HAFNIUM-BASED BULK METALLIC GLASSES FOR KINETIC ENERGY PENETRATORS

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ABSTRACT

A new family of quinary, hafnium-based, bulk-metallic-glass-forming alloys has been developed for use in composite kinetic-energy penetrators. The alloys are based on an invariant point identified in the hafnium-copper-nickel ternary system. They are denser than zirconium-based glass-forming compositions, and exhibit a higher reduced glass-transition temperature than alloys prepared by 1:1 hafnium substitution into the zirconium-based alloys. The combination of density and glass-forming ability exhibited by this alloy moves the composite technology closer to being a viable substitute for depleted-uranium penetrators.

1. INTRODUCTION

1.1 Criterion for Effective Kinetic Energy Penetrator Performance

The lethality of depleted uranium-based (DU) and tungsten-nickel-iron (W-Ni-Fe) composite kinetic energy (KE) munitions is primarily ascribed to their high densities (U: \( \rho = 18.95 \text{ g/cm}^3 \), and W: \( \rho = 19.3 \text{ g/cm}^3 \), respectively). Additionally, DU’s material characteristics give it greater penetration ability than W-Ni-Fe. The increased performance is attributed to a localized flow-softening behavior, more commonly referred to as adiabatic shear (AS) (Magnes and Farrand, 1990). Localization occurs when the rate of thermal softening exceeds that of the rate of strain and strain-rate hardening. In ballistic tests with semi-infinite targets, the transformed zones tend to occur at oblique planes with respect to the penetrator-target interface that renders the DU alloy penetrator, unlike W-Ni-Fe, able to maintain a "chiseled-nose" shape favorable for enhanced penetration. However, environmental hazards and the cleanup of spent munitions impose additional costs on the use of DU.

A long-standing goal of current research is to achieve localized flow softening in non-DU materials. Conventional W-Ni-Fe composites are two-phase composites of nearly unalloyed W particles embedded in a Ni-alloy matrix. Because the W phase itself is very resistant to AS localization, efforts over the past decade have primarily focused on replacing the Ni-alloy matrix with one having a greater susceptibility to AS failure.

As conceived, this W-based composite would combine the desirable properties of DU (i.e., increased penetration and AS) and W (i.e., density and non-toxicity) as a new class of high density, high strength, and high hardness KE penetrator. It is hoped that, by emulating the preferred erosion behavior in a comparable-density composite, the ballistic performance of DU penetrators can be matched.

1.2 Bulk Metallic Glass Alloys for Kinetic Energy Penetrator Applications

Alongside other possible candidate matrix materials, such as titanium (Ti), zirconium (Zr), hafnium (Hf), or certain steels with strong shear-localization susceptibility, the use of bulk metallic glasses (BMGs) has also been suggested. Unlike typical metals, BMGs do not have a crystalline structure. Their disordered atomic arrangement results in unusual mechanical behaviors. For example, when subjected to a compressive mechanical load, the BMG deforms by shear localization and fracture, in a similar manner to that exhibited by DU alloys at impact.

Shear localization in BMGs was first reported in Zr alloys which have densities of ~ 6.7 g/cm³ (Bruck et al., 1994; Bruck, et al., 1996). Because of its low density, a Zr-alloy BMG alone would be ineffective as a penetrator material. However, it has been suggested that the combination of W with a BMG matrix would achieve the required combination of density and deformation mechanism to compete with DU. Nevertheless, the use of the low-density Zr alloy limits composites to densities ~ 15.5 g/cm³.

An alloy of sufficient density and glass-forming ability (GFA) is thus crucial to matching the performance of DU. GFA refers to the fact that the nature of metallic glasses restricts the sizes in which they can be made. Any metal can be prepared with a glass structure, provided that it can be cooled (quenched) from a melt rapidly enough. In practice, most metals and alloys require quench rates so high that glasses of metals and alloys are typically thin ribbons or foils. BMGs are prepared from alloys, which
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yield glass at much lower cooling rates, and can thus be made in larger dimensions. Increasing alloy density without compromising GFA thus poses a challenge to the metallurgist.

