BULK METALLIC GLASSES

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This book is fondly

DEDICATED

to the memory of

Professor T.R. Anantharaman

(November 25, 1927–June 18, 2009)

who pioneered research on metallic glasses in India

Foreword

Metallic glasses with amorphous structures, first discovered in 1960, have both scientific and technological interest. The successful synthesis of bulk metallic glasses during the late 1980s has stimulated great enthusiasm in the study of this class of metallic materials. Substantial progress has been made in the understanding of physical, chemical, and mechanical properties of bulk metallic glasses since the beginning of the 1990s. Characterization on the atomic scale indicates the formation of tightly bonded atomic clusters and loosely bonded free-volume zones in the amorphous state. Various polyhedral packings have been observed in these clusters, which are also confirmed by atomic simulations. Contrary to crystalline materials with periodic lattice structures, the plastic deformation of bulk metallic glasses proceeds via localized shear bands, resulting in inhomogeneous deformation at ambient temperatures. Bulk metallic glasses show extremely high strength, close to the theoretical strength of solids in the glassy state, and superplastic behavior in the supercooled liquid state. Both experimental studies and theoretical analyses reveal shear transformation zones, instead of dislocations, as the basic unit for plastic deformation in bulk metallic glasses. Furthermore, recent studies indicate that bulk metallic glasses possess attractive physical and mechanical properties for high-tech applications in micro/nanosystems. All these interesting results, as well as all fundamental and applied topics, are systematically described in 11 chapters in this book authored by Professor Suryanarayana from the University of Central Florida in Orlando, Florida and Professor Inoue from Tohoku University, Sendai, Japan.

Professor Inoue has conducted pioneering work on the synthesis and development of bulk metallic glasses during the past 20 years. He is familiar with all aspects of properties and behaviors of these materials. There is no doubt that Professor Inoue is the right person to lead the effort in writing this book. In contrast to the edited book published previously, this book covers all topics in a coherent manner. At present, bulk metallic glasses are emerging as a new class of metallic materials with unique physical and mechanical properties for structural and functional use. This book is suitable for young researchers in materials science and applied physics, who are interested in learning about bulk metallic glasses and are looking for a guidebook to launch research into this exciting materials field. Also, this book can be perfectly used as a textbook for students in graduate schools.

C. T. Liu
Hong Kong Polytechnic University
Hong Kong
Auburn University
Auburn, Alabama

On September 3, 1960, there appeared in print a short article, barely over one column long, that shifted a paradigm: Klement, Willens, and Duwez reported that the alloy $Au_{75}Si_{25}$ (composition in atomic %) could be obtained in glassy form by rapid solidification of the liquid [*Nature* 187, 869 (1960)]. It was already known that metallic alloys could be obtained in unstable noncrystalline form by vapor deposition onto cold substrates, but the realization of a metallic *glass* (formed when a liquid solidifies without crystallization) was a surprise. At first, the very possibility of a metallic glassy state was disputed, but the active research stimulated by that 1960 paper has gone on to show not only that metallic alloys can form true glasses, but also that such glasses can be formed in bulk without the need for rapid solidification, that they have distinctive sometimes record-breaking properties, and that they have and will find a wide range of applications.

It is time for a golden jubilee celebration!—and we find one well executed in the form of this book that comprehensively covers the modern field of bulk metallic glasses. Still better, that the book's authors have prominent and complementary profiles in the field. With publication records spanning some 80 man-years, the authors can put metallic glasses into context in the broad fields of advanced metallic materials and nonequilibrium processing in which they have both been so active.

