CHAPTER I

Introduction, Motivation, and Key Contributions

Abstract

As a unifying summary of the thesis, Chapter I explains the logic underlying the conducted research in chronological order. A brief background about metallic glass is first introduced and followed by the recent progress in the bulk metallic glass development. The discussion on alloy development by design is the subject matter of Chapter II. Chapter III focuses on one outcome of Chapter II – the discovery of gold-based bulk metallic glass which could be cast fully amorphous up to 5 mm level.

Chapter IV concentrates on the similarities and differences of two recently developed high Poisson's ratio bulk metallic glasses based on Au and Pt. Comparisons were made to other known systems where appropriate. The studies reveal some unique behaviors of these high Poisson's ratio alloys. One of the most striking findings is the strain rate induced crystallization, which is discussed in detail in Chapter V. Chapter VI switches gears to the engineering and manufacturing aspect of these precious bulk metallic glasses. A novel approach to metal-to-metal joining technique is introduced. Our recent experimental successes using Au-BMGs and Pt-BMGs indicate that the method could be used as a reliable alternative to Pb-free soldering.

1. Background

When conventional metal alloys are cooled from their molten state, atoms will quickly rearrange themselves into ordered lattice spaces and crystallize. This crystallization process could be completely avoided, as discovered by Duwez in 1960 at Caltech, in the gold-silicon system, if the cooling rate is fast enough to "freeze" the melt in its amorphous state. It was the first time that highly disordered arrangements of the atoms could be observed in solid metallic alloy [1]. The early metallic glasses remained of only academic interest because a cooling rate of at least 10^6–10^8 °C per second is required to suppress the crystallization. The dimension of the specimen was therefore limited to a few microns in at least one dimension to provide such rapid heat extraction. The need for a high cooling rate was the key obstacle to the connection between academic research and viable commercial applications.

The term "bulk" metallic glass was later introduced to distinguish a good glass forming alloy that could be cast into one or more millimeter-thick samples. One of the first bulk metallic glasses (BMGs) was discovered in 1971 when Chen and Turnbull stumbled on the unusual glass forming ability in Pd-(Cu,Ag,Au)-Si alloys, which could be cast into thicknesses greater than 1 mm using a cooling rate as low as 100 ˚C/sec. Since the discovery, BMG research has been gaining traction in the scientific community. During the past two decades there have been many contributions from all over the world, for example, Pd alloy systems by Drehman et al. in 1982 [2], the pioneering systematic studies on La, Mg, Zr alloy systems by Inoue at Tohoku University, and the discovery of Zr-based BMGs (Vitreloys) by Peker and Johnson at California Institute of Technology.

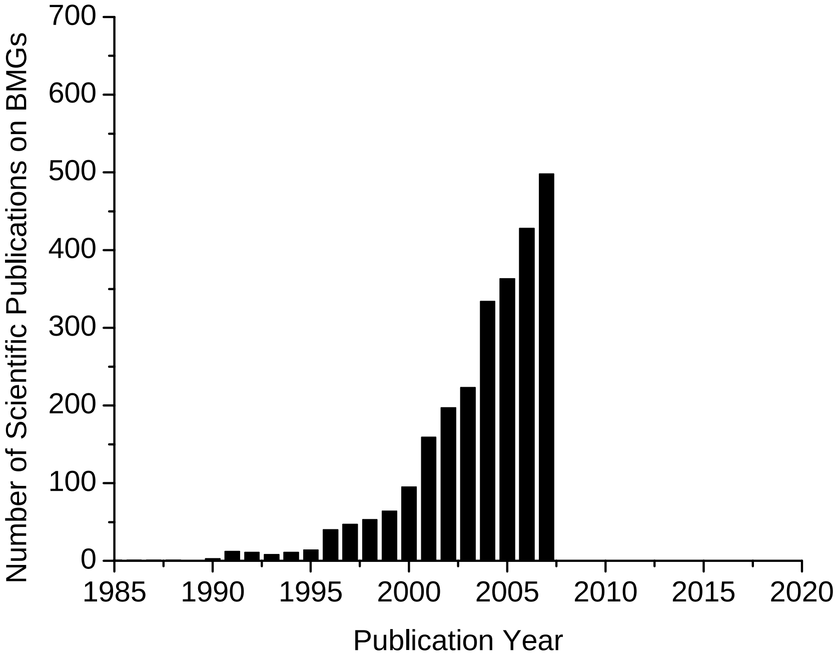

Figure I-1: The number of publications based on bulk metallic glass per year are plotted to show advances in BMG discoveries.

