DEVELOPMENT OF NOVEL BINARY AND MULTI-COMPONENT
BULK METALLIC GLASSES

Thesis by
Donghua Xu

In Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California
2005
(Defended May 17, 2005)
Acknowledgements

Caltech is such an enthralling place. During my five years as a student here, so many times, lying in bed, I could not fall asleep, being either too excited about my new results or overly eager to figure out the solutions to the problems in my research. Being stingy with my time spent beyond research, I found myself deeply indebted to my family (my wife, parents, brother, sister etc.) for their great understanding and love. It is to them that go my deepest acknowledgements.

This thesis could not have become a reality if Professor Bill Johnson had not offered me the opportunity to come to Caltech. Bill’s erudition and insights, enthusiasm and optimism provided me with such an endless source of knowledge and energy. His real scholarly generosity made it possible for me to freely enjoy my research. Bill is the very first person at Caltech who deserves my full gratitude.

Among many colleagues, Haein Choi-Yim, Jan Schroers, Sven Bossuyt, Paul Kim, Andy Waniuk, Dale Conner, Boonrat Lohwongwatana (my long time officemate), Greg Welsh, Chris Veazey, Sundeep Mukherjee, Gang Duan, Mary Laura Lind and Jin-Woo Suh in the Johnson group; Seung-Yub Lee, Robert Rogan and Can Aydiner in the Ustundag group; Jason Graetz and Olivier Delaire in the Fultz group; and Shiming Zhuang and Theresa H. Kidd in the Ravichandran group are all acknowledged for their kind assistance in experiments and/or for their friendly company in the laboratories.

My gratitude also goes to the many faculty and staff members in the department who helped me in various ways. For example, Carol Garland helped me take TEM images of
many of my samples, and Robin Hanan and Elizabeth Welsh offered me their patient assistance in purchasing materials required for my research.

Although I did not socialize a lot, I did make some good friends whose company and friendship made my life in California easy and colorful. These include Boonrat Lohwongwatana, Seung-Yub Lee, Ling Li, Xin Yu, Bingwen Wang, Tingwei Mu, Yajuan Wang, Hao Jiang, Yong Hao, and Peng Xu at Caltech, and Dawei Ren and Qi Yang at the University of Southern California.

Most of this thesis work was supported by the Defense Advanced Research Projects Agency, Defense Sciences Office, under ARO Grant No. DAAD19-01-1-0525.
Bulk Metallic Glasses (BMGs) have been drawing increasing attention in recent years due to their scientific and engineering significance. A great deal of effort in this area has been devoted to developing BMGs in different alloy systems. BMGs based on certain late transition metals (e.g., Fe, Co, Ni, Cu) have many potential advantages over those based on early transition metals. These advantages include even higher strength and elastic modulii, and lower materials cost, to name but a few that are highly preferable for a broad application of BMGs as engineering materials. Nevertheless, these ordinary-late-transition-metal-based BMGs generally have quite limited glass-forming ability (GFA). In particular, for the Ni-based and Cu-based alloys reported prior to this research, the maximum casting thickness allowed to retain their amorphous structures is only ~2 mm (or lower) and ~5 mm (or lower), respectively.

The first important finding during this research was that certain quinary Ni-based alloys in the Ni-Cu-Ti-Zr-Al system can be cast into 5 mm diameter amorphous rods. This critical casting thickness is the highest for any reported Ni-based BMG’s, indicating that these alloys are the easiest metallic glass formers based on Ni discovered to date. Secondly but more interestingly, certain binary alloys in the Cu-Zr and Cu-Hf systems were found to form bulk amorphous samples with casting thicknesses as high as 2 mm. The discovery of these binary BMGs was very surprising since it had been widely considered that only multi-component (having at least three elements) alloys could form bulk metallic glasses. These new binary BMGs have not only challenged the traditional concept about bulk metallic glass formation, but also provided interesting subjects for
future theoretical studies such as molecular dynamics simulations since they possess both the simplicity of binary alloys and the good GFA of multi-component BMGs. As a matter of fact, these binary BMGs have also led to a third and perhaps most significant discovery during this research: the family of Cu-based BMGs in the Cu-Zr-Al-Y system that possesses a critical casting thickness up to 1 cm. These quaternary Cu-based alloys, together with some complicated Fe-based alloys reported by two other groups during the course of this research, are the first centimeter-level BMGs based on the ordinary late transition metals.

