Bulk Metallic Glass Composites

A dissertation submitted to the
Swiss Federal Institute of Technology Zurich

for the degree of
Doctor of Sciences

presented by
Marco E. Siegrist

Dipl. Werkstoff-Ing. ETH
born September 17th, 1977
citizen of Hanover NH, USA and Fahrwangen AG, CH

accepted on the recommendation of
Prof. Dr. Jörg F. Löffler, examiner
Prof. Dr. Andreas Mortensen, co-examiner
Prof. Dr. Ludwig J. Gauckler, co-examiner

2007
Preface

Look around you. Unless you are reading this dissertation in the middle of a desert or a rain forest, chances are that you are surrounded by man-created material. Some of these materials may be traditional, such as the ceramic coffee cup sitting on your desk, whereas others are apt to be more technological materials that a lot of material scientists and engineers put in uncountable hours developing.

Materials have always fascinated me. As a child I enjoyed working with wood, a natural material. As a teenager I was more fascinated by bicycles and motorbikes and was confronted with metals. Later I became a sailor and windsurfer which confronted me with a lot of repairs on polymer matrix composites. Materials have always fascinated me and during my studies in Materials Engineering at ETH Zurich I began to appreciate them even more, as I learned to understand what is responsible for their bulk properties. In 2001 I had my first own little research project, investigating the electrical properties of varistor composites supervised by Dr. Felix Greuter at ABB Corporate Research. This is where I started to learn about particle-matrix interfaces, a very important topic for this dissertation. But more important; it was during that research project that I realized how much I really enjoyed Research and Development.

In the Summer of 2003 I first met Prof. Jörg Löffler on recommendation of Prof. Peter Uggowitzer. He had just been assigned an assistant professorship at ETH Zurich and was looking for PhD students to start his new research group. I was lucky to be in Jörg’s group from the very beginning. This gave me the chance to take part in launching a new research group, a task which I enjoyed very much. Once things had settled a bit I was able to do research in a very dynamic environment, because new people with good ideas were joining the group almost weekly. Additionally, I was confronted with a fully new research field; namely, bulk metallic glass composites. I was immediately fascinated by the possibility of directly tailoring the mechanical properties of the materials by adjusting their microstructure. To me this has always been the coronation of material science.
During the past three years of research, I have met many people within and outside of our research group who have strongly contributed not only to this thesis, but to my life in general. I am very proud that I may call many of them friends and look forward to interacting with them in the future.
Acknowledgements

I would like to start by thanking Prof. Jörg Löffler for advising this thesis. He has given me a lot of freedom in my research and multiple opportunities to present my results to an international audience at conferences. The time and energy he has put into starting the new research group over the past three years has been absolutely incredible.

I would like to thank Prof. Andreas Mortensen and Prof. Ludwig Gauckler for their part as co-referees for this thesis.

Prof. Peter Uggowitzer always found the right words when I ran out of motivation. Thank you for all your advice, also well beyond metallurgy!

Dr. Florian Dalla Torre and Dr. Andreas Kündig have contributed greatly to this thesis with their scientific advice. Thank you very much.

We have had a great group of PhD students at LMPT over the last three years. Every one of you has somehow contributed to this thesis! Special thanks to Edward Arata for introducing me to the field of bulk metallic glass processing as well as to Dirk Uhlenhaut and Bruno Zberg for many fruitful discussions also well beyond material science. I had a great time sharing an office with Alban Dubach and Fabian Eckermann.

I have had the pleasure of supervising many students during my thesis who have contributed significantly to this work. A big thank you to Christian Zink, Richard Darby and Michael Siegfried who worked on mechanical amorphization and consolidation of bulk metallic glass; David Steinlin, who worked on melt processing of diamond-reinforced bulk metallic glass and Petra Gunde, Pascal Wolfer, Wendy Mac and Esther Amstad who contributed to the thermophysical, mechanical and tribological properties of graphite-reinforced bulk metallic glasses.

Further I would like to thank Dr. Simon Kleiner for his help with the mechanical amorphization, Dr. Peter Wägli for his excellent supervision on the scanning electron microscope, Edward Schaller for much metallographic advice and Roman Heuberger for his help with the micro-tribological tests.
Efficient research is not possible without talented technicians. Special thanks to Christian Wegmann, Erwin Fischer, Joseph Hecht, Markus Müller and Nickolaus Koch for your invested time. I learned a lot from you guys!

Special thanks to Katherine Hahn for correcting the English in all of my publications. I have learned a lot from you!

_A lot of people helped me make the right decisions and be successful during my education;_

I would like to thank my dear friends Herbi and Eva Hartmann as well as my “Bezirksschul” teacher Beni Reimann for helping me with the integration in the Swiss school system after my family relocated from Vermont (USA) to Switzerland.

Many thanks to Konrad Hirlacher and Waldemar Feller of Kantonsschule Wohlen for laying the foundation for a scientific career and Hansjörg Künzler also of Kantonsschule Wohlen for encouraging me to visit the Department of Materials at ETH Zürich in 1997, where I was supervised by Dr. Markus Diener, who, today has his office right down the hall.

Special thanks to Dr. Urs Gonzenbach. I would not have survived the first years at ETH without our learn sessions!

Dr. Felix Greuter who supervised my internship at ABB Corporate Research was the person who gave me the “final push” to do a PhD. Thank you very much for your motivating words.

_There is much more to life than a career;_

I would like to thank all my windsurfing, sailing and riding friends for helping me keep my life balanced during my PhD and also Jassir, a very special horse; he has enriched my life in a way only a horseman or horsecwoman can understand.
What the following three people have contributed to my life cannot be put in words:

I would like to thank my parents Edwin and Ursula Siegrist for supporting me over the last 29 years. I hope that you can be proud of how things turned out.

Dear Yael, life has had more meaning since I met you 10 years ago. Thank you for everything you have given. There will always be a special place in my heart for you.
Seite Leer / Blank leaf
Summary

Bulk metallic glasses (BMGs) are a new class of metallic alloys displaying an amorphous atomic structure. These alloys typically display more than double the yield strength and up to four times the elastic limit compared to their crystalline counterparts. However, due to the lack of crystal structure, deformation by dislocation movement is not possible and monolithic samples fail on a single or few shear bands, leading to a brittle fracture behavior. This has hindered the technological breakthrough of these alloys as a structural material. The primary aim of this thesis is improving the plastic strain of BMGs and further tailoring their mechanical and tribological properties.

One approach for increasing the plasticity and in general tailoring the mechanical properties of BMGs is the development of foreign-particle-reinforced composites. The reinforcement particles interact with the shear bands, arresting them and also aid the initiation of multiple shear bands due to local stress concentrations in the material. This allows deformation on multiple shear bands leading to a significant increase in plastic strain because the deformation energy is distributed over more sample volume. Such composites can be produced either by means of melt processing or powder consolidation. Both approaches are discussed within this thesis.

Graphite-reinforced Zr$_{52.5}$Cu$_{17.9}$Ni$_{14.6}$Al$_{10}$Ti$_5$ (Vit 105) was developed with the aim of increasing the plastic strain of the amorphous alloy. These composites, produced by melt processing, were shown to display a maximal plastic strain of up to 18.5% combined with a yield strength of 1.85 GPa. This is to our knowledge the highest combination of yield strength and plasticity ever reported for foreign-particle-reinforced BMGs. Further, the mechanical properties of theses composites can be tailored by transforming part of the graphite to ZrC during processing. We have shown that a higher carbide content leads to an increase in hardness accompanied by a decrease in plasticity of the composite.

The graphite-reinforced composites also display very interesting micro-tribological properties. Graphite with its self-lubricating properties and ZrC...
reinforcement both lead to a significant decrease of the coefficient of friction of the glassy alloy when paired against bearing steel. A minimal coefficient of friction of 0.2 was measured in a three-phase composite (graphite and ZrC in the amorphous matrix) compared to about 0.8 for bearing steel on bearing steel. We also found that in ball-on-disc tests the composites showed lower wear rates than bearing steel, making these BMG-graphite composites a promising material for self-lubricating frictional bearings.