The number of publications based on BMGs have been increasing exponentially, as shown by the bar chart in Figure I-1. The number of hits[A] was counted year by year using Web of Science database to search the keywords "bulk metallic glass." Starting in 1990, there is an exponential increase of BMG discoveries based on Pd-, Zr- and La-alloy systems which have branched out into several alloy families. There have been

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[A] The 2007 number was 83 as of March 20, 2007. By assuming that the delay between paper submission and database update is 2-3 weeks, we deduce that 83 should represent accurately the number of publications submitted during the first two months of the year. Therefore the yearly publication is projected to be about 498 (6 x 83).

numerous reports on alloy compositions that were improved glass formers created by only slightly altering or adding the alloying elements.

On the contrary, there are only a handful reports on BMG systems that were formulated around lightweight structural metals, for example, aluminum and titanium. Evidently there have been great efforts [3, 4] in the scientific community to understand and develop the glass forming alloys formulated around Al, as indicated by numerous publications on Al-based metallic glasses [5-20] – all of which are just nominal glass formers and require a significant cooling rate.

To date, no Al-based BMG has been found. Several attempts were made by the Inoue group at Tohoku University, and their best Al alloys were ductile but could only be made in thin ribbons and flakes. Researchers have to employ exotic techniques to make use of these Al metallic glasses, for example, atomization and powder consolidation, pulsed laser sintering [21], and solid-state amorphization [22].

There were only a few reports on titanium BMGs. A Ti-based BMG developed by Zhang and Inoue [23] in 1998 was claimed to be a very good glass former which could be cast fully amorphous into 6 mm strip. However there have been reports disputing that the published alloy composition could not be cast fully amorphous beyond the 2 mm level [24]. Recent developments by Kim and Johnson, and by Kim and collaborators [25], show that beryllium addition could improve glass forming ability of Ti-based BMGs. Unfortunately, Be is a respiratory toxin and poses health-related risks when processed.

Mg-based BMGs are another possible candidate for lightweight structural BMGs, because their densities are below 4 g/cc. Unfortunately, among the reported Mg-based BMG compositions most do not have the required mechanical properties for structural materials, while the glass transition temperatures are usually below 150 ^{o}C [26-28]. Such low Tg puts the material at crystallization risk, i.e., Mg-BMGs may crystallize under a hot desert heat.

The quest for lightweight structural BMG continues.

2. Quest for BMGs as Lightweight Structural Materials

Sponsored by the Defense Advanced Research Projects Agency (DARPA), the author's early research work was concentrated on the search for lightweight structural BMG. During the early alloy development process, there were a few occasions when we found that our "freshly developed" alloy design ideas had already been tested by another research group elsewhere. Nearly all eutectics which are available in ternary Al-based alloy database (ASM Handbook) were tried without success. A conventional, straight-forward approach would lead one down the same path that other researchers followed without finding bulk glass formers. This project required out-of-the-box thinking. Some of the tried approaches include:

- Redesign of Be-free Vitreloy-type composition (Zr-Ti-Cu-Ni-Al) by introducing more Al and Ti
- Ti-Cr-V alloy systems formulated around the inverse melting concept which suggests that certain crystalline structures could be made amorphous by thermal annealing or slow cooling [29]

- Al-RE-TM alloy systems (RE – Rare Earth metals, TM – Transition metals) formulated with Al content less than 75% atomic, while the majority of published compositions have Al content at 75% or above

After two years and over five hundred alloy compositions tested[B], sub-millimeter-level Al-based metallic glasses that possess sizeable supercooled liquid regions were discovered. It must be noted that the majority of published Al-based metallic glasses will crystallize rapidly when the specimen is heated slowly (20 K/min) from room temperature to glass transition. In other words, there is no separation between Tg and Tx. As illustrated [30] in Figure I-2, there are two main kinetic control mechanisms for the suppression of crystallization in undercooled liquids. For most Al-based metallic glasses, a growth control (G) of crystallization allows some crystallites to form initially during rapid quenching, but their growth is restricted by rapidly rising viscosity during cooling. Upon reheating the sample, these "quenched-in" nuclei [30] undergo rapid crystal growth near Tg, which concurs with Tx.