In addition to being high, the quench rates used in metallic glass preparation are difficult to measure directly. However, an easily measured parameter of the glass, the reduced glass-transition temperature (T_{rg}), correlates with quench rate. Typically, the larger T_{rg} is, the smaller the critical cooling (or quench) rate needs to be. T_{rg} is the glass-transition temperature, T_g, normalized to the liquidus temperature, T_l, of the alloy. Both parameters can be measured with commonly available thermal analysis equipment. A T_{rg} between 0.63 and 0.67 represents a BMG alloy with good GFA (Johnson, 1999).

### 1.3 Composition Rules for Bulk Metallic Glass Alloys

A large T_{rg} translates into a low T_g value for a given alloy family. Typically in multicomponent systems, the compound with the lowest T_l corresponds to a eutectic composition.

At the eutectic composition, there is a strong competition between several crystalline phases to nucleate, grow, and accommodate one another in the solid phase. The required atomic rearrangement for crystallization and solidification takes time. Therefore, the atoms may be in a thermodynamically more favorable state if they remain in the liquid. If being in the liquid phase is more stable, the stability would be manifested as a greater depression in the melting point (Johnson, 1999). Increased stability in the liquid near a eutectic composition could then also be interpreted as a higher propensity for bypassing crystallization, and hence improved GFA as well.

There is considerable discord in the BMG community regarding the location of the ideal alloy composition that has an optimum GFA. Arguments for the use of the eutectic composition (Li, 2001) have been opposed with examples of hypo- or hypereutectic compositions (Wang et al., 2004; Xu et al., 2004).

In addition to locating systems with deep eutectics, other topological and empirical rules also aid BMG formation. These include the use of at least three elements, dissimilar crystal structures, negative heats of mixing, and large- and small-sized atoms. Such factors are designed to increase the competition between phases and raise the chemical disorder in the liquid, thereby destabilizing the formation processes of possible crystalline phases. Any complication, frustration, or confusion of the solidification process near the eutectic composition, cause the nucleation kinetics to become more sluggish and crystallization then can be avoided.

### 1.4 Zr- and Hf-Based Bulk Metallic Glass Alloys

Our initial efforts to develop higher-density BMGs centered on two quinary alloys of Zr with good GFA: Zr_{52.5}Ti_{5}Cu_{17.9}Ni_{14.6}Al_{10} (Vit105) and Zr_{57}Ti_{5}Cu_{20}Ni_{8}Al_{10} (JHU Zr57). It was felt that, based on the strong chemical similarities between Zr and Hf, direct substitution of Hf for Zr would be a straightforward approach. Replacing Zr with Hf in 20-at. % increments, we produced alloy ingots with densities ranging from 6.7 to 11.1 g/cm^3.

We were able to prepare glass for all compositions in the (Hf_xZr_{1-x})_{52.5}Ti_{5}Cu_{17.9}Ni_{14.6}Al_{10} series. In contrast, in the (Hf_xZr_{1-x})_{57}Ti_{5}Cu_{20}Ni_{8}Al_{10} series, compositions of x > 0.6 could not be quenched to a uniform glass structure (Kecskes et al., 2002). As shown in Fig. 1, in the (Hf_xZr_{1-x})_{52.5}Ti_{5}Cu_{17.9}Ni_{14.6}Al_{10} series, T_{rg} declined from 0.628 (x = 0) to 0.608 (x = 1) with increasing x. The decline from an initial T_{rg} of 0.588 (x = 0) was more pronounced in the other series.

![Graph of T_{rg} vs Hf Mole Fraction, x](image)

Fig. 1. T_{rg} of (Hf_xZr_{1-x})_{52.5}Ti_{5}Cu_{17.9}Ni_{14.6}Al_{10} and (Hf_xZr_{1-x})_{57}Ti_{5}Cu_{20}Ni_{8}Al_{10} BMGs. Note the gradual decline with increasing Hf mole fraction.