This thesis first reviews the fundamentals related to BMG development, then reports in detail the formation and properties of the above-mentioned binary and multi-component BMGs based on Ni and Cu. A generalized geometric model for the critical-value problem of nucleation developed in this research is also presented.
Contents

Acknowledgements ........................................................................................................... ii

Abstract ......................................................................................................................... iv

Contents ......................................................................................................................... vi

List of Figures ................................................................................................................ x

List of Tables .................................................................................................................. xii

Chapter 1: Introduction ................................................................................................. 1

1.1 Basic concepts about glasses and metallic glasses .............................................. 1

1.1.1 Glass and glass transition .............................................................................. 1

1.1.2 Glass formation and glass-forming ability ..................................................... 4

1.2 History of metallic glass research and motivation for this thesis .................... 7

1.3 Thermodynamics and kinetics related to glass formation and TTT
(Time-Transformation-Temperature) diagram ........................................................... 10

1.3.1 Thermodynamics of an undercooled liquid ................................................... 10

1.3.2 Kinetics of an undercooled liquid ................................................................. 12

1.3.3 Classical theory for crystal nucleation and growth from
an undercooled liquid and TTT diagram ............................................................... 17

1.4 Frequently used criteria for the development of BMGs .................................. 26

1.4.1 Reduced glass transition temperature ......................................................... 27

1.4.2 Multi-component rule (confusion principle) ............................................... 31

1.4.3 Atomic size mismatch .................................................................................. 32

1.4.4 Chemical interactions among constituent elements ..................................... 34

1.4.5 Considerations based on phase diagrams ................................................... 35
Chapter 2: Formation and properties of Ni-based BMGs in Ni-Cu-Ti-Zr-Al system

2.1 Introduction .................................................................................................................45
2.2 Experimentals ..............................................................................................................46
2.3 Results and Discussion .............................................................................................47
   2.3.1 Ternary Ni₄₅Ti₂₀Zr₃₅ alloy ....................................................................................47
   2.3.2 Quaternary Ni₄₅Ti₂₀Zr₃₅₋ₓAlₓ alloys ......................................................................50
   2.3.3 Quinary NiₓCuₐ₋ₓTiₓZr₃₋₅Al₁₀ alloys (a~b~45) .......................................................51
   2.3.4 Effect of small Si additions .................................................................................54
   2.3.5 Mechanical tests .................................................................................................55
2.4 Conclusions ...............................................................................................................57
References .........................................................................................................................58

Chapter 3: Formation of bulk metallic glasses in binary Cu-Zr and Cu-Hf systems

3.1 Introduction ...............................................................................................................60
3.2 Experimentals ............................................................................................................61
3.3 Results and discussions ...........................................................................................61
   3.3.1 Glass-forming abilities .......................................................................................61
   3.3.2 Thermal analyses with DSC ................................................................................65
   3.3.3 Mechanical properties of the three best glass formers ........................................69
3.4 Conclusions ..............................................................................................................71
References .......................................................................................................................72
Chapter 4: A generalized model for the critical-value problem of nucleation

4.1 Introduction .............................................................................74
4.2 Model construction ...............................................................77
4.3 Model solution and interpretation .........................................77
4.4 Conclusions .........................................................................85

References ..................................................................................87

Chapter 5: Centimeter size BMG formation in Cu-Zr-Al-Y system ..........88

5.1 Introduction .............................................................................88
5.2 Experimentals .........................................................................89
5.3 Results and discussions .........................................................90
5.4 Conclusions .........................................................................100

References ..................................................................................101

Chapter 6: Concluding Remarks ....................................................102
List of Figures

Chapter 1

1.1 Plots of viscosity data scaled by values of $T_g$ for different glass-forming liquids…..14
1.2 Plots of the three terms in Eq. (1.13) vs. nucleus radius $r$………………………...19
1.3 Nucleation rate $I_v$ and crystal growth rate $u$ as a function of temperature for the
   BMG alloy Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$……………………………………………………….22
1.4 TTT (Time-Temperature-Transformation) diagram of Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ calculated
   using a crystallized volume fraction $f = 10^{-6}$ ......................................................24
1.5 Logarithm of nucleation rate (in cm$^3$s$^{-1}$), log $I_v$, vs. the reduced temperature, $T_r$,
   calculated at different values of the reduced glass transition temperature $T_{rg}$ ........30
1.6 Binary phase diagram of Zr-Be system .................................................................36
1.7 Binary phase diagram of Ti-Be system.................................................................36
1.8 Binary phase diagram of Zr-Cu system...............................................................37
1.9 Binary phase diagram of Zr-Ni system...............................................................37
1.10 Binary phase diagram of Zr-B system..............................................................39

Chapter 2

2.1 XRD patterns of selected ternary and quaternary alloys taken with a Co K$\alpha$
   source..................................................................................................................49
2.2 DSC scans of selected ternary and quaternary alloys at a heating rate of 0.33 K/s…..49
2.3 XRD patterns of selected quaternary and quinary alloys taken with a Co K$\alpha$
   source..................................................................................................................52
2.4 Electron diffraction pattern taken from the transverse cross section of a 5mm
Chapter 3