By contrast, our recently developed Al-based and Al-Ti-based metallic glasses have better stability against crystallization, as schematically illustrated in the nucleation control case shown in Figure I-2. In a nucleation control mechanism, both nucleation and growth noses in the TTT diagram are shifted towards longer time. This allows the molten

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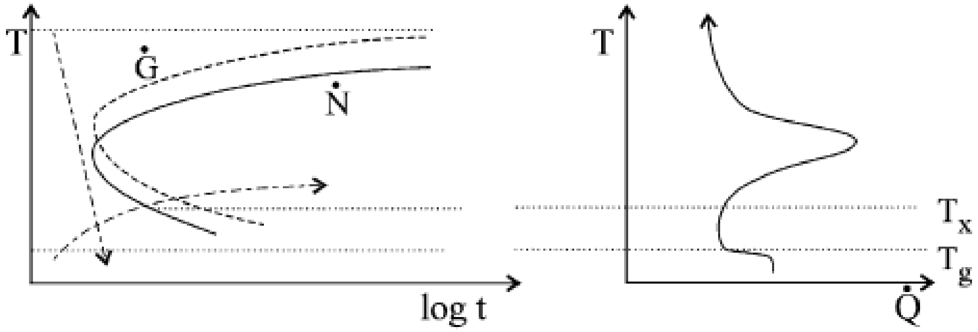
[B] The development and assessment of nominal glass formers must first be done using rapid quenching technique to screen alloys with potentially good GFA. The author's very first task at Caltech was to refurbish the splat-quenching machine. The "renewed" splat quencher was later used extensively to expedite many alloy development projects and to provide rapid quenching tools for examining different aspects of glass formation at high cooling rates. The splat-quenched liquid undergoes a 10^6 K/s cooling rate, which is the high end of the cooling rate spectrum available in the laboratory.

alloy to be quenched rapidly while the crystal nucleation reaction is bypassed. As a result, there is no precursor reaction to influence the evolution of crystalline clusters during reheating, and clear separation between Tg and Tx can be observed [30].

Nucleation control



Growth control

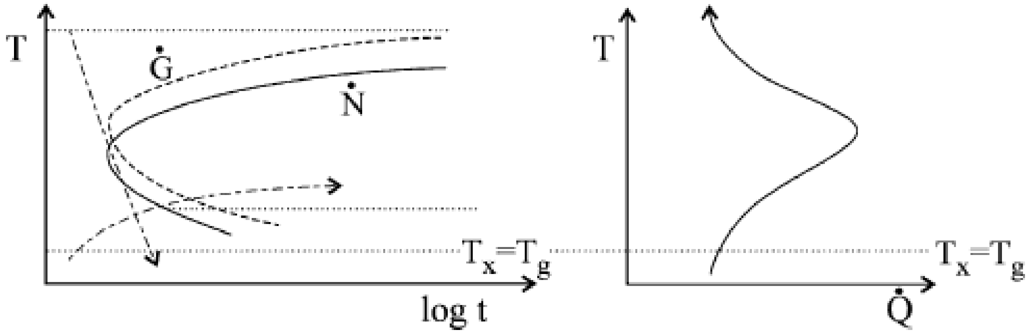


Figure I-2: Schematics showing kinetics of metallic glass formation: nucleation control vs. growth control. Quenching and reheating paths are shown on the TTT diagrams and T-dQ/dt thermograms (dQ/dt = heat evolution rate) [30].

The width of the supercooled liquid region, ΔTx = Tx-Tg, indicates the alloy's stability against crystallization. From the metallic glass processing point of view, the supercooled liquid region in time-temperature space allows the glassy alloy to be post-processed. Foaming, thermoplastic stamping, plastic injection molding, and powder consolidation are just a few examples of post-processing techniques available to glassy alloys that possess a supercooled liquid region.