Diamond-reinforced Vit 105 composites were developed with the aim of increasing the hardness and improving the cutting properties of the amorphous alloy. They were produced by powder consolidation and melt processing techniques. For the consolidation route, amorphous Vit 105 powder was produced by mechanical amorphization of crystalline pre-alloys. Data on the amorphization rate could be fitted with an exponential relaxation function. Further, a processing window for consolidation was determined by calorimetric analysis of the amorphous powder and composite samples. With these parameters local densification was achieved; however, the bulk density remained below 75% due to an inadequate temperature control of the pressing setup. Melt processed diamond-reinforced BMGs showed a significant increase in hardness and good particle-matrix adhesion. Thus, BMGs reinforced with high volume contents of diamond close to the surface have high potential to be used as a cutting tool material.
Zusammenfassung

Metallische Massivgläser sind eine neue Klasse metallischer Werkstoffe, welche sich durch ihre amorphe Atomstruktur auszeichnet. Die fehlende Kristallstruktur hat neuartige Materialeigenschaften zur Folge. Versetzungsdеformationen, wie wir sie in kristallinen Metallen kennen, sind nicht möglich, was zu höherer Festigkeit und Elastizität des Materials führt. In der Tat weisen metallische Gläser typischerweise etwa die doppelte Streckgrenze und bis zu viermal die elastische Dehngrenze ihrer kristallinen Pendants auf.

Aufgrund der fehlenden Kristallstruktur läuft die Deformation in sogenannten Scherbändern ab. Scherbänder sind niederviskose Volumen innerhalb des Festkörpers, welche sich in Ebenen mit der höchsten Scherspannung und in Regionen mit viel freiem Volumen bilden. Monolithische Massivglaslegierungen können auf nur einem oder wenigen solcher Scherbändern versagen, was zu einem spröden Bruchverhalten führt. Dieses spröde Bruchverhalten hat die Verwendung der metallischen Gläser als kommerzieller Strukturwerkstoff bis heute stark gehindert. Das Hauptziel dieser Arbeit ist die Erhöhung der plastischen Dehngrenze der metallischen Massivgläser und zusätzlich die Verbesserung der mechanischen und tribologischen Eigenschaften durch Modifizierung der Mikrostruktur.


Seite Leer / Blank leaf
# Table of contents

Preface .......................................................................................................................... I  
Acknowledgements ........................................................................................................ III  
Summary .......................................................................................................................... VII  
Zusammenfassung .......................................................................................................... IX  

1 General introduction ................................................................................................... 1  
1.1 Metallic Glasses .................................................................................................... 2  
1.2 Aim and outline of the thesis .............................................................................. 29  

2 Mechanical amorphization ....................................................................................... 31  
2.1 High-purity amorphous Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_{15} powder via mechanical amorphization of crystalline pre-alloys ................................................................. 32  

3 Diamond-reinforced bulk metallic glass composites ................................................ 45  
3.1 Production of diamond-reinforced Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_{15} composites by consolidation technique ................................................................. 46  
3.2 Melt processing of diamond-reinforced bulk metallic glass composites ......... 54  

4 Graphite-reinforced bulk metallic glass composites ................................................ 67  
4.1 Ductile bulk metallic glass-graphite composites ............................................... 68  
4.2 Tailoring the mechanical properties of graphite-reinforced bulk metallic glass composites ...................................................................................................... 80  
4.3 Micro-tribological properties of graphite- / ZrC-reinforced bulk metallic glass composites ...................................................................................................... 92  

5 Conclusion and outlook ............................................................................................ 113  
5.1 General conclusion .............................................................................................. 114  
5.2 General outlook .................................................................................................. 116  
Curriculum Vitae ......................................................................................................... 121  
Publications ................................................................................................................ 122  

XIII
1 General introduction

Metallic glasses are a new class of metallic alloys displaying an amorphous atom structure. The amorphous microstructure leads to unique combinations of material properties. Chapter 1.1 gives an introduction to metallic glasses and metallic glass composites with emphasis on their mechanical properties. Subchapter 1.2 states the aim of the thesis and gives an overview of the outline.
1.1 Metallic Glasses

Metallic glasses are a new class of metals that show an amorphous structure in the solid phase. They have no crystal structure, grain boundaries or crystal defects. This leads to interesting mechanical and thermophysical properties.

In these metastable materials, the crystalline phase is energetically favored over the amorphous one as is shown in Fig. 1.1.1. An amorphous solid phase can be achieved either by rapid quenching of the liquid phase or by mechanical amorphization of a crystalline solid. In metallic glasses produced by melt processing, glass-forming ability of an alloy is generally described by either the critical cooling rate or the critical casting thickness. The critical cooling rate is the cooling rate which is necessary to hinder crystallization, whereas the critical casting thickness is the maximum dimension that an alloy can be cast to without crystallizing. Alloys displaying good glass-forming ability typically have a small energy difference between the amorphous and crystalline solid phases ($\Delta E_{ac}$) leading to a smaller driving force for crystallization. Further, good glass formers generally have high viscosities which hinders diffusion of atoms, slowing crystallization.
Fig. 1.1.1 Energy levels of crystalline and amorphous phases in metals and description of the transformations between them.

During rapid quenching the amorphous phase is “frozen in” once the metallic melt is quenched below the glass transition temperature, because diffusion processes are too slow at this temperature to allow rearranging of atoms. Depending on the glass-forming ability of the metallic glass, different rapid quenching techniques such as melt spinning, splat quenching or copper mold casting must be applied to prohibit crystallization during solidification. Metallic glasses displaying sufficient glass-forming ability for copper mold casting are especially interesting for net-shape processing because no crystallization shrinking takes place during casting.

An alternative to the melt processing route is mechanical amorphization of crystalline powders followed by consolidation. Mechanical energy transferred into the sample by ball milling leads to a transformation from the stable crystalline to the metastable amorphous state. The grain size of the crystalline powder is decreased with milling time until the amorphous state is achieved. Different consolidation routes lead to bulk amorphous samples.

The thermophysical particularities of metallic glasses do not only display new challenges in material processing but also open new opportunities, such as deformation above the glass transition temperature but below the onset of crystallization.
Deformation in the undercooled liquid region allows similar processing steps as are common in the polymer industry.

Due to the lack of crystal structure classical deformation based on dislocation movement is not possible. This leads to very high strength and elasticity (~2% elastic strain compared to 0.5% –1% for crystalline alloys) but also to a more brittle fracture behavior as will be discussed repeatedly within this thesis. This brittle fracture behavior has hindered the technological breakthrough of metallic glasses as a structural material. This thesis is devoted to improving the plasticity of amorphous alloys and herewith making them more attractive for structural applications.

1.1.1 History and future of metallic glasses

Metallic glasses were discovered in 1960 by Pol Duwez at Caltech (Pasadena CA, USA) in the Au-Si binary system [1]. Since then there has been an ongoing search for compositions with higher glass-forming ability. It was shown by Turnbull in 1969 that glasses showing a high ratio of the glass transition temperature ($T_g$) to the melting temperature ($T_m$), $T_g / T_m$, display good glass-forming ability [2]. Since $T_g$ shows small dependency on composition whereas $T_m$ can be influenced significantly with only small shifts in composition, there has been an ongoing search for low melting multi-component alloys. An elegant experimental approach to finding low lying eutectics in multi-component systems is centrifugal processing, where the eutectic composition of a multi-component system can be determined by cooling from the melt under high gravity to separate the crystallizing phases by their melting temperature [3]. Since 1960 there has been very rapid development in increasing glass formation properties as can be seen in Fig. 1.1.2. It is shown that the critical casting thickness of metallic glasses was increased by over three orders of magnitude in the 40 years after their discovery.
It is often said that the bulk metallic glass (BMG) era began in 1984 with the development of the Pd$_{40}$Ni$_{40}$P$_{20}$ alloy at Harvard University (Cambridge MA, USA), which, when processed by a fluxing technique could be cast to 1 cm [5]. The first report of metallic glass formation significantly above 1 cm without the use of a fluxing technique was in the early 90’s in Zr$_{41.2}$Ti$_{13.8}$Cu$_{12.2}$Ni$_{10.0}$Be$_{22.5}$ (Vitreloy 1) developed by the Johnson group, once again at Caltech [6], where the first metallic glass was discovered.

In the past decade, BMGs have been developed in many alloy systems. The highest glass-forming ability ever achieved is reported in literature by the Inoue group at Tohoku University (Sendai, Japan) in the Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ system with a critical casting thickness of 72 mm [7] and even 80 mm with fluxing [8]. Mg, Al, Fe, La, Ce and Ni-based systems with bulk glass-forming ability have also been developed. A much more detailed overview of the improvement of glass-forming ability over the past 45 years is given in [4].