Obviously, this approach would not result in an improvement in GFA. Subsequently, we observed that the Zr:Cu:Ni ratio of Zr_{52.5}Ti_{5}Cu_{17.9}Ni_{14.6}Al_{10} (Vit105), Zr_{57}Nb_{5}Cu_{15.5}Ni_{12.6}Al_{10} (Vit106), or Zr_{57}Ti_{5}Cu_{20}Ni_{8}Al_{10} (JHU Zr57) alloy is near the Zr-Cu-Ni ternary eutectic point (Fig. 2). It was hypothesized that the low T_{rg} of the substitutionally obtained Hf alloys was attributed to being too far from the corresponding Hf-Cu-Ni ternary eutectic point. However, a Hf alloy with Hf:Cu:Ni ratio near the Hf-Cu-Ni eutectic point would be a good glass-former.

Because no ternary Hf-Cu-Ni phase diagram could be found in the literature, we undertook a study of the Hf-Cu-Ni phase equilibria. Once the invariant points were identified, we applied the BMG formation rules to develop a Hf alloy with improved GFA. We used, differential thermal analysis, a well-established technique, for the determination of phase equilibria in alloys (Pope...
and Judd, 1977). We also relied on X-ray diffraction, scanning and transmission electron microscopies to determine and verify the structure of the alloyed and glassy materials. We report these results here.

![Diagram](image)

**Fig. 2.** Zr:Cu:Ni ratios of common Zr alloys, mapped onto the two-dimensional plane projection of the Zr-Cu-Ni liquidus surface (taken from Takeuchi, 1968). Note all are near the eutectic point (E).

### 2. EXPERIMENTAL PROCEDURES

#### 2.1 Invariant-Point Identification

Identifying invariant points in the Hf-Cu-Ni system entailed synthesizing ternary compositions, and measuring their melting behavior using differential thermal analysis. Elemental metals were pickled in an acidic solution, and arc melted under a Ti-gettered, partial-vacuum argon atmosphere. The ingot buttons were flipped and remelted several times (typically 6 melts) to ensure complete alloying of the elements.

Thermal analysis was conducted using a Netzsch Instruments STA 409C differential thermal analyzer (DTA) configured with a high-temperature (1600 °C) furnace, Type S thermocouples, graphite crucibles, and an argon atmosphere. Heating rates were 10 °C/min. To establish good thermal contact between the crucible and the sample, alloy samples were melted, allowed to cool, and solidify in the DTA furnace prior to the analysis scan.

Backscatter scanning electron microscopy (SEM) was used to examine the phase assemblage of samples cooled in the DTA. We used a Hitachi S-4700 field-emission scanning electron microscope, with a tungsten electron source and a YAG backscatter detector.

#### 2.2 Quaternary and Quinary Alloy Development

Once the invariant point was identified, further alloying additions were made. The goal of alloying additions was to lower the liquidus temperature while retaining the congruent nature of the melt.

5 and 10 atomic % (at. %) Ti, niobium (Nb), aluminum (Al), and chromium (Cr) were substituted for Hf at the invariant composition (Hf$_{55}$Cu$_{30}$Ni$_{15}$, see Results and Discussion), or mixed proportionally while maintaining the Hf:Cu:Ni ratio fixed. In addition, a 15-at. %-Al, proportionally substituted ingot was prepared. The resulting ingots were subjected to the same thermal analysis procedure described above.

Glass-forming ability was determined by suction casting 3-mm-diameter rods. Suction casting was performed by arc-remelting ingot pieces in Ti-gettered purified argon, followed by drawing and quenching the melt into a water-cooled Cu mold. The suction-casting apparatus has been described elsewhere (Gu, et al., 2002).

#### 2.3 Bulk Metallic Glass Characterization

Due to the high strengths and large elastic limits of metallic glasses, a simple screening procedure to determine whether or not a suction-cast rod might be glassy is to bend it in one’s hands. If it breaks, it is not glass. All suction-cast rods were subjected to this test.

Segments of rods, which passed the initial screening, were subjected to differential scanning calorimetry analysis. To determine glass-transition temperature, the STA 409C was configured with an argon atmosphere, Type E thermocouples, and copper crucibles. Heating rate was 10 °C/min.

Alloy density was determined using the Archimedes method in water.