Figure I-3 shows typical differential scanning calorimetric (DSC) curves for Al-rich BMGs – most do not have supercooled liquid region [31]. There are only a limited number of Al-based systems—for example, Al-La-Ni systems [19] developed by Inoue and coworkers in 1989 with ΔTx of 0-17 °C [32] – figure I-4 shows the DSC thermal profile of melt spun $Al_{86}La_5Ni_9$ ribbon, which exhibits a narrow [32] glass transition region prior to crystallization.

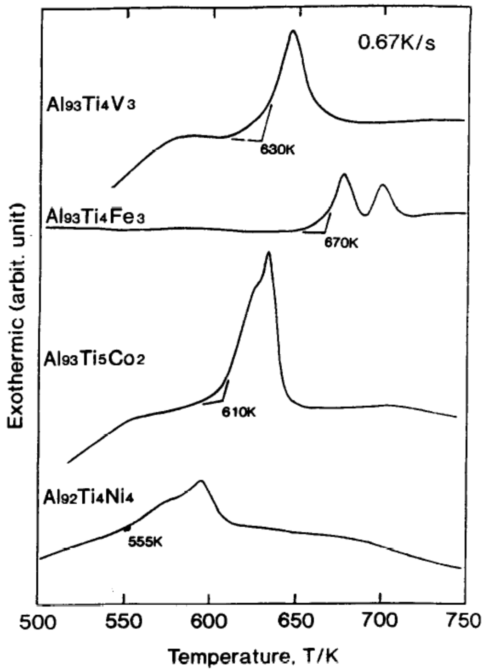


Figure I-3: DSC curves of melt spun $Al_{93}Ti_4V_3$, $Al_{93}Ti_4Fe_3$, $Al_{93}Ti_5Co_2$, and $Al_{92}Ti_4Ni_4$ alloys showing no supercooled liquid region (reproduced after [31])

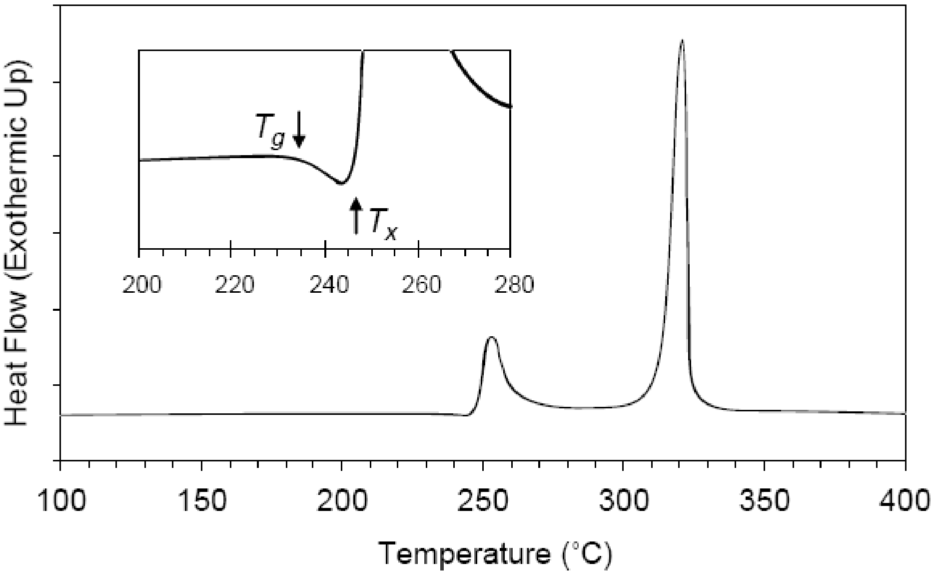


Figure I-4: DSC curve of $Al_{86}La_5Ni_9$ alloy during 20 K/min heating. The narrow glass transition region is magnified in the inset (reproduced after [32]).

