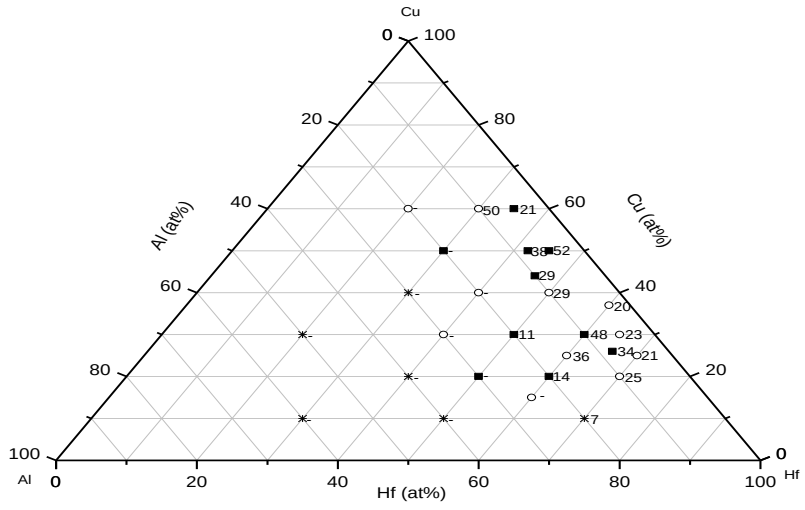
(b)

Figure 2: Values of T_g attained by DSC at a heating rate of 20K/min for a) Hf-Al-Ni, and b) Hf-Al-Cu melt spun ribbon.

APPENDIX III



(a)



(b)

Figure 3: Values of ΔT_x (supercooled liquid region, T_x-T_g) at a heating rate of 20K/min for a) Hf-Al-Ni, b) Hf-Al-Cu melt spun ribbon.