X-ray diffraction patterns were recorded using Philips PW 1729 x-ray generator, with a typical copper K$_\alpha$ tube source, scintillation detector, and low-background sample holder. Scans were taken over a 2-Θ scattering angle range of 20 to 120 °, with a step size of 0.025 °, and 5-s dwell time.

A sample of the suction-cast glass-forming alloy was thinned with an FEI-200 focused ion beam milling device until electron transparent, and examined using a 300-kV FEI Technai F30 high-resolution transmission electron microscope.
3. RESULTS AND DISCUSSION

3.1 Invariant-Point Identification

Each point on the ternary Hf-Cu-Ni plot (Fig. 3) represents a composition for which an ingot was made and subjected to thermal analysis. The dashed lines represent a series of pseudo-binary compositions, wherein the mole fraction of the third component is fixed. The intersections of the dashed lines are compositions, which were observed to melt congruently. Figure 4 illustrates melting point data along these composition lines, indicating how the solidus and liquidus converge at one of these invariant points.

Fig. 3. The locus of all experimentally fabricated Hf-Cu-Ni alloy points, depicted on the Hf-Cu-Ni ternary composition triangle. The two sets of intersecting lines, labeled as (a) and (b), and (c) and (d), respectively, define the invariant points found in our study.

The DTA thermographs for Hf50Cu30Ni15 and Hf70Cu5Ni25 are exhibited in Fig. 5. It may be noted that although data in Fig. 4 infers that the invariant point is at Hf75Cu5Ni25, the convergence of the solidus and liquidus occurs over a wider composition range. For clarity, heretofore, we designate the nominal eutectic composition as Hf50Cu30Ni15. For Hf50Cu30Ni15, the onset of melting was 1150 °C, while the endpoint was at 1165 °C. For Hf50Cu30Ni25, they were 1130 and 1144 °C, respectively. We have not yet developed a glass-forming alloy based on Hf70Cu5Ni25, so we will limit our discussion to alloys based on Hf50Cu30Ni15.

3.2 Quaternary and Quinary Alloy Development

Figure 6 presents the thermographs for the 5 at. % Ti and 10 at. % Al alloying additions to Hf50Cu30Ni15. The ingot compositions are Hf50Ti5Cu30Ni15 and Hf50Cu27Ni13.5Al10. The concentrations of these elements reduced the liquidus temperature of Hf50Cu30Ni15 as shown, while maintaining the congruent melting behavior. The other alloying elements (Nb and Cr) and other concentrations of Ti or Al elements resulted in moving the composition away from a congruent melt. The typical result of the other alloying additions was the appearance of a shoulder on the high-temperature side of the melting peak (not shown). This would be consistent with the persistence of a small amount of higher-melting-point
material after the initial melting began.

Because 5 at. % Ti and 10 at. % Al had the effect that they did in quaternary ingots, we prepared suction-cast rods of Hf₄₄.₅Ti₅Cu₂₇Ni₁₃.₅Al₁₀. Rods of this nominal composition passed the simple mechanical screening described above, and were subjected to the glass-characterization tests.

3.3 Metallic Glass Characterization

The density of the metallic glass is 10.9 g/cm³. As shown in Fig. 7, the X-ray diffraction pattern from a suction casting exhibits a broad, diffuse ring with no Bragg peaks. A selected-area electron diffraction pattern, Fig. 8 (a), showed similar features. The corresponding bright-field, high-resolution image in Fig. 8 (b) reveals no evidence of crystallites or ordering. DTA determined Tᵩᵡ to be 500 °C, Tᵩ = 984 °C, making Tᵩᵡ = 0.615 (Fig. 9).

Fig. 6. Alloying effect of Ti and Al on the solidus and liquidus of Hf₅₅Cu₃₀Ni₁₅.

Fig. 7. X-ray diffractogram of the Hf₄₄.₅Ti₅Cu₂₇Ni₁₃.₅Al₁₀ glass.

Fig. 8. Electron diffraction pattern and high-resolution transmission electron micrograph, shown in (a) and (b), demonstrate no long-range crystalline order in the alloy.
Fig. 9. DTA thermograms exhibiting a glass transition point and a single exothermic peak, shown in (a), and an endothermic peak defining the solidus and liquidus of the alloy in (b).

