On the thermodynamic and kinetic properties of bulk glass forming metallic systems

Dissertation

zur Erlangung des Grades

Doktor der Naturwissenschaften (Dr. rer. nat.)

der

Naturwissenschaftlich-Technischen Fakultät III Chemie, Pharmazie und Werkstoffwissenschaften

der

Universität des Saarlandes

vorgelegt von

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Saarbrücken

Juni 2012

Tag des Kolloquiums:	18.10.2012

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Saarbrücker Reihe

Materialwissenschaft und Werkstofftechnik

Band 35

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Shaker Verlag

Aachen 2012

Bibliographic information published by the Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at http://dnb.d-nb.de.

Zugl.: Saarbrücken, Univ., Diss., 2012

Printed in Germany.

ISBN 978-3-8440-1483-9
ISSN 1860-8493

Shaker Verlag GmbH • P.O. BOX 101818 • D-52018 Aachen
Phone: 0049/2407/9596-0 • Telefax: 0049/2407/9596-9
Internet: www.shaker.de • e-mail: info@shaker.de

Abstract

Bulk metallic glasses (BMGs) are typically formed from the rapid quenching of multicomponent metallic melts. Good BMG-forming systems are associated with a large atomic size mismatch and deep eutectic formation between the constituent elements. As such, these densely packed BMG-forming liquids can be characterized through sluggish kinetics, which impedes the nucleation and growth of crystals, as well as a low driving force for crystallization that is present in the undercooled liquid.

In this work, the equilibrium thermodynamic and kinetic properties of certain BMG-forming liquids are analyzed at temperatures near the melting point and in the deeply supercooled state near the glass transition. This includes determination of the viscosity and thermodynamic functions of the liquid. The non-equilibrium properties of the glassy state are also studied, looking at the phenomenology of structural relaxation as it relates to viscosity, enthalpy and free volume. A look at viscous flow in terms of configurational entropy and various models of the free volume is given.

Finally, the molten viscous behavior of various BMG-forming alloys is investigated at temperatures above the melting point. The kinetics in the melt at high temperatures reveals a distinctively more fragile liquid state than at low temperatures near the glass transition. This behavior is revealed to be the result of a fragile-to-strong transition in the undercooled liquid, possibly due to polyamorphism.

Zusammenfassung

Metallische Massivgläser (MMG) entstehen üblicherweise durch schnelles Abkühlen mehrkomponentiger metallischer Schmelzen. Ein großer Unterschied in den jeweiligen Atomradiien und die Bildung tiefer Eutektika sind typische Kennzeichen guter MMG-bildener Systeme. Dementsprechend werden solche MMG-bildenen Schmelzen durch eine langsame Kinetik, sowie eine geringe treibende Kraft zur Kristallisation, gekennzeichnet.

In dieser Arbeit werden bei Temperaturen in der Nähe des Schmelzpunktes, sowie bei sehr tiefen Unterkühlungen nahe des Glasübergangs, die thermodynamischen und kinetischen Gleichgewichtseigenschaften bestimmer MMG-bildener Schmelzen untersucht. Es werden die Viskosität und die thermodynamischen Funktionen bestimmt. Nichtgleichgewichtseigenschaften des Glaszustandes werden auch berücksichtigt und die Phänomenologie struktureller Relaxation in Bezug auf Viskosität, Enthalpie und freies Volumen untersucht. Eine Beschreibung viskoses Fließen mittels der Konfigurationsentropie sowie verschiedener Modelle des freien Volumens werden auch diskutiert.

Es wird schließlich das viskose Verhalten verschiedener MMG-bildener Schmelzen bei Temperaturen nahe des Schmelzpunkts untersucht. Die Kinetik der Schmelze bei diesen hohen Temperaturen zeigt ein kinetisch fragileres Verhalten als es bei niedigeren Temperaturen in der Nähe des Glasübergangs zu beobachten ist. Dies deutet auf einen Fragil-Stark-Übergang in der unterkühlten Schmelze hin, der eventuell auf Polyamorphismus beruht.

for my grandfather...

Acknowledgments

I would first like to express my sincerest gratitude to my supervisor Ralf Busch for his guidance throughout this project and for allowing me the opportunity to make these last five years at the *Lehrstuhl für Metallische Werkstoffe* some of the most challenging and productive I've had thus far. Above all, I'm thankful to have had the chance to gain invaluable practical experience and the freedom to pursue my own ideas.

My colleagues and co-workers at the LMW have been a great source of inspiration and insight for me and I would like to thank them all for their cooperation and the friendship that we've developed over the years. In particular, I am grateful for the support and training provided by Isabella Gallino, who mentored me during my first year at the department and has been a constant source of optimism. I would especially like to thank Dr.-Ing. Frank Aubertin for the many productive and insightful conversations we've had together, as well as his willingness in helping me to answer some of the great many questions that I have encountered during this project. I would like to recognize and thank Hermann Altmeyer and Jörg Eiden of the LMW technical staff for putting forth the hard work necessary to keep everything running and having the patience to help me improve my own technical competence as well. I would also like to thank Martina Stemmler for her help in carrying out the XRD measurements. It also goes without saying that the time and effort put in by our *HiWis* in casting and preparing samples is greatly appreciated.

I am thankful for also being able to have as my peers some genuinely good friends. I would like to acknowledge Jochen Heinrich, whom I have known since our year at OSU together and would like to thank him for the help and guidance he's given me towards understanding the ins and out of Germany. I am happy to have also had the chance to work with Moritz Stolpe, someone who has never failed at putting a smile on my face or leading an interesting conversation. I am very thankful for the friendship I've had with Will Hembree over these past years and consider him a close companion. I would also like to thank Shuai Wei for the many insightful discussions we've had together in our collaborations and I wish him all the best in his scientific endeavors.