For comparison, Figure I-5 shows two DSC thermal profiles for two splat-quenched samples – both of which have sizeable supercooled liquid region. The author developed these two alloy families based on light weight structural material requirements (e.g., low density, and a supercooled liquid region large enough for post-processing, etc.) The density for the Al-rich and Al-Ti-rich alloys – $Al_{67}Fe_{20}Ce_3B_{10}$ and $(Al_{½}Ti_{½})_{55}Zr_{12.5}Ni_{32.5}$ – is approximately 3.75 g/cc and 5.35 g/cc, respectively (see density approximation in Appendix A). The alloy development aspect of our Al-based metallic glass study will be discussed briefly in Chapter II.

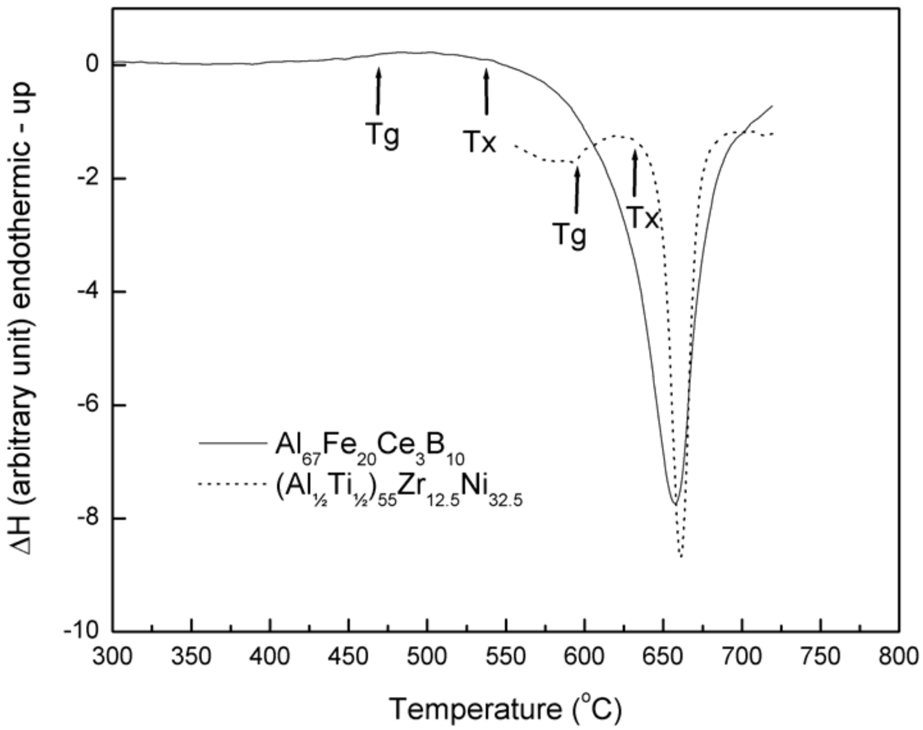


Figure I-5: DSC thermal profiles for $Al_{67}Fe_{20}Ce_3B_{10}$ *and* $(Al_{½}Ti_{½})_{55}Zr_{12.5}Ni_{32.5}$ *splat quenched samples using 20K /min heating rate. Contrary to most Al-based metallic glasses, these two alloys exhibit a supercooled liquid region which suggests their potential usage as structural material after post-processing – e.g., thermoplastic forming, thermoplastic sintering, and powder consolidation – all of which techniques require stable feedstock glass to have considerable supercooled liquid region.* [C]

[C] The detailed results and discussion of Al-based and Al-Ti-based metallic glasses are outside the scope of this thesis and shall be separately reported in forthcoming publication.

3. Relationship between Poisson's Ratio and Desired Mechanical Properties

Most of the metallic glasses synthesized during DARPA's lightweight BMG project were found to be brittle. Many of the splatted Al metallic glass foils would crumble easily, however a few compositions exhibited some plasticity. Undeniably, the plastic or brittle behavior of BMGs is of engineering significance.

Limited plasticity at room temperature is known to be the Achilles' heel for many bulk metallic glasses (BMGs). For instance, the iron-based BMGs [33] discovered by researchers at the University of Virginia were not immediately useful for engineering applications because of their extremely brittle nature.