3.1 Binary Cu-Zr phase diagram (reproduced from Ref. [17]) ........................................62
3.2 Binary Cu-Hf phase diagram (reproduced from Ref. [17])..............................62
3.3 X-ray (taken with a Cu K\(\alpha\) source) and electron diffraction patterns of
\(\text{Cu}_{40}\text{Zr}_{54}\) (A1), \(\text{Cu}_{64}\text{Zr}_{36}\) (A2) and \(\text{Cu}_{66}\text{Hf}_{34}\) (A3)..........................63
3.4 XRD patterns taken from 0.5 mm thick strips of \(\text{Cu}_{100-x}\text{Zr}_x\) (\(x=34, 36, 38.2, 40\)
at.\%) using a Cu-K\(\alpha\) source.................................................................66
3.5 XRD patterns taken from the cross sections of the 2mm thick cast strips of
\(\text{Cu}_{100-x}\text{Zr}_x\) (\(x=34, 36, 38.2, 40\) at.\%) using a Cu-K\(\alpha\) source..........................66
3.6 DSC scans of the 0.5mm thick strips of \(\text{Cu}_{60}\text{Zr}_{40}\), \(\text{Cu}_{61.8}\text{Zr}_{38.2}\), \(\text{Cu}_{66}\text{Zr}_{34}\), and
the 2mm thick strip of \(\text{Cu}_{64}\text{Zr}_{36}\) obtained at a heating rate of 0.33K/s..............68
3.7 Variations of \(\Delta T\) and \(T_{rg}\) with respect to Zr content \(x\) in alloy series
\(\text{Cu}_{100-x}\text{Zr}_x\) (\(x=34, 36, 38.2, 40\) at.\%).................................................................68
3.8 Compressive stress vs. strain curves of the three best glass formers in Cu-Zr
and Cu-Hf systems obtained at a strain rate of \(\sim 4\times 10^{-4}\) s\(^{-1}\) at room temperature....70

Chapter 4

4.1 The geometric factor as a function of contact angle \(\theta\) in the large-wall
heterogeneous solution......................................................................................76
4.2 (a) the geometric construction for the generalized nucleation model; (b) an illustration of the mechanical equilibrium at point S in part (a).........................78

4.3 (a) 3D image of the bivariate function $g(R, \theta)$; (b) 2D plots of $g(R, \theta)$ vs. $R/r_c$ at different values of $\theta$; (c) 2D plots of $g(R, \theta)$ vs. $\theta$ at different values of $R/r_c$ ...........................................................................................................................................83

Chapter 5

5.1 (A) Pictures of three cast samples of Cu$_{46}$Zr$_{42}$Al$_7$Y$_5$, with different diameters:

S1, 10mm; S2, 12mm; S3, 14mm; (B) XRD patterns obtained from 10mm (S1); 12mm (S2) and 14mm (S3) diameter rods of Cu$_{46}$Zr$_{42}$Al$_7$Y$_5$; and from 3mm (M1) and 4mm (M2) diameter rods of the matrix alloy Cu$_{46}$Zr$_{47}$Al$_7$ .............91

5.2 DSC scans of selected alloys at a constant heating rate of 0.33K/s. The upward arrows refer to the glass transition temperatures and the downward arrows refer to the onset of the first crystallization events. The inset at the lower right corner is the isothermal DSC profile of the 10mm diameter rod of Cu$_{46}$Zr$_{42}$Al$_7$Y$_5$ at a constant temperature of 739K ..........................................................93

5.3 Melting behaviors of selected alloys measured at a heating rate of 0.33K/s. The arrows refer to the liquidus temperatures......................................................95

5.4 TEM image (a), Cu K\(\alpha\)1 X-ray dot map image (b) and Y K\(\alpha\)1 X-ray dot map image (c), of as-cast Cu$_{46}$Zr$_{42}$Al$_7$Y$_5$. The ripples and scratches in the images were caused by the ultramicrotomy sample preparation method.................98
Chapter 2

2.1 Examples of the new Ni-based amorphous alloys developed in this work (T_g and T_{x1} were measured with DSC at a heating rate of 0.33K/s) ..........................48

2.2 Some measured mechanical properties of selected alloys .................................55

Chapter 3

3.1 Thermal properties of three best glass formers in Cu-Zr and Cu-Hf systems ........67

3.2 Mechanical properties of three best glass formers in Cu-Zr and Cu-Hf systems ......69

Chapter 5

5.1 A list of representative alloys and selected properties .................................92