Over the last 50 years, interest has waxed and waned, but surveying the field at this point, we can see not only that metallic glasses are an important new class of material, but also that their appearance has transformed fundamental understanding in a wide range of areas. For example, studies of the structure of metallic glasses have stimulated much work on equilibrium and supercooled metallic liquids. The structure of such liquids was first described by Bernal as dense random packing. While a high packing density is a characteristic of metallic liquids and glasses, it is now better appreciated that high densities are not associated with randomness, but rather with high degrees of order, albeit noncrystalline. The kinetics of crystallization of liquids is often discussed in terms of time–temperature–transformation diagrams. Whereas such diagrams were once purely schematic, glass-forming metallic systems allow them to be determined experimentally. Transmission electron microscopy of metallic glasses has permitted atomic-level investigations of crystal nucleation, relevant for standard solidification yet difficult or impossible to conduct on the liquids themselves. Comparison of metallic glasses with other longer-established members of the broad family of glasses has improved understanding of the glass transition, and has revealed remarkable correlations of thermal, elastic, and mechanical properties that hint at fundamentals of the glassy state spanning different bonding types.

Metallic glasses are of interest in establishing the fundamental basis of physical, mechanical, and chemical properties. In their early days, for example, they were important in showing something not universally expected at the time—that crystallinity is not a prerequisite for ferromagnetism. And at the present time, the distinctive shear-band deformation mode of metallic glasses is stimulating the development of theory on the ultimate strength of materials.

Such contributions to the broader understanding of condensed matter can only support interest in the metallic glasses themselves as new materials. This book covers their remarkable development since 1960: production methods, understanding of structure and glass-forming ability, composition ranges available, and properties. Above all, it is the availability of many metallic glasses in bulk form (with minimum dimension exceeding 1 mm to 1 cm) that has stimulated the current intense research on these materials.

Among the reasons for study of the crystallization of metallic glasses is that thereby attractive microstructures can be obtained. The metallic glasses can act as precursors, rather as oxide glasses do in the production of conventional glass ceramics. There are, indeed, several ways in which composites based on metallic glasses are of interest. Among those covered in this book are dispersions of a primary ductile crystalline phase in a metallic-glass matrix, composites that show remarkable combinations of strength and toughness. Also covered is the emerging topic of metallic-glass foams.

Very early in studies of metallic glasses, it was recognized that they would have properties attractive for applications. Their excellent soft-magnetic properties were the first to be exploited on a large commercial scale. As made clear in this book, their physical and mechanical properties, and their corrosion resistance, can also be highly attractive. So much of our technology is limited by materials performance. The present time of challenges in clean power generation and other aspects of sustainability may yet be materials science's finest hour, when solutions emerge in the form of new materials and new processing routes: bulk metallic glasses will surely have a prominent role. They may not be used on the largest scales associated with structural steels, but on the scales associated with personal items such as sports equipment down to micro- and nano-devices they have much to offer.

In this important reference work for the field, the authors provide comprehensive yet critical coverage of all major aspects of bulk metallic glasses. They recognize that it is important to understand the drawbacks as well as the advantages of these materials. They also show that while there have been great advances in understanding, many challenges remain. Bulk metallic glasses are at the heart of an exciting field with much still to deliver.

A. Lindsay Greer
Cambridge

The future of metallurgy lies in mastering disorder. In fact, one can argue that the trajectory of our field has followed a path of increasing topological disorder ever since the realization that pure metals are crystalline. Although crystallinity provides symmetry and order, it is the regions where ideal crystalline packing is disrupted that capture our attention. Metallurgists focus on "defects," including dislocations and grain boundaries, recognizing that these positions of broken periodicity, even when present in vanishingly small volume fractions, utterly dominate the most important properties. Recently, the interest in so-called nanocrystalline or nanostructured metals has driven attention to a regime where more atoms than not lie in disordered regions, evoking a variety of new mechanisms and properties of immediate technological interest.

In this landscape, amorphous metals are a limit—they are completely noncrystalline, with a negligible fraction of atoms sitting in a symmetric, crystalline environment. They are a mystery—their structure is often more definable in terms of what it is not, than what it is. When first discovered in the 1950s, they were rare and unusual; today they are pervasive, and can be produced by a wide array of synthesis routes. Their properties are not limited by the presence of lattice defects; they promise a suite of genuinely exceptional properties. Extreme values of strength, fracture toughness, magnetic properties, corrosion resistance, and other properties have been recorded in amorphous metals. In some cases, these come not individually, but in combinations unparalleled by any other material known to humankind.