Recent study on brittle-to-ductile transition in BMGs by Lewandowski et al. [34] shows that there is a strong correlation between plasticity and the elastic modulus ratio, G/B, when G is the shear modulus and B is the bulk modulus. The value of G/B less than 0.41-0.43 has been found necessary in order for bulk metallic glasses to exhibit plasticity.

Based on Lewandowski's finding, the G/B value of less than 0.41-0.43 is equivalent to the υ of more than 0.31-0.32. The concept was recently confirmed by Gu and colleagues at the University of Virginia [35] who doped $Fe_{65}Mo_{14}C_{15}B_6$ bulk amorphous steel with lanthanide metals to modify the value of υ. They demonstrated that there existed a brittle-to-ductile transition in that particular Fe-based BMG system – when υ is less than 0.32, specimens tend to be extremely brittle. A detailed discussion of the correlation can be found in Chapter IV of this thesis.

The high Poisson's ratio seems to be the key to plasticity in metallic glasses. Prior to the author's Au-based BMGs discovery [36], there were only two families of BMGs that exhibited exceptionally high Poisson's ratio ($\upsilon > 0.4$), they are the BMG systems based on palladium (~0.41) and platinum (~0.43) [37], both of which showed extensive ductility. In the periodic table, there are only three pure elements that have a Poisson's ratio greater than 0.4 – 0.45 for Tl, 0.44 for Pb, and 0.44 for Au. Because of the toxicity and health problems found with Tl and Pb, Au-based BMG seemed to be the ideal alloy candidate for investigating the relationship between plasticity and Poisson's ratio.

The development of Au-based BMG would require a significant effort. With the recent success in Pt-based BMGs development by Schroers and Johnson [38], Liquidmetal Technologies received funding to develop a Au-based BMG with at least 18 karat gold content (75 wt%) for jewelry application. With financial support from Liquidmetal Technologies, the author collaborated with Dr. Schroers and systematically developed gold-based BMGs that could be cast fully amorphous up to 5 mm in strip geometry.

A general alloy design, strategies, techniques, and obstacles will be included in chapter II of this thesis, while Chapter III focuses on the development of gold a based bulk metallic glass and its characteristic temperatures.

Chapter IV offers a detailed thermodynamics and kinetics study and necessary comparisons between the two recently developed high Poisson's ratio systems – Pt-based and Au-based BMGs. The chapter ends with a comparison of the Gibbs free energy difference between liquid and crystalline mixture among four different bulk metallic glasses (two from this work and two from literature), using the original Turnbull's free energy change approximation as a driving force for nucleation (equation (3) in [39]). The normalized comparison suggests that all liquid and crystalline mixtures have the same Gibbs free energy difference at the high-temperature region (near the melting temperature), which is contrary to the commonly used glass forming ability benchmark methodology using $\Delta G^{l\text{-}x}$.

4. Anomalous Behaviors of Gold-Based BMG

Despite the fact that our Au-based BMGs have high Poisson's ratios (0.40-0.41), their mechanical properties are not as desirable as originally expected. Often, the correlations among various mechanical properties showed Au-based BMGs to be outliers. For example, Novikov and Sokolov reported the correlation between Tg and mechanical properties B, G, and the average atomic volume, V. V is equal to M/ρ where M is the average atomic mass and ρ is density [40]. The plot in Figure I-6 shows a correlation between Tg and V(B+3.4G) for almost 50 BMGs. The two points that deviate from the correlation correspond to $Au_{49.5}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ and $Au_{55}Cu_{25}Si_{20}$. The relationship between Tg and V(B+3.4G) is derived using two purely graphically fitted correlations introduced in [40], and the assumption that the activation energy of viscous flow in metallic liquids is proportional to the shear modulus.

The main portion of Chapter V will be devoted to explaining one of the anomalies found in the Au-based family, which will be based on the manuscript in [41].

