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A Brief Study Of Zr- and Pd-based Bulk Metallic Glasses To Glass Forming Ability And Critical Cooling Rate

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Abstract

The structure of bulk metallic glasses is not regular like crystalline structure and there is diversity in the pattern of their structure, GFA and critical cooling rate are important contributors to their formation. This transformation necessitates cooling the metallic melt well below the glass transition temperature (Tg) to achieve the glassy state. A diverse range of alloy systems, including binary, quaternary, ternary, and high-order alloys, have been extensively utilized for synthesizing metallic glasses in vast quantities. The key requirement for the successful formation of bulk metallic glasses is a favorable ability to solidify into a glassy structure.

Keywords: **Alloys, Thermal Conductivity, Crystal Structure, Glass-Forming, Critical Cooling Rate**

1. Introduction

Glass formation is characterized by the ability of metallic alloys to undergo a transition into a glassy state. When the formation of crystal nuclei is effectively suppressed, the process of glass formation can be successfully achieved. The detection threshold for the minimum volume fraction of crystals is typically around 10^{-6}. To achieve this, the liquid alloy must be significantly under-cooled below its glass transition temperature (Tg). This significant under-cooling is typically accomplished through rapid solidification of the liquid alloy. Successful glass formation is contingent upon the melt being solidified at a rate above the critical cooling rate (Rc), which varies depending on the specific alloy system and its composition. The critical cooling rate (Rc) is influenced by three factors, namely: the rate of crystal growth and its temperature dependence, g(T), the relationship between X and the two latter quantities, and the rate of nucleation and its variation in temperature, I(T). Is there any effect of the crystal structure, thermal coefficient of thermal expansion, thermal conductivity, and covalent radius on

the glass forming ability and crystal cooling rate through the following points is study in the article especially for Zr- and Pd-based BMGs.

2. Objectives

To study the dependence of Glass forming ability on the crystal structure, thermal coefficient of thermal expansion, thermal conductivity, and covalent radius of the additional elements added.

3. Research Methodology

The following different steps have been followed during this theoretical study:

- The data used in the study for the Zr- and Pd-based BMG has been on the basis of available standard data.
- The data has been classified on the basis of various GFA and cooling rate R_c.
- Various deviations have been studied with the help of graphs, keeping the classification in the form of a table.

4. Results And Discussion

4.1 Kinetics Of Glass Formation

The kinetics of crystallization was first explained by Turnbull. The following assumptions were formed:

1. The composition of the crystals set up is equivalent to the liquid.

2. Nucleation transients are immaterial.

3. The change in bulk free energy correlated with the transformation into the crystal phase from the under-cooled liquid, ΔG_v, is given by the linear roughly, $\Delta G_v = \Delta H_f$.

The expression for the volume fractions (X) of the solid crystalline phase, formed under the condition of non-crystalline isothermal, if the melt of an alloy is solidified from the temperature T_l (above the liquidus temperature) to T_g (below the glass transition temperature) is-

$$X = \frac{4}{3}\pi R^{-4} \int_{T_l}^{T_g} I\,(T') \left[\int_{T'}^{T_g} g\,(T'')\,dT' \right] dT$$

Here: I- Rate of study state nucleation.
R- Rate of cooling.
g(T″)- Rate of crystal growth.
T′- Constant cooling rate, constant assumed for calculation purpose only, imposed on the melt.

For critical cooling rate R_c, X is 10^{-6}, So,

$$R_C = \left[\frac{4}{3}\pi 10^6 \int_{T_l}^{T_g} I\,(\mathrm{T}') \left[\int_{T'}^{T_g} g\left(T^{''}\right)\mathrm{dT}'\right]\mathrm{dT}\right]^{\frac{1}{4}}$$

The term I and g depends upon, ΔS_f, the entropy of fusion, η, the viscosity of super cooled liquid and so on. R_c, rate of critical cooling decreases with increasing ΔS_f and η, and decreasing T_l, liquidus temperature.

As indicated by the entropy model of the liquid state or the free-volume model, it is requisite that every liquid undergoes a transition to the glassy state, whether the crystallization can be avoided or bypassed. Thus, the problem of glass formation comes out to be exclusively kinetic in nature. So, in the event that a fluid could be cooled adequately quickly to forestall the development of a perceptible measure of a crystalline phase, glass arrangement could be accomplished. Therefore, regardless of whether the glass forms or not, it is interrelated to the rapid with which the liquid can be cooled and furthermore to the kinetic constants.

4.2 Available Data

Available data in various types of research for Zr- and Pd-based bulk metallic glasses are shown in the following table-1. The data for crystal structure, thermal expansion coefficient, thermal conductivity, and covalent radius of constituent elements of bulk metallic glasses is shown in table-2.

