

Overview

A new methodology of predicting specific compositions for glass forming alloys based on elemental cluster selection, liquidus lines, atomic packing efficiency and ab initio calculations is presented and discussed. The proposed composition selection model has led to the discovery of a number of new Mg, Cu, Zn and Ag-based ternary and quaternary bulk metallic glasses (BMGs).

Alloy Design Theory

In 1960, Hume-Rothery plotted the frequency of binary eutectic compositions and found clear maxima corresponding to simple, whole number atomic ratios.^[1] Dong et al. developed a criterion based on atomically close-packed binary icosohedral clusters that correspond to binary eutectic compositions and glass-forming ability.^[2] Related to this work, Miracle et al. (2004) developed a model to calculate the radius ratio, R of a nominal number of atoms N around a central atom, to give the highest degree of geometric packing efficiency shown in Equation (1).^[3]

$$N = \frac{4p}{p(2-q) + (2q)\arccos\left\{\left(\sin p/q\right)\left[1 - 1/(R+1)^2\right]^{1/2}\right\}} \quad (1)$$

The model presented in this work considers liquidus lines to be representative of the most stable liquid composition and atomic configuration for a given region upon cooling and atomic relaxation. In accordance with Eq. (1), efficiently-packed ternary atomic clusters in close proximity to liquidus lines are considered to be the 'stable', building block of glass-forming alloys.

Experimental Methodology

The Cu-rich region of the Ca-Cu-Mg ternary system was chosen to demonstrate this alloy design method as Ca, Mg and Cu have a difference in atomic radius of at least 20% which is kinetically favourable for glass formation and geometrically allows for a larger compositional range of efficiently packed clusters. Various efficiently-packed clusters that correspond to liquidus lines in the Ca-Cu-Mg system are shown in Figure 1(a). Over 30 alloys of both stoichiometric cluster compositions and intermediate compositions were prepared and cast into a copper wedge mould to determine their relative glass-forming ability, thermal stability and physical/mechanical properties.

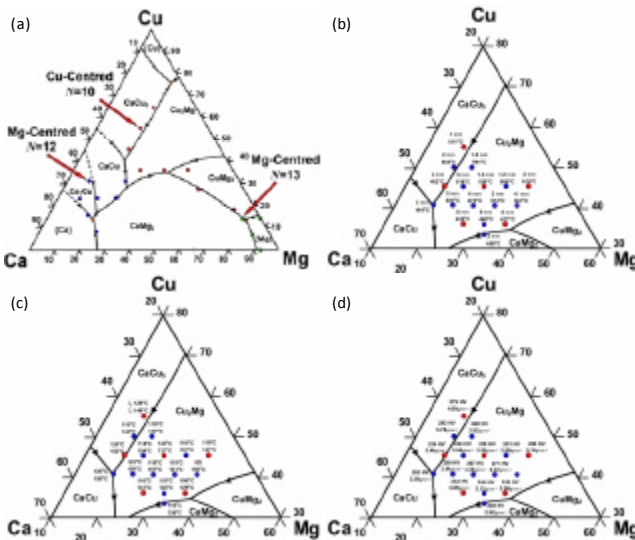


Figure 1: (a) Ca-Cu-Mg ternary system liquidus surface and various efficiently-packed cluster compositions, (b) Critical casting diameter (glass-forming ability) and liquidus temperature data, (c) Thermo-physical data including the glass transition temperature (T_g) and crystallisation temperature (T_x) and (d) Alloy hardness and density for selected Cu-rich alloys.

Experimental Results

The critical casting thicknesses (a measure of glass-forming ability) and liquidus temperatures for both cluster compositions (red points) and intermediate alloy compositions (blue points) are shown in Fig. 1(b). Thermo-physical parameters of these amorphous alloys including: (i) the glass transition temperature (T_g) above which an alloy shifts from being a vitreous solid to a supercooled liquid that may be deformed superplastically and (ii) the crystallisation temperature (T_x), above which the amorphous state is no longer stable and the alloy begins to crystallise. Figure 1(d) shows results for Vickers hardness and alloy density.

Computational Analysis

To further assess this method of glass-forming alloy prediction, ab initio-type calculations of the highlighted clusters were carried out to determine: (i) their energetically favourable atomic configuration (there is <5% difference in binding energy between all possible orientations for atomic species for any given cluster); (ii) binding energy (resistance to dissociation), (iii) surface area to volume ratio (measure of reactivity in a local environment) and (iv) the presence and/or degree of polarity of these clusters (measure of inter-cluster binding). Results are represented in Figures 2 (a)-(d)

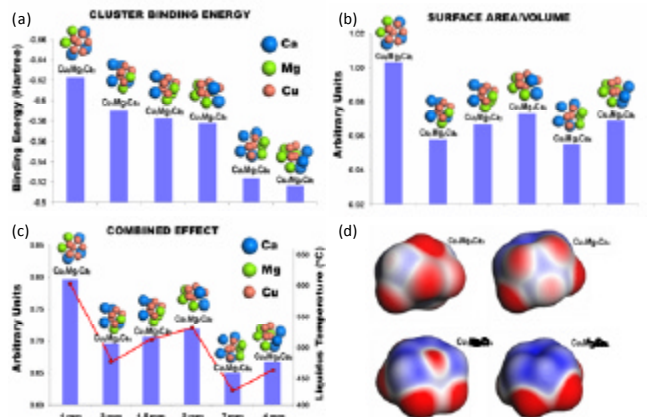


Figure 2: (a) The binding energy (Hartree), (b) Surface area to Volume ratio, (c) The combined effect of binding energy and surface area/volume ratio and relationship between liquidus temperature (red dots) and glass-forming ability (x-axis) and (d) Electro negativity/Polarity iso-surfaces of the selected atomic clusters.

Discussion & Findings

Cluster-Based Alloys: A strong correlation between liquidus lines and alloy compositions that correspond to efficiently-packed ternary atomic clusters has been observed. Liquidus temperatures and glass-forming ability correspond well with the combined effects of cluster binding energy and the surface area/volume ratio. The glass transition temperature of these cluster-based alloys is believed to be related to cluster polarity/inter-cluster binding, further, their strength/hardness and density appears to be dependent on stoichiometry.

Intermediate Cluster Alloys: The nearest stable cluster is thought to dominate the structure of intermediate cluster alloy compositions and the stoichiometric remainder of atoms to reside interstitially between clusters. This may account for:

- Higher bulk alloy densities due to less free volume in the structure.
- Higher strength/hardness due to a higher degree of inter-cluster binding.
- The adoption of, or increase in the T_x value of the nearest stable cluster-alloy.
- T_g values that relate to interstitial binding rather than cluster polarity.

References

- [1] W. Hume-Rothery, E. Anderson, *Phil. Mag.* 5, (1960) 383-405
- [2] Q. Wang, J.B. Qiang, J.H. Xia, J. Wu, Y.M. Wang, C. Dong, *Intermetallics*, 15 (2007) 711-715
- [3] D.B. Miracle, O.N. Senkov, W.S. Sanders, K.L. Kendig, *Mat. Sci. and Eng. A*, 375-377 (2004) 150-156