Lately the primary aim of alloy development has not only been to further improve the critical casting thickness but much more to improve certain properties of the metallic glasses such as strength, plasticity, low temperature formability and
biocompatibility. Recently a Co-based BMG displaying a fracture strength of 5.2 GPa was reported by the Inoue Group. [9]. This is not only the highest value ever reported for a metallic glass but one of the highest values ever reported for any bulk material. The Johnson Group reported the first fully dense, monolithic BMG displaying major compressive plastic strain of 20% based on the high Poisson’s ratio of Pt-based alloys [10]. B. Zhang et al of the Chinese Academy of Science (Beijing, China) reported the development of a Ce-based BMG with a glass transition temperature of 68°C which allows deformation in the undercooled liquid region in hot water [11]. And finally, the development of a Ni-free Zr-based BMG by the Löffler Group at ETH Zurich [12] has opened the field for biocompatible BMGs.

1.1.2 Current and future applications

Metallic glasses display very soft magnetic properties due to the lack of grain boundaries which interact with the magnetic domains (domain pinning) in crystalline alloys. This led to the first large-scale application of metallic glasses for the use as a precursor material for the production of soft magnetic, nanostructured Fe-based ribbons, used mainly for noise reduction applications. This technology is produced by Hitachi Metals Ltd. under the brand name FINEMET®. Ref. [13] shows how the magnetic properties of metallic glasses can be tailored by inducing nanocrystallization and adjusting the grain size in the nm-range.

Metallic glasses are also candidates for demanding structural applications due to their high yield strength and elastic strain. Fig. 1.1.3 shows an Ashby plot of the elastic limit (yield strength) of conventional engineering materials and metallic glasses plotted against their Young’s modulus [14]. It can be seen that metallic glasses show yield strengths which are far superior to conventional engineering materials. This gives them great potential as a new structural material.
Displaying two to four times the elastic strain of crystalline alloys, metallic glasses have the potential of storing one order of magnitude more energy than steel for instance. This high elasticity of metallic glasses led to their first structural application, namely golf club heads produced by Liquidmetal Technologies, who hold the patent for Vitreloy 1, the best non-precious-metal-based glass former known today. Another large advantage of the Vitreloy 1 alloy is that it is not necessary to use high purity elements to process it, which keeps costs as low as about $30 per kilogramm (stated by Liquidmetal Technologies, May 2006). Nevertheless, this is still almost one order of magnitude more expensive than stainless steel. Further, sporting goods such as a metallic glass reinforced tennis racquet produced by Head are being introduced into the market.

The high strength and surface quality combined with the excellent formability, due to the lack of crystallization shrinkage during casting has led to the market introduction of other structural materials, such as casings for electronic components, cell phone hinges and jewelry. Additionally, the self-sharpening effect known for metallic glasses [15] has led to the first medical applications in the form of a surgical cutting instruments produced by Surgical Specialties Corporation in collaboration with Liquidmetal Technologies.
It has been reported that metallic glasses display frictional properties superior to those of bearing steel [16]. However, very little work has been done on the tribology of metallic glasses. It is imaginable that the more homogenous surface of metallic glasses (no grain orientation and grain boundaries) may have a positive effect on tribological properties; however, the possibility of crystallization due to frictional heat has to be considered. The tribological investigations presented in Chapter 4.2.6 give evidence that graphite-reinforced metallic glasses may be a suitable material for dry frictional bearing applications.

What will the future bring? I believe that micro-forming of metallic glasses is a promising topic for future applications [17]. Very precise structures can be made in the undercooled liquid region due to the lack of crystal structure. Such micro-formed metallic glasses could for instance be used as a tool for micro-structuring of polymers. Further, the performance of small springs could be improved by over one order of magnitude if made from metallic glass [18] instead of steel due to the much higher elasticity of the amorphous material. This could be interesting for springs in the watch industry. The development of bulk components for structural applications is mainly dependent on the progress in the search for tensile plasticity in BMGs. An excellent contribution by M.F. Ashby and A.L. Greer [14] discusses possible future applications.

1.1.3 Mechanical properties of metallic glasses

As has been mentioned earlier bulk metallic glasses display very interesting mechanical properties due to their lack of crystal structure and defects. The yield strength of amorphous alloys is typically more than double as high as in their crystalline counterparts as can be seen in Fig. 1.1.4. The metallic glasses display an average specific strength of about 337 MPa/(g/cm) compared to 154 MPa/(g/cm) for crystalline alloys.
This high specific yield strength combined with their high elastic limit should predestine them for structural applications. However, their technological breakthrough has been greatly hindered by their lack of plastic strain to failure. In order to increase the plastic strain of metallic glasses one must first understand the cause of this brittle fracture behavior.

1.1.3.1 **Deformation of metallic glasses**

Due to the lack of crystal structure, dislocation movement is not possible in amorphous alloys. A deformation model for metallic glasses was first proposed by Spaepen in 1974 [19]. It is based on the concept of free volume in liquids and glasses described by Morrel and Turnbull [20] in 1959. 11 years later the same two scientists revisited the topic of free volume to explain the liquid-glass transition [21]. In 1977 Spaepen presented a deformation mechanism map of metallic glass [22] shown in Fig. 1.1.5.
The deformation mechanism map gives an overview of the deformation mechanisms taking place in dependence of temperature, stress and strain rate. In general, homogeneous flow takes place at low stress and high temperatures, whereas inhomogeneous flow takes place at high stresses and low temperatures.

Above the liquidus temperature ($T > T_l$) the material has a viscosity of $\eta \approx 1 \text{ Pa s}$ (compared to $10^{-3} \text{ Pa s}$ for conventional metallic melts) and deforms like a Newtonian liquid. In the range of the glass transition temperature ($T \approx T_g$), the material has a viscosity of $\eta \approx 10^{13} \text{ Pa s}$ by definition. It can be described as a non-Newtonian viscous material. In the temperature range above $T_g$ the viscosity decreases drastically with increasing temperature leading to the steep incline in the strain-rate contours. Between the glass transition temperature and the onset of crystallization ($T_g < T < T_x$) the material behaves Newtonian at low strain rates and non-Newtonian at high strain rates.

Below the glass transition temperature ($T < T_g$) the material has a viscosity $\eta < 10^{15} \text{ Pa s}$ and acts like a solid. The viscosity does not change much as a function of temperature. At low temperatures ($< 0.7 T_g$) inhomogeneous flow takes place at high stress and high strain rates. This flow regime is decisive for structural applications of
metallic glass, and will be addressed in great detail within this thesis. In this region deformation is highly localized in very thin shear bands often leading to catastrophic failure on one or few such bands, especially under tensile loading.

1.1.3.1.1 Inhomogeneous flow

The deformation mechanism taking place during inhomogeneous flow is based on local softening of the material due to inhomogeneous distribution of free volume. Such regions where softening takes place are called shear bands. Under load, regions of high free volume experience local stress concentrations and undergo structural changes leading to a strong decrease in viscosity. Polk and Turnbull have suggested that the structural change is a result of two competing processes, namely; a shear-induced disordering and a diffusion-controlled reordering process [23].

A possible mechanism for creation of free volume due to shear (shear induced disordering) is shown in Fig. 1.1.6. In this model an atom with a volume $V_a$ is squeezed into a neighboring hole with a smaller volume $V_h$ due to shear. This makes the neighboring atoms move out and new volume is created ($\Delta V = V_a - V_h$). The lowering of viscosity is associated with an increase in free volume; therefore the shear-induced disordering process must be dominant. The annihilation of free volume (diffusion-controlled reordering) is based on thermally activated diffusive jumps.

![Fig. 1.1.6 Illustration of the creation of free volume by squeezing an atom into a tight hole as a result of shearing of the material (adapted from [22]).](image-url)
The Doolittle equation gives an empirical relation of the viscosity and the free volume ($\eta = \text{viscosity}, V_0 = \text{volume occupied by atoms}, V_f= \text{total free volume}, b$ and $\eta_0 = \text{const.}$).

$$\eta = \eta_0 \exp \left( \frac{bV_0}{V_f} \right)$$ \hspace{1cm} (1.1.1)

It can be seen that a decrease in viscosity is associated with an increase in free volume. Thus, in the case of shear bands during deformation the shear-induced disordering must dominate the diffusion-controlled reordering process.

The vein patterns found on the fracture surface of metallic glasses (shown in Fig. 1.1.7) are very similar to those obtained when pulling apart two plates with Vaseline (or another viscous layer) between them; this gives evidence that local softening takes place. Further, if no softening of the material took place one would expect fracture to occur in the plane with the highest normal stress under tensile loading (normal to the loading direction). However, under tensile conditions fracture takes place at an angle of about 45° to the loading direction, giving clear evidence that the material has weakened in this plane.