If our future is to master disorder, then amorphous metals will certainly point the way. In particular, metallic glasses (i.e., amorphous metals produced from the melt) are formed by intentionally stabilizing the disordered liquid structure, and the rules for doing so become better understood with each passing year. And, although we may glibly describe them as "disordered," metallic glasses are structured in rich and complex ways that are just beginning to be unraveled. Their properties emerge in enigmatic ways from their disordered structure, and the means of optimizing those properties remain tantalizingly out of reach.

Metallic glasses have been actively studied for decades, and with particular fervor in the one just past. With many thousands of scholarly articles on the subject, and as many more expected in the coming years, a research text that overviews the entire field is overdue. Although there have been conference proceedings, edited collections, and review articles on metallic glasses, this book is unique in that its authors have designed a text that systematically covers each of the important aspects of the field, from processing, to structure, to properties. The authors have been at the center of this field through its most crucial period, have extensive experience in writing reviews, and bring complementary views to bear in the book. Each of the chapters presents a balance of breadth and depth: the coverage of the field is extensive with copious citation to the research literature and extensive compilation of data on glass properties. Attention is paid to critical nuances that highlight the complexity of glasses, such as the difference between "bulk" glass-forming alloys formed by casting (which is the principal focus of the book), and similar alloys with subtly different structures produced by rapid solidification or solid-state routes.

With all of these qualities, this book is sure to be a welcome source of reflection for those already immersed in the field, and an inspiration to those entering it. I expect that this book will be an important milestone on the path to mastering disorder.

Christopher A. Schuh
MIT, Cambridge, Massachusetts

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It is with great pleasure that we acknowledge the invaluable assistance we have received from many colleagues and friends, who have contributed, in different ways, to the successful completion of this book.

Both of us have been involved with the synthesis, characterization, and applications of rapidly solidified materials, in general, and metallic glasses, in particular, for over three decades. During this long journey, we had the good fortune of interacting with a number of leaders in this field from whom we have learned immensely and benefited greatly in understanding the complexities of metallic glasses. In alphabetical order, they are T.R. Anantharaman, R.W. Cahn, H.S. Chen, P. Duwez, T. Egami, H. Fujimori, A.L. Greer, K. Hashimoto, C.T. Liu, T. Masumoto, J.H. Perepezko, S. Ranganathan, K. Suzuki, and A.R. Yavari. We are pleased to have had their guidance and advice at different stages in our professional careers.

Some chapters of the book were read by colleagues. We are grateful to Professor Dmitri Louzguine-Luzgin and Dr. Nobuyuki Nishiyama of Tohoku University, Sendai, Japan, and Professor R. Vaidyanathan of the University of Central Florida, Orlando, Florida, for their critical comments and constructive suggestions. The incorporation of these suggestions has certainly improved the clarity and readability of the book.

Many of the figures in this book have been prepared by friends and students. We are thankful to Dr. Akira Takeuchi, Dr. Ichiro Seki, C.L. Qin, and Dr. U.M.R. Seelam for their hard work and patience in preparing the several iterations of the figures. The aesthetics of the figures are mostly due to their skills. Professors Dmitri Louzguine-Luzgin and Yoshihiko Yokoyama have also provided some figures used in this book. We are also grateful to the authors and publishers from whom we have borrowed several figures.