3.4 Detailed Study of Hf55Cu30Ni15 Invariant Point

Attempts to reproduce the thermograph of Fig. 5 revealed a small endotherm at 1085 °C (not shown). Subsequent measurements revealed that this endotherm appears in most nearby compositions, including the compositions through which the dotted lines are drawn in Fig. 3. Figure 10 illustrates the variation of solidus and liquidus lines with composition for these alloys.

If the Hf55Cu30Ni15 were a eutectic, the liquidus would converge to the solidus at that composition (see Fig. 4). As is clear from Fig. 10, it does not. The presence of the small endotherm at 1085 °C also means that Hf55Cu30Ni15 is not a eutectic.

Backscattered SEM micrographs of a furnace-cooled ingot of Hf55Cu30Ni15 are exhibited in Fig. 11. It is clear from Fig. 11 (a) that the composition is off eutectic, although there is a eutectic microstructure present. The eutectic region probably corresponds to the 1085 °C endotherm observed in thermal analysis. Figure 11 (b) is a higher magnification study of the eutectic region.

Fig. 10. Plots of solidus and liquidus versus composition for (a) Hf55Cu45-xNix, and (b) Hf70-xCu30Nix.

The fact that Hf55Cu30Ni15 is not a eutectic composition has important consequences for the development of metallic glasses. It appears from the asymmetric nature of the 1160 °C endothermic peak (Fig. 5) and the appearance of the microstructure that the peak most likely is a peritectic point resulting from the interaction of the a small amount of eutectic liquid with an incongruently melting compound. While such an alloy does not have the advantages that a eutectic would have for forming glass, peritectic points still involve considerable atomic rearrangement. If quenching is sufficiently rapid to prevent such rearrangement, it appears from the evidence presented here that peritectic points are also promising candidates for the development of glass-forming alloys. If this can be shown to be widely true, the opportunities for making bulk metallic glasses will have expanded greatly.
The significance of this discovery in the development of high-density BMGs is twofold. First, it implies that a Hf-alloy BMG could be formed into bulk objects with dimensions equivalent to those only previously available to Zr-alloy BMGs. Second, and more importantly, it has enabled fabrication of 17-g/cm³ composites, which approach the density of WHA KE penetrators. Ballistic tests of the first composites prepared showed penetration was more pronounced than would be expected from density alone.

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**Hf-Based BMGs**

**Motivation**

Develop enhanced tungsten-based kinetic energy penetrator materials that replicate the deformation and flow behavior of depleted uranium (DU) materials.

It is inherent that if imitation of the ballistic deformation behavior is successful, the ballistic performance will follow…

DU outperforms tungsten as localized deformation causes the bulging tip to remain sharp.

**Goal:** Reproduce uranium-like behavior with non-uranium material
**Hf-Based BMGs**

**Motivation**

**Uranium-Like Behavior:** i.e., Self-Sharpening

ARO funded SBIR program at CalTech
Zr-Ti-Cu-Ni-Be: castable bulk metallic glass alloy

'chisel' nose on monolithic BMG

reduced mushrooming on W-wire-reinforced-BMG composite

**Tutorial: History**

Crystalline

atoms arranged into a structure with order

Glassy

atoms in liquid-like disordered arrangement

**Amorphous Structures:**

- **Types:**
  - 1960's: first metallic glass Au-Si by Klement et al. - binary
  - 1980's: Pd$_{40}$Ni$_{40}$P$_{20}$ - ternary
  - 1990's: Vitreloy1 (Zr$_{41.2}$Ti$_{12.8}$Ni$_{10}$Cu$_{12.5}$Be$_{22.5}$) - quinary

- **Forms:**
  - Thin Films (nm) → Ribbon (µm) and Wire (µm)
  - **Bulk Metallic Glasses (BMG)** (mm)

**Cooling Rate**

$10^6 - 10^9$ K/s

$10 - 1$ K/s
**Hf-Based BMGs**

**Tutorial: Undercooling and Selection Rules**

**Binary Eutectic**
- Eutectic is the lowest melting point alloy
- Behaves as a ‘pure’ element
- Rearrangement during transformation from liquid to solid: **slow process**