Fig. 1.1.7 Vein patterns on the fracture surface of a Zr$_{52.4}$Cu$_{17.6}$Ni$_{14.6}$Al$_{10}$Ti$_5$ (Vit 105) BMG

Lately there has been a lot of discussion concerning the adiabatic temperature rise in shear bands during deformation [24,25]. A simple experiment where the surface
of a compression sample was coated with tin and investigated by SEM after deformation has given clear evidence of a significant temperature increase (> 200 °C) in and close to shear bands during deformation [25]. Such a temperature increase becomes more plausible if one considers the extremely high strain rates taking place, particularly if a sample fails on a single shear band with a thickness of merely 20 nm [25,26]. The droplets seen on the fracture surface shown in Fig. 1.1.7 are a hint that the temperature in the shear band may have exceeded the melting temperature during deformation.

In crystalline metals deformation leads to an increase of the dislocation density and dislocations start hindering each other. This leads to an increase in strength with ongoing deformation, a mechanism known as work hardening on a macroscopic scale. This is not the case in amorphous alloys because in contrast to dislocations, shear bands lead to local softening, not hardening of the material. Additionally, the shear band density in monolithic metallic glasses is too small that shear bands would interact with each other.

1.1.3.2 Approaches for improving plasticity

Brittleness is often observed in monolithic metallic glasses because the entire deformation energy is concentrated on only one or few shear bands, which represent a very small volume fraction of the material. Plastic strain can be improved by any means of increasing the shear band density in the metallic glass leading to a better distribution of the deformation energy within the sample.

Under uniaxial compression a glassy alloy is elastically loaded until the local stress somewhere within the material (in a region of high free volume) reaches a critical value and a shear band is initiated. As the shear band propagates the load drops and the material elastically recovers leading to an arrest of the shear band and the process begins again. This mechanism leads to fluctuations in the load during compression testing (serrated flow) and typically results in ~1-2% plastic strain before failure in monolithic alloys. Under tensile loading no plastic strain is observed in
monolithic samples because serrated flow does not take place and samples fail on one single shear band.

Further, it has been observed that in contrast to a thick BMG plate, which displays brittle fracture under bending load, a thin metallic glass ribbon displays significant plasticity [27]. This is because in bending, shear band spacing correlates with the sample thickness as is shown in [27,28]. Smaller shear band spacing allows a smaller shear offset per shear band under the same bending conditions. If one considers that crack nucleation takes place at a critical shear offset, it can be understood that plastic strain must not only correlate with shear band spacing but also with sample thickness. This is “good to know” and helps us understand that we must increase the shear band density during deformation, but it is of no help in bulk samples where the shear band density must be increased by micro-structural engineering.

The shear band density can be increased by hindering the propagation of shear bands and at the same time aiding the nucleation of new shear bands. The propagation of shear bands can be hindered by any means of reducing the stress at the tip of the shear band, for instance by placing obstacles in their way. Shear bands can be initiated by introducing sites of local stress concentration in the material. A possible mechanism leading to deformation on multiple shear bands is shown in Fig. 1.1.8.
Fig. 1.1.8 Possible mechanism for increasing the shear band density in metallic glasses (I: shear band initiation site, O: obstacle, SB: shear band) resulting in stress fluctuations during deformation as can be seen in the corresponding stress-strain diagram.

Under uniaxial compression a first shear band (SB₁) initiates at the initiation site with the highest stress concentration (I₁). The shear band propagates until it interacts with an obstacle (O₁) and its propagation is hindered by reducing the stress at the tip of the shear band. As soon as the stress in the initiation site with the next highest stress concentration (I₂) reaches a critical value, a new shear band (SB₂) is initiated and propagates until it is once again hindered by an obstacle (O₂). The third shear band (SB₃) that is initiated at I₃ is not hindered by an obstacle but interacts with another shear band (SB₁). This once again influences the propagation of the shear band. Termination, splitting or deflection will take place depending on the contact angle and the exact morphology of the arrested shear band (SB₁). It is thought that if the temperature rise in SB₁ was high enough to inhibit local nanocrystallization or growth of existing nanocrystals, it may act like a reinforcement particle hindering the propagation of SB₃.

It can be seen in the corresponding stress-strain diagram that the stress initiation and propagation of a shear band is associated with a stress drop. Once the shear band is arrested, the stress once again increases to the level necessary for new shear band
initiation, and so on. The smaller the strain during the stress fluctuations ($\Delta \varepsilon$), or in other words, the higher the shear band density, the more homogeneous the deformation and the larger the increase in plastic strain will be. In order to increase plastic strain at all, $\Delta \varepsilon$ must be smaller than in the case of normal serrated flow in monolithic glasses. $\Delta \varepsilon$ can be decreased by decreasing the spacing and increasing the effectiveness of obstacles and initiation sites.

Effective initiation sites should be densely spread throughout the material and initiate shear bands at similar stress levels. Possible initiation sites are pores or second phase particles with a Young’s modulus significantly different of the matrix material, leading to interfacial stresses. Effective obstacles such as pores or second phase particles should arrest shear band propagation or at least split up propagating shear bands. The more initiation sites and obstacles are present in the material the shorter is the propagation distance of a single shear band and the higher the resulting plastic strain.

\subsection{1.1.3.2.1 Approaches for improving plasticity by second phase reinforcement}

The most common way of improving plasticity in metallic glasses is adding second phase particles to the amorphous matrix. It is expected that soft particles will lower the stress at the tip of a propagating shear band, hindering its propagation whereas stiff particles will tend to lead to deflection and splitting up of shear bands. Additionally, particles with a stiffness significantly different from that of the matrix material may lead to local stress concentrations in the particle-matrix interface during deformation (for simulations see [29]). These stress concentration sites act as nucleation points for shear bands. Both effects lead to multiplication of shear bands during deformation. In Chapter 4.1 it is argued that soft reinforcement particles (with a Young’s modulus significantly lower than that of the matrix material) are more effective in hindering shear band propagation due to the generation of tensile stress fields between particles as has been simulated for arrays of pores in a brittle material [30]. These tensile stress fields and their effect on shear band propagation is illustrated in Fig. 1.1.9. Considering the Mohr-Coulomb criterion, shear band propagation is less
hindered under tensile conditions. With this in mind it is thought that shear bands will preferably propagate in the tensile stress fields and that these stress fields will guide the shear bands in direction of neighboring reinforcement particles, leading to very small $\Delta e$ (see Fig. 1.1.8).

Fig. 1.1.9 During compression of a porous material tensile stress fields form between pores [30]. This is also the case for very soft reinforcement particles. These tensile stress fields are thought to lead propagating shear bands into neighboring pores or particles because their propagation is favored.

Second phase reinforced BMGs (BMG composites) are split into two categories; namely, foreign-particle-reinforced composites and *in-situ* formed composites. These materials are discussed in great detail in Chapter 1.1.5. An example of the effect of graphite reinforcement in a Zr-base BMG is shown in Fig. 1.1.10. It can be seen that the shear band density is increased significantly within the vicinity of the reinforcement particle and that many secondary shear bands have formed.
Generally a second phase which is significantly larger than the width of a shear band (~20 nm) is used for reinforcement because larger particles are expected to be more efficient in halting shear band propagation (this is also the case for the graphite particle shown in Fig. 1.1.10). However, lately it has been suggested, that nanocrystals smaller than the width of a shear band may also be effective in arresting shear band propagation. In-situ deformation experiments have shown that if very low volume fractions of nanocrystals (1.5 nm) are present in an amorphous matrix, these crystals will grow in the heated area of a shear band during deformation \[26\]. If we consider that there are for instance 0.1 vol.% nanocrystals of 1.5 nm in the amorphous matrix, their content will locally (within the vicinity of the shear band) increase to almost 30 vol.% if the crystals grow to 10 nm. As a consequence the viscosity in the shear band will increase significantly and its propagation will be hindered. At the same time the hardening of the shearing matter leads the localized deformation to deviate into undeformed regions, widening the shear band.

### 1.1.3.2.2 Approaches for improving plasticity in monolithic alloys

Recently there have also been reports of improving plasticity in monolithic BMGs. One approach is by producing porous materials. First attempts with 36 - 64 vol.% pores in a Pd\(_{42.5}\)Cu\(_{30}\)Ni\(_{7.5}\)P\(_{20}\) led to high plastic strain but very low yield strength
More recently it was shown that the same alloy with a porosity of only 4 vol.% and a pore size of 20-30 μm still displays up to 18% plastic strain combined with a yield strength of 1.52 GPa (compared to 1.63 GPa for the monolithic alloy) in compression [32]. Pores act like very soft second phase reinforcement particles. Under mechanical loading the pores lead to local stress concentrations in the metallic glass which leads to nucleation of multiple shear bands. At the same time the pores hinder the propagation of the nucleated shear bands, because when a shear band interacts with a pore the stress at the tip of the shear band is reduced. Further, the stress fields illustrated in Fig. 1.1.9 are thought to favor the simultaneous stopping and nucleating of new shear bands leading to a very high shear band density.