APPENDIX IV

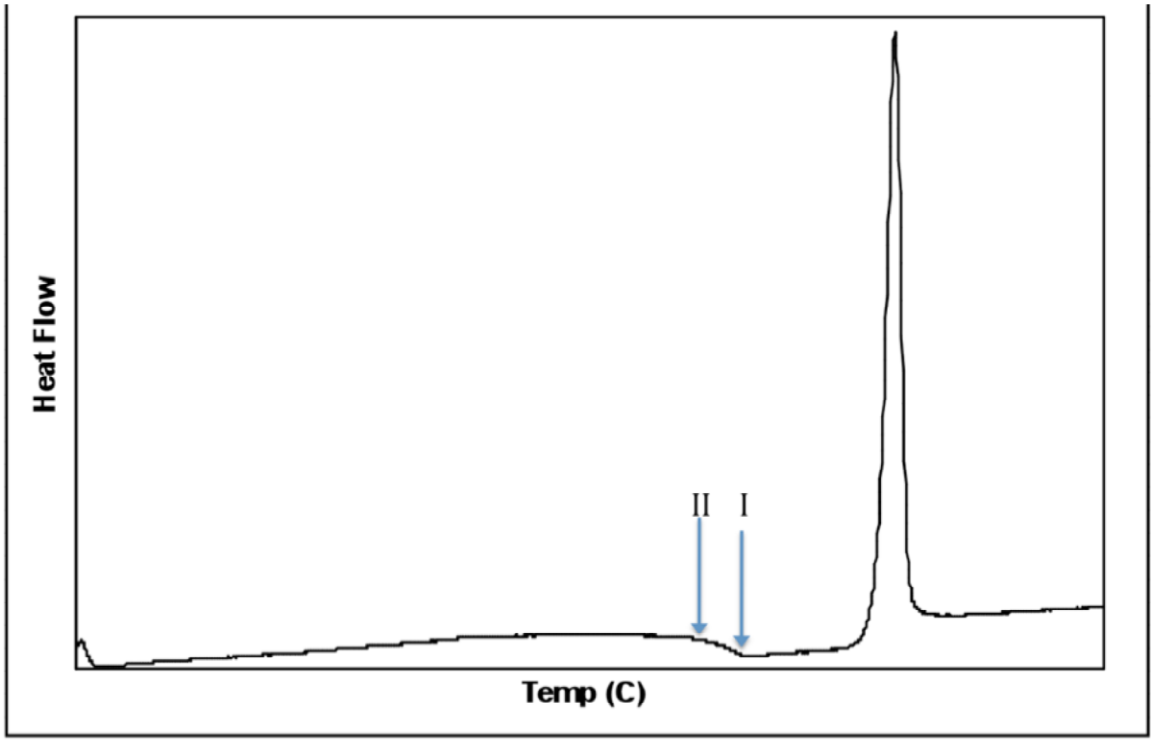
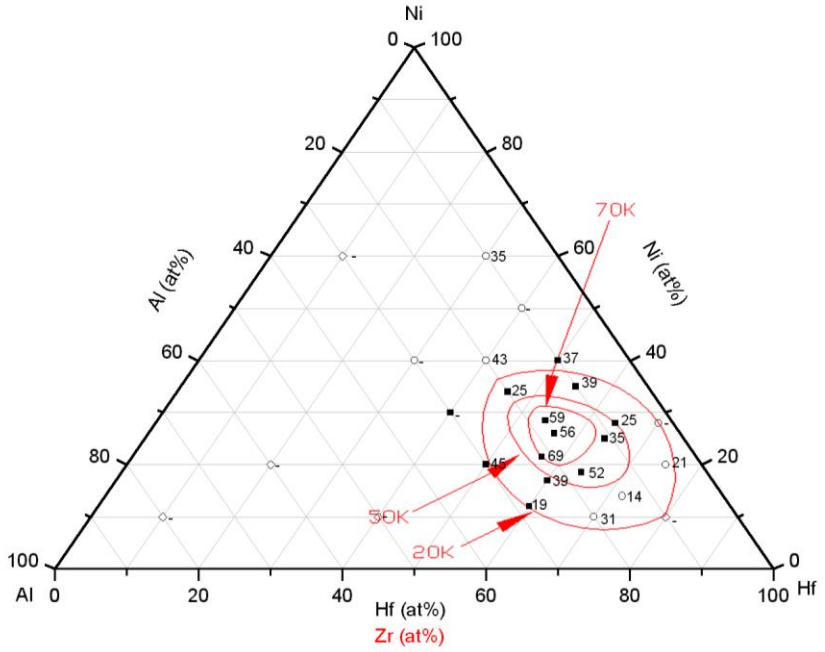
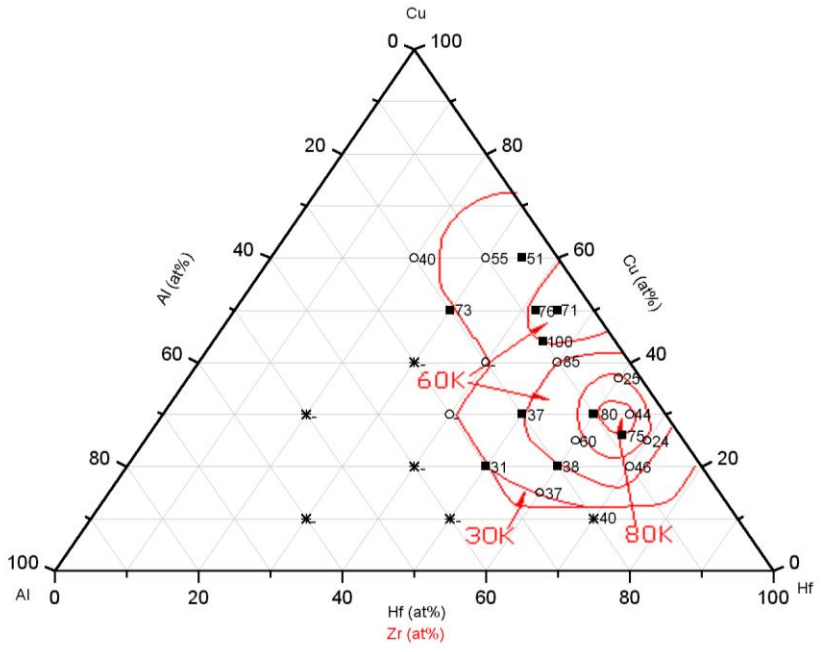


Figure 4: DSC plot of Hf-Al-Ni melt spun ribbon showing I, the offset of glass transition, giving T_g as chosen for Hf-based results presented, and II, the onset of glass transition, giving T_g as used in fig. 5 for comparison purposes.

APPENDIX V



(a)



(b)

Figure 5: ΔT_x for melt spun a) Hf-Al-Ni, and b) Hf-Al-Cu using the onset of glass transition for T_g (40K/min). Also shown (boundary lines) is ΔT_x (approximate) for melt spun Zr-Al-Ni[6] and Zr-Al-Cu[7] ribbon (40K/min).