**Metallic Glass Synthesis Rules**
- Near deep eutectics
- More than three constituents
- Competing crystalline structures
- Atomic size difference between main constituents more than 12%
- Negative heats of mixing between constituents

**Metallic Glass** forms when a liquid alloy becomes increasingly viscous on cooling and fails to **crystallize**

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**Key Metallic Glass Properties**

- **Vitreloy 1**
  - X-ray Profile

- **Vitreloy 105**
  - Thermal Profile
  - DTA Signal [µV/mg]

**Entry Criteria for Penetrator Applications**
- Increase density from 7 g/cm³ to 11 g/cm³
- Improve thermal stability and glass forming ability;
  - high \( T_{\text{liquid}} \)
  - large \( T_r \approx T_g/T_{\text{liquid}} \)
- Environmental and systemic compatibility (i.e., non-toxicity, non-reactive with reinforcement)
Trg of (Hf\(_x\)Zr\(_{1-x}\))\(_{52.5}\)Ti\(_5\)Cu\(_{17.9}\)Ni\(_{14.6}\)Al\(_{10}\) and (Hf\(_x\)Zr\(_{1-x}\))\(_{57}\)Ti\(_5\)Cu\(_{20}\)Ni\(_8\)Al\(_{10}\) BMGs. Note the gradual decline with increasing Hf mole fraction.

Zr:Cu:Ni ratios of common Zr alloys, mapped onto the two-dimensional plane projection of the Zr-Cu-Ni liquidus surface. All are near the eutectic point (E).
**Hf-Based BMGs**

*The Search for the Invariant Points*

The locus of all experimentally fabricated Hf-Cu-Ni alloy points, depicted on the Hf-Cu-Ni ternary composition triangle. The sets of intersecting lines, define the invariant points found.

**Hf-Based BMGs**

*The High-Hf Eutectic*

Plots of solidus and liquidus versus composition for
(a) Hf$_{75}$Cu$_{25-x}$Ni$_x$, and
(b) Hf$_{95-x}$Cu$_5$Ni$_x$. 

Hf$_{75}$Cu$_5$Ni$_{20}$
**Hf-Based BMGs**

*Thermal Characteristics of the Invariant Points*

![Graph showing DTA thermographs of two ternary alloys.]

DTA thermographs of the two congruently melting ternary alloys.

**Hf-Based BMGs**

*Alloying Effects*

![Graph showing alloying effects of Ti and Al on solidus and liquidus.]

Alloying effect of Ti and Al on the solidus and liquidus of Hf$_{55}$Cu$_{30}$Ni$_{15}$. 
**Hf-Based BMGs**

End Point: X-ray Amorphous

X-ray diffractogram of the Hf_{44.5}Ti_{20}Cu_{27}Ni_{13.5}Al_{10} glass

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Electron diffraction pattern and high-resolution transmission electron micrograph, shown in (a) and (b), demonstrate no long-range crystalline order in the alloy.
Hf-Based BMGs
A Real BMG

DTA thermograms exhibiting a glass transition point and a single exothermic peak, shown in (a), and an endothermic peak defining the solidus and liquidus of the alloy in (b).

Hf-Based BMGs
A Real BMG - Why?

Plots of solidus and liquidus versus composition for (a) Hf_{55}Cu_{45-x}Ni_x, and (b) Hf_{70-x}Cu_{30}Ni_x.
SEM micrographs of the Hf$_{55}$Cu$_{30}$Ni$_{15}$ alloy sample with an overview shown in (a) and an enlarged view shown in (b).

This is not a eutectic-like structure

This is the eutectic-like structure

Hf-Based BMGs
Things Get Complicated

Melt behavior and as-cooled phase morphology resembles that of a different type of reaction:

Liquid + Solid A → Solid AB

The reaction appears to be sluggish

Significant undercooling is possible

BMG compositions are not limited to deep eutectics

Number of potential systems increases
Greater flexibility of finding higher density systems
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