It has also been reported that a monolithic Pt$_{57.5}$Cu$_{14.7}$Ni$_{5.3}$P$_{22.5}$ BMG displaying a high Poisson’s ratio ($\nu = 0.42$) shows up to 20% plasticity under compression [33]. The high Poisson’s ratio, manifested in a low ratio of shear modulus (G) to bulk modulus (B), is claimed to be responsible for the high plasticity. The Pt-based alloy displays $G/B = 0.165$ compared to $G/B = 0.31$ for the Zr-based Vitreloy. It is argued that the small $G/B$ ratio allows for shear collapse before the extensional instability leads to crack formation, allowing the tip of a shear band to extend rather than initiating a crack. Compressive ductility in BMGs with a high Poisson’s ratio has only been reported in the Pt-based system. The Poisson’s ratio of metallic glasses correlates well with the main element, so we might expect a similar effect in Pd- ($\nu = 0.39$) and Au- ($\nu = 0.44$) based BMGs. Unfortunate, the Poisson’s ratio of the elements seems to correlate with their market price.

There have been other reports of monolithic metallic glasses displaying significant plasticity in compression [34,35]. Even though these materials show deformation based on shear banding, it can be argued that they are not true metallic glasses due to significant short to medium-range order. Cu$_{47.5}$Zr$_{47.5}$Al$_{5}$ has not only been shown to display significant plasticity under compression but also a work-hardening-like behavior [34]. It is argued that the easy nucleation of shear bands may be due to the heterogeneous amorphous structure of the glass, which promotes the nucleation of shear bands throughout the material rather than triggering the nucleation of cracks. Intersecting shear bands are declared to be responsible for the work-
hardening. Similar mechanical properties were also reported in Cu_{50}Zr_{50} metallic glass [35]. Here it is argued that the medium-range order (1-2 nm) of the metallic glass is responsible for the ductile and work-hardening-like behavior.

1.1.4 References

1.1.5 **Bulk metallic glass composites**

Composite materials are generally developed with the aim of achieving material properties which cannot be realized in a monolithic material. An excellent overview is given by Ashby in Ref. [1]. Monolithic engineering materials often do not show a very good combination of two material properties as is shown in the schematic in Fig. 1.1.11. If the values of two desired properties (for instance fracture strength and inverse specific density) are plotted against each other for various monolithic materials, the data points often lay on a hyperbola as is the case for the materials a-e in the schematic. However, often a better combination of material properties can be achieved by combining two (or more) monolithic materials to form composites, as is shown for composite ae, produced by combining the monolithic material a and e.

![Schematic showing some combinations of material properties are only accessible with composite materials (a-e: monolithic materials).](image)

Bulk metallic glass composites were mainly developed with the hope of increasing the plasticity of the amorphous alloys. However, the plastic strain should be increased without sacrificing the high yield strength of the materials. The problem of limited plastic strain in amorphous alloys has been discussed extensively in Chapter 1.1.3. There are two different types of BMG composites; namely, foreign-particle-reinforced BMGs and *in-situ* particle-reinforced BMGs.

Foreign-particle-reinforced BMGs are alloys that are reinforced with particles or fibers as is common in crystalline Metal Matrix Composites (MMCs), where the
particles are often of ceramic nature [2]. Such composites can be produced by powder consolidation or melt processing, whereas melt processing is more common.

*In-situ* formed BMG composites are produced by mixing a substance to the matrix that reacts with one or more of the matrix components to form a crystalline phase in the amorphous matrix during processing. These composites can only be produced by melt processing, and their microstructure is strongly dependent on the cooling conditions.

### 1.1.6 Foreign-particle-reinforced bulk metallic glass composites

Foreign-particle-reinforcement of metallic glasses (and metals in general) allows direct tailoring of the microstructure by changing the type of particle (hard, soft, affinity to matrix etc.) as well as particle shape, size and volume content. This has been standard procedure for a long time in crystalline metals (see [3,4,5] for reviews) leading to the development of today’s metal matrix composites (MMCs) which have found a wide range of industrial applications especially in the automotive industry (cylinder liners, pistons, brake calibers, pushrods, brake discs, drive shafts, etc.).

First foreign-particle-reinforced metallic glasses were prepared by mechanical alloying because at that time, the glass-forming ability of the potential matrix materials was insufficient for melt processing of bulk composites. However, many of the reports in literature are only of composite powders (as for instance [6]) and not consolidated metallic glass composites and are thus not further discussed.

With increasing glass-forming ability over the years it became possible to add second phase particles to the melt without leading to crystallization of the matrix material. This led to the development of many melt processed foreign-particle-reinforced composites. However, there are restrictions because very small particles and high reinforcement volume contents lead to a high nucleation surface and promote crystallization of the matrix material.
1.1.6.1 Foreign-particle-reinforced bulk metallic glass composites produced by consolidation techniques

Due to the difficulties that go along with the traditional consolidation technique (see Chapter 3.1) there have been very few reports of metallic glass composites produced in this manner. However, lately, reports of Cu-reinforced Ni-Zr-Ti-Si-Sn BMG composites produced by warm extrusion [7] and magnetic compaction [8] have been reported to show interesting mechanical behavior. The extruded composite displays some plastic strain under compression whereas the composite produced by magnetic compaction even showed a plastic strain of ~23% combined with a yield strength of ~800 MPa under tensile loading. This result is promising; however, one must consider that 60% Cu was used for reinforcement which questions the term “BMG composite”.

1.1.6.2 Foreign-particle-reinforced bulk metallic glass composites produced by melt processing techniques

One of the first reports of melt processed foreign-particle-reinforced BMG composites was by the Johnson Group in 1997 [9]. They reported the use of SiC, TiC, WC, W and Ta as reinforcement particles in Cu and Zr-based alloy systems. Zr_{57}Nb_{5}Al_{10}Cu_{15.4}Ni_{12.6} (Vit 106) was shown to display especially high resistance against crystallization due to the increased nucleation surface. Mechanical tests showed that the developed composites display either high yield strength or high plastic strain [10,11], but never a very good combination of both. A high plastic strain of 24% was achieved in compression by reinforcing the BMG with 50 vol.% Nb particles of 200 μm. However, this high reinforcement content led to a decrease of the yield strength to about 500 MPa (compared to 1.8 GPa for the monolithic alloy). None of the foreign-particle-reinforced glasses displayed any tensile plasticity.

Carbon nanotubes have also been used as reinforcement particles in Zr-based BMGs [12]. This led to an increase in stiffness but not in plasticity of the material. Not many foreign-particle-reinforced BMGs have been reported in other alloy systems. TiB-reinforced Mg-based BMGs have been shown to display a major increase in yield
strength and plastic strain in compression (1.2 Gpa and 3.2% respectively) compared to the monolithic alloy (~550 MPa and 0%) [13].

Fiber-reinforced BMGs shall be mentioned here, even though they are not the topic of this dissertation, because they have led to superior mechanical properties compared to particulate-reinforced BMGs. Plastic strains of up to 17% combined with a yield strength of 1.3 GPa [14] were achieved with 60% W-fiber-reinforced Vit 1 under compression. The fracture strength of the composite is even higher (~2.1 GPa) than in the monolithic matrix material (~1.9 GPa). However, no major tensile plasticity was achieved.

1.1.7 In-situ formed bulk metallic glass composites

Many in-situ formed metallic glass composites have been developed in the past few years [15,16,17,18,19,21]. Some of them show a tremendous increase in plastic strain compared to the monolithic matrix material.

In-situ formed metallic glass composites have the advantage that a homogeneous particle distribution is easily achieved without complicated mixing procedures as are common for foreign-particle-reinforced metallic glass composites. Further they display excellent chemical bonding between the matrix and the reinforcement particles.

The disadvantages of the in-situ formed composites lie in the delicate processing and the fact that the microstructure cannot be tailored as precisely as in foreign-particle-reinforced metallic glass composites. Often the chemistry, size and shape of the crystalline particles are dependent on the cooling rate or the heat treatment of the composites, making their reproducibility very difficult. Especially, the achievement of a homogeneous microstructure in cast components of varying wall thickness is very challenging.