Alloy Composition	R_c (Ks^{-1})	Reference
Zr- based BMG		
$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$	1.4	[5]
$Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$	1.5	[4]
$Zr_{57}Cu_{15.4}Ni_{12.6}Al_{10}Nb_5$	10	[7]
$Zr_{46.2}5Ti_{8.25}Cu_{7.5}Ni_{10.0}Be_{27.5}$	28	[5]
$Cu_{48}Zr_{48}Al_4$	<40	[16]
Pd- Based BMG		
$Pd_{42.5}Cu_{30}Ni_{7.5}P_{20}$	0.067	[3]
$Pd_{40}Cu_{30}Ni_{10}P_{20}$	0.1	[3]
$Pd_{40}Cu_{25}Ni_{15}P_{20}$	0.15	[3]
$Pd_{40}Cu_{30}Ni_{10}P_{20}$	1.58	[8]
$Pd_{40}Ni_{40}P_{20}$	128	[8]
$Pd_{78}Cu_6Si_{16}$	550	[14]
$Pd_{82}Si_{18}$	$1.8x10^3$	[15]

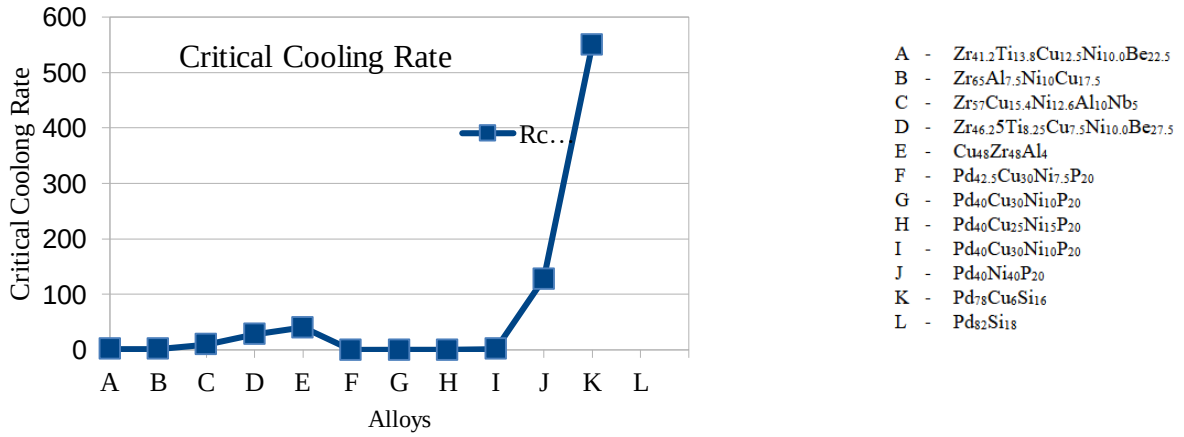
Table-1: Critical Cooling Rates For Different Alloy Systems Under The Formation Of Glassy Phases.

Elements	Crystal Structure	Thermal expansion μm/(m·K)	Thermal Conductivity W/(m·K)	C. Radius (pm)
Zr	hcp	5.7	22.6	148
Al	fcc	23.1	237	118
Ni	fcc	13.4	90.9	121
Cu	fcc	16.5	401	138
Ti	hcp	8.6	21.9	136
Pd	fcc	11.8	71.8	131
P	bcc	-	white-0.236, black-12.1	106
Si	Fc-diamond cubic	2.6	149	111
Be	hcp	11.3	200	**90**

Table-2: Data For Individual elements

4.3 Analysis Of Data

The value of the critical cooling rate changes with the changing of the friction of constituent elements in bulk metallic glasses, and also changes with the replacing of the constituted elements with others. Adding the new constituent elements in the bulk metallic glasses also changes the critical cooling rate.The base element in $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ and $Zr_{46.25}Ti_{8.25}Cu_{7.5}Ni_{10.0}Be_{27.5}$ is zirconium. The crystal structure, coefficient of thermal expansion, thermal conductivity, and covalent radius of base element zirconium are hcp, 5.7µm/(m-K), 22.6 W/m-K, and 148pm respectively. The crystal structure, coefficient of thermal expansion, thermal conductivity, and covalent radius of element titanium are hcp, 8.6µm/(m-K), 21.9 W/m-K, and 138pm respectively. The value of fraction of zirconium is increasing in bulk metallic glass $Zr_{46.25}Ti_{8.25}Cu_{7.5}Ni_{10.0}Be_{27.5}$ as compared to BMG $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ and the value of fraction of titanium is decreasing. The value of quantities thermal conductivity and covalent radius for zirconium is more than that of titanium. The effect is that the BMG $Zr_{46.25}Ti_{8.25}Cu_{7.5}Ni_{10.0}Be_{27.5}$ will have a higher cooling rate value as compared to BMG $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$.