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C. Suryanarayana is a Professor of Materials Science and Engineering in the Department of Mechanical, Materials and Aerospace Engineering of the University of Central Florida in Orlando, Florida. He has conducted research investigations in the areas of rapid solidification processing, mechanical alloying, innovative synthesis/processing techniques, metallic glasses, superconductivity, quasi-crystals, and nanostructured materials for more than 40 years and has concentrated his research efforts on bulk metallic glasses and mechanical alloying and milling for the past 15 years. He has published more than 330 technical papers in archival journals and authored/edited 19 books and conference proceedings. Earlier, he was a Professor of Metallurgy at Banaras Hindu University in Varanasi, India. He held visiting assignments at the University of Oxford, Oxford, United Kingdom; the Atomic Energy Center in Mol, Belgium; the Wright-Patterson Air Force Base in Dayton, Ohio; the University of Idaho in Moscow, Idaho; the Colorado School of Mines in Golden, Colorado; the GKSS Research Center in Geesthacht, Germany; the Helmut Schmidt University in Hamburg, Germany; Tohoku University in Sendai, Japan; the National Institute for Materials Science in Tsukuba, Japan; Chungnam National University in Taejon, Korea; and Shenyang National Laboratory for Materials Science in Shenyang, China.

Professor Suryanarayana is on the editorial boards of several prestigious materials science journals. He has received several awards for his research contributions to nonequilibrium processing of materials, including the Young Scientist Medal of the Indian National Science Academy, the Pandya Silver Medal of the Indian Institute of Metals, the National Metallurgists Day Award of the Government of India, the Distinguished Alumnus Award of Banaras Hindu University, and the Lee Hsun Research Award from the Chinese Academy of Sciences. The ISI recently announced that Professor Suryanarayana is one of the most cited researchers in the field of materials science and engineering. He is a fellow of ASM International and also of the Institute of Materials, Minerals and Mining, London, United Kingdom. He received his BE in metallurgy from the Indian Institute of Science, Bangalore, and his MS and PhD in physical metallurgy from Banaras Hindu University, Varanasi, India.

A. Inoue is the President of Tohoku University, Sendai, Japan. Professor Inoue has conducted research investigations on rapidly solidified glassy alloys; nanocrystalline alloys for engineering applications; iron and steel metallurgy; metallic glasses; superconductivity; and synthesis, characterization, and commercialization of metallic glasses in general, and bulk metallic glasses (BMGs) in particular. He has pioneered the field of BMGs through systematic synthesis, characterization, and applications for the past 20 years. He has published more than 2000 papers in archival journals and edited several conference proceedings and books. He also holds over 200 patents and has been a member of the editorial boards of several archival journals.

Professor Inoue held visiting assignments at the Royal Institute of Technology, Stockholm, Sweden; the Swedish Institute of Metals Research; AT&T Bell Laboratories, Murray Hill, New Jersey; and the Institute für Forschung Werkstoff (IFW), Dresden, Germany. He was awarded honorary doctorate degrees from the Swedish Royal Institute of Technology, Stockholm, Sweden, and from Dong-Eui University, Busan, Korea. He holds honorary professor positions in several prestigious universities.

Professor Inoue has received several awards and recognitions for his research contributions. He is a member of the Japan Academy and a foreign member of the U.S. National Academy of Engineering. Some of the most important awards he has received include the Japan Academy Prize (in recognition of his outstanding scholarly contributions to the pioneering development of BMGs), the Japan Prime Minister's Prize (in recognition of his outstanding Industry–University–Government Cooperation Achievement of BMGs), and the James C. McGroddy Prize for New Materials (in recognition of the development of slow cooling methods for the fabrication of BMGs with remarkable mechanical properties and the characterization and applications of these materials) from the American Physical Society. He was most recently awarded the 2010 Acta Materialia, Inc. Gold Medal. He has also delivered the Kelly Lecture (University of Cambridge, Cambridge, United Kingdom) and the Dr. Morris Traverse Lecture (Indian Institute of Science, Bangalore, India). The ISI has selected him as one of the most cited researchers in the field of materials science and engineering. He received his BS in metallurgical engineering from the Himeji Institute of Technology and his MS and PhD in materials science and engineering from Tohoku University, Sendai, Japan.

Contents