It is difficult to define a clear boundary between in-situ formed metallic glass composites and multi-phase nanocrystalline materials. There are reports in literature of “metallic glass composites” not only displaying high plastic strains but also work hardening [20]. Even though such materials are of great fundamental and technological value they may not be called metallic glass composites because work hardening does not lie in the nature of the metallic glass (see Chapter 1.1.3).
One of the first reports of *in-situ* formed metallic glass composites was also by the Johnson group in 1999 on the Zr-Ti-Nb-Cu-Ni-Be system where a dendritic Ti-Zr-Nb phase was precipitated in the amorphous matrix [15]. This was the starting point for a whole new field in increasing the ductility of bulk metallic glasses.

The next step in tailoring the microstructure of *in-situ* formed composites was performed by the Inoue group who developed a very interesting ZrC-reinforced Zr-Al-Ni-Cu composite in 2000 [21]. These *in-situ* composites were not formed in the classical way by crystallizing part of the matrix but by melting the matrix material together with graphite particles and letting them react to carbides depleting the matrix of Zr. This is a very elegant procedure because the carbide size and content can be varied by adjusting the graphite particle size and content. This system will be revisited in Chapters 4.2 4.2 and 4.3.

Theses events were followed by further reports on *in-situ* composites in the Zr [15,16,17,18] system and new developments in the Cu [19,22,23,24], Ti [20] Fe [25] and Ni [26] metallic glass systems. *In-situ* composite formation has shown a very high potential in increasing the plastic strain of metallic glasses. Plastic strains of up to 20% have been achieved under compression [27] by dispersing of 30 vol.% spherical β-Zr solid solution in a glassy Zr-based matrix. However, to our knowledge there have been no reports of significant tensile plasticity.

### 1.1.7.1 *In-situ* carbide formation in Zr-based metallic glasses

The possibility of *in-situ* carbide formation in Zr-based metallic glasses is of great importance in the graphite-reinforced BMGs discussed in Chapter 4. *In-situ* carbide formation as described in [21] is generally triggered by adding small graphite particles (<10 μm) to a Zr-based alloy melt. Zr being the element in the matrix with the most negative enthalpy of formation with graphite ZrC is formed. Even in the Zr-Ti-Ni-Cu-Al alloy system we observed only ZrC formation even though Ti displays an energy of formation with graphite which is not much less negative than that of Zr ($H_{\text{for}}(\text{Zr}) = -106 \text{ kJ/mol}$, $H_{\text{for}}(\text{Ti}) = -77 \text{ kJ/mol}$ [28]). This is also discussed more detailed in Chapter 4.2 where we will show that it is possible to control the carbide
formation by varying the size of the graphite particles and in particular the processing temperature. In a further step this led to the development of a novel three-phase composite with graphite and ZrC in the amorphous matrix which is presented in Chapter 4.3.

1.1.8 References

1.2 Aim and outline of the thesis

The global aim of this thesis is to tailor the mechanical properties, especially increasing the plastic strain of bulk metallic glasses by second phase reinforcement. Foreign particle reinforcement was chosen because it allows direct tailoring of the composite microstructure and, thus, properties by adjusting the reinforcement particle type, size and volume content. Graphite particles were used for reinforcement.

1.2.1 Diamond-reinforced bulk metallic glass composites

With diamond reinforcement we have two things in mind; namely, the development of a composite with high thermal conductivity for heat sinks and to improve the cold cutting properties of BMGs.

Heat sinks have become very important in high-end electronic components. Due to the ongoing miniaturization, heat is concentrated on less surface and materials with very high thermal conductivity are demanded as heat sinks. Diamond reinforcement of crystalline alloys has been proposed as a possible solution. We believe that reinforcement of metallic glasses would be promising due to their superior formability, especially in small dimensions.

Bulk metallic glasses show a self-sharpening effect, which is of great interest for technological cutting applications. Recently, bulk metallic glasses have been introduced as a new material for surgical scalpels. We think that it might be possible to further tailor the cutting properties by reinforcing the metallic glass with diamond particles.

We attempt to process diamond-reinforced BMGs by a powder consolidation process. The first step in such a process is the production of amorphous powders. There, we want to gain a fundamental understanding for the mechanical amorphization process and show that it is possible to produce powders with very low oxygen contamination starting from crystalline pre-alloys (see Chapter 2.1).
1.2.2 Graphite-reinforced bulk metallic glass composite

Despite the high yield strength of bulk metallic glasses, its technological breakthrough as a structural material is still hindered by its lack of major plastic strain. With graphite reinforcement we want to make a contribution to increasing plasticity of metallic glasses without sacrificing their high yield strength. We chose graphite as a reinforcement particle primarily with the hope of increasing the plastic strain of the BMG. Further we expect graphite reinforcement to lead to interesting tribological properties due to its super-lubricity.

We expect the graphite particles embedded in the BMG matrix to have a self-lubricating effect during dry-sliding and thus decrease the coefficient of friction compared to the metallic glass. We think that the high yield strength and compressive plasticity (see Chapter 4.1) of these materials combined with their excellent tribological properties (see Chapter 4.3) make them a possible candidate for dry frictional bearings.

1.2.3 Outline of the thesis

The thesis is separated the following way. Chapter 2 describes mechanical amorphization, a technique used to produce amorphous powder for the production of BMG composites by consolidation technique. In Chapter 3 the production and properties of diamond-reinforced BMGs produced by powder consolidation (Chapter 3.1) and melt processing technique (Chapter 3.2) are discussed. Graphite-reinforced BMGs are the topic of Chapter 4. The subchapters focus on mechanical properties (Chapter 4.1), tailoring of the mechanical properties (Chapter 4.2) and the tribological properties (Chapter 4.3) of these composites. And, finally, Chapter 5 consists of a conclusion and an outlook.
2 Mechanical amorphization

In this chapter the processing of metallic glass powders is discussed. Amorphous metallic powders are used for the production of bulk metallic glass composites via a powder consolidation route.
2.1 High-purity amorphous Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_{5} powder via mechanical amorphization of crystalline pre-alloys\(^1\)

Abstract

Fully amorphous Zr\(_{52.5}\)Cu\(_{17.9}\)Ni\(_{14.6}\)Al\(_{10}\)Ti\(_{5}\) (Vit 105) powder with very low oxygen contamination was successfully produced from pre-alloyed crystalline material. A yield of over 80\% was achieved without the use of a milling agent. The amorphization process was observed by differential scanning calorimetry and x-ray diffraction. The extremely fast amorphization rate was shown to be fitted by an exponential relaxation function. A partial TTT diagram was obtained from isothermal annealing experiments based on the Johnson-Mehl-Avrami model. Further, the microstructure of the powder was observed by scanning electron microscopy, and gas analysis was conducted at various stages of the powder process.

2.1.1 Introduction

Ball milling (mechanical alloying) is a common method for producing amorphous metallic powders [1]. In many cases these are used for the production of Bulk Metallic Glass (BMG) composites via powder consolidation [1, 2, 3]. Depending on the alloy system the range of compositions which can be mechanically amorphized is similar [4] or wider [5, 6] than in melt processing. Producing BMG composites via powder consolidation also has the advantage that reinforcement particles can be more

easily distributed. There is no critical casting thickness as in the melt processing of metallic glass-forming alloys [7,8]. A successful consolidation process requires, however, information about the thermal properties and crystallization kinetics of the amorphous powders.

Up to now, Zr-based amorphous powder has generally been produced by ball milling of elemental powders [1,2,6,9,10,11]. In this project, however, we mechanically amorphized crystalline Zr$_{52.5}$Cu$_{17.9}$Ni$_{14.6}$Al$_{10}$Ti$_5$ (Vit 105) pre-alloys by ball milling. This method leads to shorter milling times and lower oxygen contamination than in previous studies. X-ray amorphous powder with only 650 ppm of oxygen contamination was achieved after 12 h of milling with a yield of over 80%. Our method also allows the investigation of the amorphization process without having to consider the effect of powder mixing. The amorphization rate, microstructure, oxygen / nitrogen contamination, and crystallization kinetics of the powders are presented for various stages of the ball-milling process.

2.1.2 Experimental procedure

Pre-alloys with the atomic composition Zr$_{52.5}$Cu$_{17.9}$Ni$_{14.6}$Al$_{10}$Ti$_5$ (Vit 105) were prepared by arc melting of high-purity elements (> 99.95%) in an Ar 6.0 atmosphere and casting into a 13 mm Cu mold in a Bühler arc melting system. The as-cast samples were crystallized at 465 °C for 90 min under a vacuum of < 5 × 10$^{-5}$ mbar to enable crushing of the sample into pieces smaller than 5 mm for ball milling. The crushed powder was placed into a ball-milling crucible in a Mecaplex glove box filled with Ar 4.8. Ball milling with a Retsch PM 100 planetary ball-mill was performed in a 125 ml steel vial at 400 rpm with a ball-to-powder ratio of 7.5:1. No milling agent was used. Periodic interruptions during milling hindered sticking of the material to the balls and the vial.