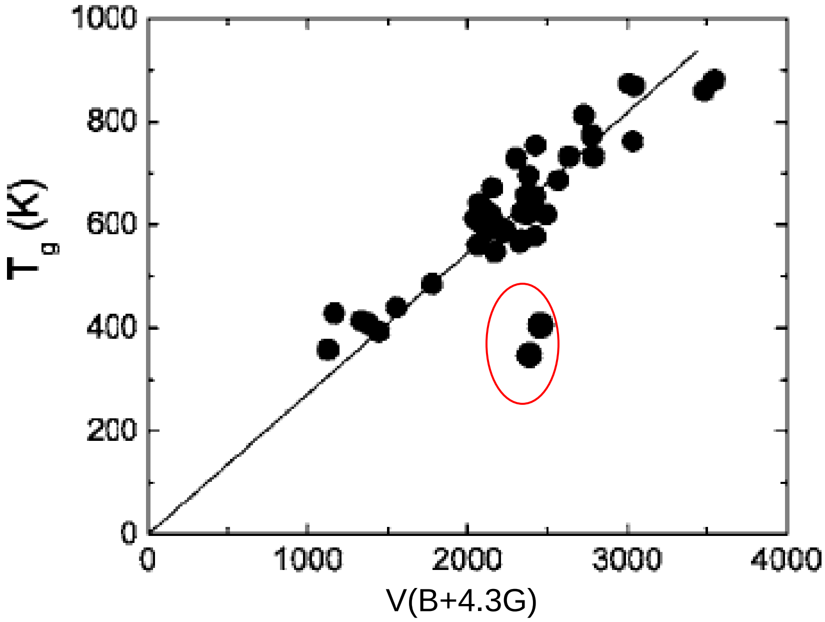


Figure I- 6: Correlation between Tg and V(B+4.3G) (unit = au cm^3 GPa/g). Respective BMGs and the values of the parameters can be found in [40]. The two outliers circled are the data points representing two Au-based metallic glasses.

5. Gold and Platinum BMGs as an Alternative to Lead-Free Solders – a Novel Approach for Metal-to-Metal Joining

There has been ongoing research to find adequate substitute for Pb solder for many years, but until now there has been no clear solution to the problem. In the current transition stage, commercial Pb-free solders for reflow application in electronics packaging include a few varieties of near ternary eutectic of tin (Sn), silver (Ag), and/or copper (Cu) alloys with possible minute additions of elements such as bismuth (Bi), indium (In), zinc (Zn), and antimony (Sb).

These Sn-Ag-Cu (SAC) and Sn-Ag-Bi (SAB) solders are only partial solutions to issues posed by RoHS. SAC solders are inferior to Pb-Sn solder in terms of solderability (wetting, spreading, and low melting) and reliability. Because an optimized replacement for Pb-Sn solder has not been found, the European Commission (EC) has granted exemptions for specific usage of lead solder in “high-performance products” and in areas where the replacement solder would potentially pose greater risk than the use of lead.

Intel Corporation and our Caltech group have joined hands in search of lead-free solder alternative by utilizing metallic glasses. The two main approaches were (1) to develop a alloy that not only melts at around 230-270 ^{o}C[D], but also vitrifies to form an amorphous joint, and (2) to develop feedstock metallic glass solder for a thermoplastic soldering process.

Chapter VII will briefly explain the background of RoHS and existing problems found in current lead-free solder alternatives, followed by the discussions of recent results on possible approaches utilizing metallic glasses. The chapter will disclose novel methods and processing conditions for soldering and universal metal-to-metal joining developed in this thesis. The methods rely on the superior mechanical properties of bulk metallic glasses, and the softening behavior of metallic glasses in the undercooled liquid region near the glass transition. The new method is currently being tested with Au-BMG and Pt-BMG because of their low Tg, fragile liquid nature, ample processing time allowed, and resistance to oxidation reaction. The content of this chapter is based on the two provisional patents submitted by the author and co-inventors.

[D] The 230-270 ^{o}C temperature range is what the industry is currently using for melting and reflowing solder on copper bumps to join electronic chips and components.

6. Summary

This thesis is centered around the two high Poisson's ratio BMGs based on Au and Pt. The alloy development aspect was explained to show how the Au-based BMGs were designed by raising Tg while most other alloy development techniques primarily focus on the lowering of liquidus temperatures. The alloy crystallization behavior, mechanical properties, and other kinetic and thermodynamic variables were studied. The last chapter describes the key applications and processing techniques of these precious BMGs.

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