My stay in Germany would not have been possible without the encouragement and guidance of Prof. Christian Stehr of Oregon State University. Prof. Stehr enabled me to make the first steps towards continuing my graduate education in Germany and I am indebted to him for his years of support. My deepest gratitude also goes out the many funding agencies who have provided financial support for me along the way. I would especially like to acknowledge the opportunities provided to me by the Ford Family Foundation, allowing me to carry out my undergraduate studies. Additionally, my graduate work in Saarbrücken would not have been possible without the effort put forth by the many individuals behind the AMASE Master, as well as the generous financial support provided by the Erasmus Mundus Program. I would especially like to recognize and thank Prof. Dr.-Ing. Frank Mücklich and Dr.-Ing. Flavio Soldera for their work in making this possible. Lastly, I would like to recognize the *Deutsche Forschungsgemeinschaft*, whose funding has supported a portion of this project.

My most heartfelt thanks go out to my partner, Sanja, who has shown infinite patience with me throughout this entire process. Her love and support has helped me immeasurably. Most of all though, I would like to express my deepest gratitude for the ongoing support and encouragement of my family, teachers and close friends. None of this would have been possible without them.

Z. Evenson
Saarbrücken, June 2012

Contributions and publications

The experimental results presented in Chapters 5 and 6 were collected, analyzed and interpreted by the author. A portion of the three-point beam-bending data on Vitreloy 106 and 106a were originally collected and analyzed by S. Raedersdorf [1]. The three-point beam-bending data shown in this work for Vitreloy 106 and 106a correspond to experiments and analysis that were repeated by the author. In Chapter 7, high-temperature viscosity data were taken from experiments performed by T. Schmitt [2], M. Nicola and W. Hembree [3]; the data analysis, presentation and conclusions are the author's original work. I. Gallino was responsible for assisting with and directing the experimental implementation of the calorimetric studies carried out here. The overall research direction and project administration was conducted by R. Busch.

At the time of writing this thesis, there have been five publications based on the results presented in this work:

- Z. Evenson, I. Gallino and R. Busch, The effect of cooling rates on the apparent fragility of Zr-based bulk metallic glasses, *J Appl Phys*, **107**; 123529 (2010)
- Z. Evenson, S. Raedersdorf, I. Gallino and R. Busch, Equilibrium viscosity of Zr-Cu-Ni-Al-Nb bulk metallic glasses, *Scripta Mater*, **63**; 573-576 (2010)
- Z. Evenson and R. Busch, Equilibrium viscosity, enthalpy recovery and free volume relaxation in a $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$ bulk metallic glass, *Acta Mater*, **59**; 4404-4415 (2011)
- Z. Evenson and R. Busch, Enthalpy recovery and free volume relaxation in a $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$ bulk metallic glass, *J Alloys Comp*, **509S**; S38-S41 (2011)
- Z. Evenson, T. Schmitt, M. Nicola, I. Gallino and R. Busch, High temperature melt viscosity and fragile-to-strong transition in Zr-Cu-Ni-Al-Nb(Ti) and $Cu_{47}Ti_{34}Zr_{11}Ni_8$ bulk metallic glasses, *Acta Mater*, **60**; 4712-4719 (2012)

Additionally, these results have been presented as contributions to various academic symposia:

- Z. Evenson, I. Gallino and R. Busch. The Effect of Cooling Rates on the Apparent Fragility of the $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ Bulk Metallic Glass. Poster presented at *RQ13, The 13th International Conference on Rapidly Quenched and Metastable Materials*; 2008 Aug 24-29; **Dresden, Germany**.
- Z. Evenson, I. Gallino and R. Busch. The Effect of Cooling Rates on the Apparent Fragility of the $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ Bulk Metallic Glass. Poster presented at *Glass and Time: Fragility of Liquids – Cause(s) and Consequences, International workshop*; 2008 Oct 08-10; **Copenhagen, Denmark**.
- Z. Evenson, I. Gallino and R. Busch. The Effect of Cooling Rates on the Apparent Fragility of the $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ Bulk Metallic Glass. Poster presented at *Materials Research Society Fall Meeting 2008*; 2008 Dec 01-05; **Boston, USA**.
- Z. Evenson and R. Busch. Relaxation Phenomena in a $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$ BMG Alloy as Investigated with Dilatometric Methods. Poster presented at *5th International EEIGM / AMASE / FORGEMAT Conference on Advanced Materials Research*; 2009 Nov 04-05; **Nancy, France**.
- Z. Evenson and R. Busch. Enthalpy and Free Volume Relaxation in a Zr-Ti-Ni-Cu-Be Bulk Metallic Glass Alloy. Presented at *DPG Frühjahrstagung der Sektion Kondensierte Materie (SKM)*; 2010 Mar 21-26; **Regensburg, Germany**.
- Z. Evenson and R. Busch. Enthalpy and Free Volume Relaxation in a Zr-Ti-Ni-Cu-Be Bulk Metallic Glass Alloy. Presented at *International Symposium on Metastable, Amorphous and Nanostructured Materials (ISMANAM) 2010*; 2010 July 4-9; **Zürich, Switzerland**.
- Z. Evenson and R. Busch. Structural Relaxation in a $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$ Bulk Metallic Glass. Poster presented at *International Workshop on Dynamics in Viscous Liquids*; 2011 Mar 30 - Apr 2; **Rome, Italy**.

Finally, a portion of the results presented in Section 5.1 was produced from the preliminary work that appears in the Master's thesis, "The effect of cooling rates on the glass transition of Zr-based bulk metallic glasses", by Z. Evenson (2008).

Contents