X-ray diffraction (XRD) was performed with a Siemens Diffractometer D5000 using CuK$_\alpha$ radiation, and a Setaram Labsys DSC with Ar 6.0 flow was used for differential scanning caloriometry (DSC). All experiments were run at heating and cooling rates of 20 K/min. Gas analysis was performed on a Leco TC-436 apparatus.
combined with a Leco EF-400 furnace, and a Zeiss Gemini 1530 FEG scanning electron microscope (SEM) was used for microstructure investigation.

2.1.3 Results

The amorphization process was observed by XRD and DSC. Fig. 2.1.1a shows how the XRD pattern of the powder develops with milling time. After only one hour of milling a very broad peak is obtained, suggesting that the grain size has become minute. After 12 and 30 hours of milling only a halo is observed in XRD, which suggests that the powder has become amorphous. DSC measurements performed on the same powder show the evolution of crystallization enthalpy with milling time. As can be seen in Fig. 2.1.1b, a distinct crystallization peak first appears after 4 h of milling. After 12 h a second small peak appears starting at about 580 °C. The onset of the first crystallization shifts to a higher temperature with increasing milling time and lies higher than that of the amorphous as-cast sample after 30 h of milling. After 30 h of milling the crystallization enthalpy is in the range of the amorphous as-cast sample, but the two-step crystallization at about 460 °C, common for as-cast Vit 105, is not seen in the ball-milled sample.

![Figure 2.1.1](image)

Fig. 2.1.1 a) XRD analysis showing the evolution of the amorphization process of pre-alloyed Zr$_{52.5}$Cu$_{17.9}$Ni$_{14.6}$Al$_{10}$Ti$_{5}$ during ball milling with parameters B (20 mm steel balls, paused for 3 min after every minute of milling) and b) DSC scans showing the evolution of crystallization as a function of milling time. The onset of crystallization shifts to a higher temperature for longer milling and eventually reaches the value of the as-cast amorphous sample. The two-step crystallization observed for the as-cast sample is not seen in the ball-milled samples.
Fig. 2.1.2 shows the evolution of the crystallization enthalpy measured in DSC after various milling times for different milling parameters (denoted in the following as A and B). The initial milling parameters A which allowed amorphization without sticking were three 20 mm steel balls and 30 s of milling followed by a 2.5 min pause. To improve the rate of amorphization, milling parameters B were used, consisting of five 20 mm steel balls, and the process was paused for 3 min after every minute of milling. It can be seen that an adjustment of the milling parameters, as in B, led to much faster amorphization rates. Both data sets could be fitted with an exponential relaxation function

\[ E = A(1 - \exp(-t/\tau)), \]  

(2.1.1)

with \( A = 26.5 \text{ J/g}, \ \tau = 12 \text{ h} \) for milling parameters A and \( A = 40 \text{ J/g}, \ \tau = 8.5 \text{ h} \) for milling parameters B, respectively. The powder milled with parameters B is X-ray amorphous after 12 h of milling. However, the crystallization peak still increases from 29.1 J/g to 32.6 J/g and 39.6 J/g for 18 h and 30 h of milling, respectively. The crystallization enthalpy achieved after 30 h of milling is in the range of the fully amorphous as-cast sample with 38.4 J/g in Fig. 2.1.1b.
Fig. 2.1.2  Evolution of crystallization enthalpy with time and fit using an exponential relaxation function (solid line) \( E = A(1-\exp(-t/\tau)) \) with \( A = 26.5 \text{ J/g} \), \( \tau = 12 \text{ h} \) and \( A = 40 \text{ J/g} \), \( \tau = 8.5 \text{ h} \) for milling parameters A and B, respectively.

The particle size distribution after 12 h of milling with parameters B is shown in Fig. 2.1.3a. The equilibrium between cold welding and breaking up of particles is at about 100 \( \mu \text{m} \) particle size. The arrows in Fig. 2.1.3b indicate sites where particles have been fused or where a split-up is likely to occur after further milling. At high resolution, as in Fig. 2.1.3c and Fig. 2.1.3d, very fine vein-like patterns can be seen on the particle surfaces. They are typically about one order of magnitude smaller than the vein patterns observed on the fracture surface of bulk metallic glasses [12,13,14].
Gas analysis was conducted after every processing step. The level of oxygen and nitrogen contamination can be seen in Fig. 2.1.4. All values are in weight ppm. The fully amorphous as-cast alloy contains < 200 ppm O₂ and < 50 ppm N₂, respectively. Annealing of the samples in a vacuum led to a distinctive reduction of oxygen and nitrogen in the sample. The main increase in gas contamination apparently took place during crushing of the crystalline pre-alloys, while milling for 12 h in an inert atmosphere generated only a minor increase in gas contamination, to a final value of about 650 ppm O₂ and 120 ppm N₂. Gas analysis was also conducted on the powder from the amorphization experiment shown in Fig. 3. Parameters A with 13 glove box cycles led to 3250 ppm O₂, whereas parameters B with 5 glove box cycles led to 900 ppm O₂.
Thermal experiments for investigation of crystallization kinetics were conducted on the amorphous powder according to the following thermal program: heating to 380 °C; holding 15 min; then heating to the annealing temperature (400–420 °C); and holding for 3–60 min. The sample was then cooled to 300 °C followed by two cycles to 700 °C to observe crystallization. Fig. 2.1.5a shows the measured crystallization enthalpies after annealing at different temperatures as a function of the annealing time. As expected, a higher annealing temperature leads to a faster decrease in the measured crystallization enthalpy, or in other words to faster crystallization. At 400 °C, near the glass transition temperature, crystallization starts after about 20 min of annealing, whereas at 420 °C it starts almost immediately.
An interpretation of the crystallization kinetics was possible using the Johnson-Mehl-Avrami (JMA) model [15,16]. According to this model, the time and temperature dependence of the crystalline volume fraction $X$ can be described in terms of the Avrami exponent $n$ and a kinetic constant $k$, which follows an Arrhenius relation with temperature $T$;

$$X(T,t) = 1 - \exp(-kt^n)$$  \hspace{2cm} (2.1.2)

with $k = k_0 \exp(-E_A/RT)$, $E_A = \text{activation energy}$ and $R = 8.314 \text{ Jmol}^{-1}\text{K}^{-1}$. The ratio of the residual enthalpy $\Delta H_x(T,t)$ to the initial value $\Delta H_x(t_0)$ describes the amorphous fraction and is thus equated to $1-X(T,t)$. The Avrami exponent is obtained from the slope by plotting $\ln(\ln(1/(1-X)))$ versus $\ln(t)$ as shown in Fig. 2.1.5b. At an annealing temperature of 400 °C and 420 °C, $n$ amounts to 3.0 and 1.4 respectively, although a decreasing tendency is observed for long holding-times at 400 °C. The apparent activation energy was calculated to be 1052 kJ/mol from an Arrhenius Plot.

A time-temperature-transformation (TTT) diagram for isothermal crystallization in the undercooled liquid region is exhibited in Fig. 2.1.6. Based on the JMA equation with the evaluated constants, the time in function of temperature after which 5% of the initial crystallization enthalpy is lost is calculated. An Avrami exponent of $n = 1.4$ was used for $T \geq 410$ °C and $n = 3$ for $T < 410$ °C. In the range of 400-410 °C a rather large
time window is opened where the powder can be annealed for several minutes without significant crystallization.

![Partial TTT diagram based on DSC study and Johnson-Mehl-Avrami model. The plot indicates the annealing time at a certain temperature after which 5\% of the initial crystallization enthalpy is lost; \( n = 1.4 \) was used for \( T \geq 410^\circ\text{C} \) and \( n = 3 \) for \( T < 410^\circ\text{C} \).](image)

**2.1.4 Discussion**

X-ray amorphous powder with a high yield of over 80\% was achieved after only 12 h of milling without a milling agent. This is much faster than that usually reported in literature starting from elemental powders of similar composition and milling with a planetary ball mill [6,11,17]. Rapid amorphization was also reported in [18], where amorphization started from various compounds instead of elemental powders. Even though our powder is x-ray amorphous after 12 h, the crystallization enthalpy increases by another 30\% during the next 18 h of milling, which we attribute to a further decrease in short-range order.