The value of fraction of beryllium is increasing in bulk metallic glass $Zr_{46.25}Ti_{8.25}Cu_{7.5}Ni_{10.0}Be_{27.5}$ as compared to BMG $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ and the value of fraction of copper is decreasing. The value of quantities coefficient of thermal expansion, thermal conductivity, and covalent radius for copper is more than that of beryllium. The effect is that the BMG $Zr_{46.25}Ti_{8.25}Cu_{7.5}Ni_{10.0}Be_{27.5}$ will have a smaller cooling rate value as compared to BMG $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$. Out of the coefficient of thermal expansion, thermal conductivity, and covalent radius, any two or all are more for elements zirconium and beryllium as compared

to titanium and copper. The value of the fraction of elements zirconium and copper is increasing and the value of the fraction of elements titanium and is decreasing in BMG $Zr_{46.25}Ti_{8.25}Cu_{7.5}Ni_{10.0}Be_{27.5}$ with comparison to BMG $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$.As a result, an increasing fraction of the elements in bulk metallic glasses increases the critical cooling rate of bulk metallic glass. Such a result is obtained when either two or all of the coefficients of thermal expansion, thermal conductivity, and covalent radius are more for the elements with increasing fractions. Such a result is also obtained when either two or all of the coefficients of thermal expansion, thermal conductivity, and covalent radius are less for the elements with decreasing fractions.

Critical cooling rate for $Pd_{42.5}Cu_{25}Ni_{7.5}P_{20}$ is 0.067 Ks^{-1} and that for $Pd_{40}Cu_{30}Ni_{15}P_{20}$is 0.15 Ks^{-1}. The base element in BMGs $Pd_{42.5}Cu_{25}Ni_{17.5}P_{20}$ and $Pd_{40}Cu_{25}Ni_{15}P_{20}$ is palladium. The crystal structure, coefficient of thermal expansion, thermal conductivity, and covalent radius of base element palladium are fcc, 11.8μm/(m-K), 71.8 W/m-K, and 131pm, for element nickel are fcc, 131.8μm/(m-K), 90.9 W/m-K, and 121pm, and for copper are fcc, 16.5μm/(m-K), 401 W/m-K, and 138pm respectively. The coefficient of thermal expansion, thermal conductivity, and covalent radius are more for elements copper as compared to palladium and nickel. The value of the fraction of elements copper is increasing and the value of the fraction of elements palladium and nickel is decreasing in BMG $Pd_{40}Cu_{30}Ni_{15}P_{20}$ with comparison to BMG $Pd_{42.5}Cu_{25}Ni_{7.5}P_{20}$. The critical cooling rate of BMG $Pd_{40}Cu_{30}Ni_{15}P_{20}$ is higher than that of BMG $Pd_{42.5}Cu_{25}Ni_{7.5}P_{20}$ but there is not much difference in magnitude. The similar result is obtained for BMGs $Pd_{40}Cu_{30}Ni_{15}P_{20}$ and $Pd_{42.5}Cu_{25}Ni_{7.5}P_{20}$ as obtained in BMGs $Pd_{42.5}Cu_{25}Ni_{17.5}P_{20}$ and $Pd_{40}Cu_{25}Ni_{15}P_{20}$.

The critical cooling rate for $Pd_{40}Cu_{30}Ni_{10}P_{20}$ is 0.1Ks^{-1} in one literature[3]and 1.58Ks^{-1} in another literature[8]. Compared to the quantitative fraction of the constituent element in BMG $Pd_{40}Cu_{25}Ni_{15}P_{20}$ and $Pd_{40}Cu_{30}Ni_{10}P_{20}$, the quantitative fraction of copper in BMG $Pd_{40}Cu_{30}Ni_{10}P_{20}$ is increasing while the quantitative fraction of nickel is decreasing. Based on the above analysis, the critical cooling rate should increase due to the decrease in the amount of nickel and increase in the amount of copper. Therefore, in this way the critical cooling rate of BMG $Pd_{40}Cu_{30}Ni_{10}P_{20}$ should be more than that of BMG $Pd_{40}Cu_{25}Ni_{15}P_{20}$. The critical rate of BMG $Pd_{40}Cu_{25}Ni_{15}P_{20}$ is 0.15Ks^{-1} while the values of critical cooling rate for BMG $Pd_{40}Cu_{30}Ni_{10}P_{20}$ in different literature are 0.1Ks^{-1} [3] and 1.58Ks^{-1}[8] meet. Based on the above

analysis, the value of critical cooling rate for element $Pd_{40}Cu_{30}Ni_{10}P_{20}$ can exceed that of BMG $Pd_{40}Cu_{25}Ni_{15}P_{20}$ only when $1.58Ks^{-1}$ is taken out of the two values of critical cooling rate. Thus, the value of critical cooling rate for BMG $Pd_{40}Cu_{30}Ni_{10}P_{20}$ of $1.58Ks^{-1}$ seems more likely to be correct.

5. Conclusion

From the analysis of different BMGs, it is known that the critical cooling rate is affected by the change in the quantitative fraction of the constituent element; it appears that the critical cooling rate depends on the crystal structure, coefficient of thermal expansion, thermal conductivity, and covalent radius.

6. Research Gap

What will be the change in its critical cooling rate on the addition of any element in bulk metallic glass, or the change in its quantitative fraction? It remains to study how much the critical cooling rate of metallic glass will change due to all the constituent elements whose quantitative fraction is changing. Such changes in critical cooling rate are based on the crystal structure, coefficient of thermal expansion, thermal conductivity, and covalent radius. Whether this type of process can also be done on the mechanical properties of metallic glass like Young's modulus, critical temperature, Poisson ratio, etc. is under study.

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