We have found that the amorphization rate obtained by the milling of crystalline pre-alloys can be fitted with an exponential relaxation function. This is due to the fact that relaxation proceeds from a stable crystalline state into a new metastable equilibrium. This is not the case when starting from elemental powders, because the amorphization mechanism is superimposed by the mixing of the various elements. The
crystallization enthalpy of our amorphous powder milled for 30 h is in the range of the as-cast samples; however, the crystallization sequence seems to be slightly different and the powder has a slightly larger supercooled liquid region than the bulk specimen (cf. Fig. 2.1.1b).

Our amorphous powder also has much less oxygen and nitrogen contamination than that reported in literature for similar compositions [6,19]. We also found that most contamination takes place before the milling procedure. Crushing of the crystalline pre-alloys in an inert atmosphere would presumably lead to even lower levels.

Investigation of the crystallization kinetics shows that there are two different crystallization mechanisms, depending on annealing temperature. The Avrami exponent of 3 obtained at 400 °C indicates continuous nucleation and three-dimensional growth, whereas the exponent of 1.4 at 420 °C is related to one-dimensional surface nucleation. It is assumed that heterogeneous nucleation begins with impurities such as oxides. In this case, the activation energy for crystallization of the ball-milled powder is about three times higher than the value reported in a study of non-isothermal crystallization kinetics of bulk Vit105 [20]. Finally, the TTT diagram obtained in Fig. 2.1.6 shows that there is a potential processing window for consolidation of BMG composites, from 400 °C – 410 °C.

2.1.5 Conclusions

X-ray amorphous Vit105 powder was produced with a yield of over 80% starting from melt-processed pre-alloys in only 12 h of milling time. This is much faster than the amorphization processes reported in literature starting from elemental powders with similar compositions. We found that the amorphization rate can be fitted with an exponential relaxation function, indicating that the material relaxes from a crystalline into a new metastable equilibrium. The amorphous powder further reveals much lower oxygen and nitrogen contamination than what has been reported so far. Most contamination takes place prior to the actual milling procedure.

Study of the crystallization kinetics has shown that the crystallization mechanism is dependent on the annealing temperature. The Avrami exponent of 3 obtained at 400
°C indicates continuous nucleation and three-dimensional growth for our amorphous powder, whereas the exponent of 1.4 at 420 °C is related to one-dimensional surface nucleation. A calculation of the TTT diagram (Fig. 2.1.6) shows that a rather large processing window exists for the consolidation of the powder.

2.1.6 References

Seite Leer / Blank leaf
3 Diamond-reinforced bulk metallic glass composites

In this chapter diamond-reinforced bulk metallic glass composites produced by powder consolidation and melt processing are discussed. The results presented on composites produced by powder consolidation in Chapter 3.1 were obtained in a pre-study. The aim of this pre-study was to determine if the oxygen contamination of the produced amorphous powder was low enough to allow bonding between the particles during consolidation. The consolidation route was not further followed because much progress was made with the melt processing route which is discussed in Chapter 3.2 and was also used to produce the graphite-reinforced BMGs presented in Chapter 4. We find that melt processing offers a more straight-forward approach to achieving bulk composites with today’s good glass-forming alloys.
3.1 Production of diamond-reinforced $\text{Zr}_{52.5}\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}\text{Ti}_{5}$ composites by consolidation technique

Abstract

Producing bulk metallic glass composites by consolidation of amorphous powder allows to avoid the problems of critical casting thickness and homogeneous particle distribution present in melt processing. In the described pre-study we attempted to consolidate amorphous $\text{Zr}_{52.5}\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}\text{Ti}_{5}$ (Vit 105) powder and a composite powder containing additionally 20-30 $\mu$m diamond particles. We found that bonding between the particles took place. However, the produced samples had a relative density of only about 70% and thus displayed very low yield strength.

3.1.1 Introduction

There are many reports in literature of BMGs [1,2,3] and BMG composites [4,5] which have been produced by consolidation techniques. The main advantage of this processing route is that theoretically the component dimensions are not limited to the critical casting thickness of the matrix material. In addition it is easy to achieve a homogeneous particle distribution in BMG composites by mixing the powders before consolidation. The difficulty lies in achieving fully dense samples. Increasing pressure, processing temperature and time is expected to improve densification during consolidation; however, as has been shown in [6], the latter two parameters are limited by the crystallization kinetics. More sophisticated consolidation techniques such as
extrusion [7] and pulse current sintering [8] show shorter processing times, allowing higher consolidation temperatures.

Reports of high hardness of consolidated amorphous powder are found in literature [2,3], however, very little data on the yield strength and plasticity of such consolidated samples is available. Consolidated Mg_{70}Ca_{10}Al_{20} has been reported to display very high specific yield strength [1] and Cu-reinforced Ni_{59}Zr_{20}Ti_{10}Si_{2}Sn_{3} has even been shown to display minor plasticity under compression [4]. Lately a metal matrix composite with 40 wt.% amorphous Ni_{52.62}Zr_{28.71}Ti_{13.57}Si_{1.33}Sn_{3.74} powder in a Cu matrix, prepared by magnetic compaction, was shown to display a yield strength of about 800 MPa combined with 28% plasticity under tensile conditions [5].

In this project we evaluated uni-axial pressing as a consolidation technique for processing a diamond-reinforced Zr_{52.5}Cu_{17.5}Ni_{14.6}Al_{10}Ti_{5} BMG composite. Diamond-reinforced BMGs are expected to display good cutting properties and high thermal conductivity making them an interesting material for surgical cutting tools and heat sinks, respectively.

3.1.2 Experimental

In order to minimize oxidization, the powder was filled into a pressing mold inside a glove box. Subsequently the whole mold was packed into a corrugated tube which was then sealed at both ends by flanges with copper o-rings. The mold and piston were manufactured out of Nimonic105. The individual parts of the pressing device are shown in Fig. 3.1.1.
The mold with a diameter of 5 mm was filled with about 550 mg amorphous Vit 105 powder (characterized in [6]) which was mixed with monocrystalline diamond powder (particle size 20-30 μm, Microdiamant AG, MSY 20-30) for the production of the composite samples. After sealing the casing of the mold in Ar atmosphere it was heated to around 400 °C for 45-60 min. Afterwards the casing was quickly moved from the furnace to the hydraulic press, where the powder was consolidated for 1 minute at a pressure of roughly 600 MPa.

Compression tests were performed with a Schenk Trebel tensile tester at a strain rate of $10^{-3}$ s$^{-1}$ and a CamScan scanning electron microscope was used for investigation of the microstructure.

### 3.1.3 Results

The processing parameters and the achieved densities are listed in Table 3.1.1. Due to limits of the experimental setup the applied pressure is much smaller than what is typically used for powder consolidation of metallic glasses. The densities were calculated measuring the sample weight and dimensions.
Table 3.1.1 List of consolidated samples stating processing parameters and achieved density

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>Pressing temperature [°C]</th>
<th>Pressure [MPa]</th>
<th>Achieved density [g/cm³]</th>
<th>Achieved relative density</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Vit 105</td>
<td>398</td>
<td>641</td>
<td>4.9</td>
<td>0.73</td>
</tr>
<tr>
<td>2</td>
<td>Vit 105</td>
<td>398</td>
<td>641</td>
<td>5</td>
<td>0.73</td>
</tr>
<tr>
<td>3</td>
<td>Vit 105</td>
<td>405</td>
<td>641</td>
<td>5.1</td>
<td>0.75</td>
</tr>
<tr>
<td>4</td>
<td>Vit 105</td>
<td>RT</td>
<td>534</td>
<td>4.5</td>
<td>0.66</td>
</tr>
<tr>
<td>5</td>
<td>Vit 105</td>
<td>RT</td>
<td>641</td>
<td>4.7</td>
<td>0.69</td>
</tr>
<tr>
<td>6</td>
<td>Vit 105 / 15 vol.% diamond</td>
<td>398</td>
<td>534</td>
<td>4.4</td>
<td>0.70</td>
</tr>
</tbody>
</table>

Sample 3 displays the maximum achieved relative density of about 75%. It was processed at the highest temperature (405°C) and a pressure of 641 MPa. Other Vit 105 samples processed at 398°C at the same pressure display a slightly lower relative density of 0.73. Samples 4 and 5 were processed at room temperature and display the lowest densities. However, the cohesion of the powder is still good enough that the samples do not fall apart. The composite sample 6 displays a slightly lower relative density than the monolithic Vit 105 samples processed with the same parameters. This may be due to the fine diamond particles hindering the movement of the piston.

Higher processing temperatures (significantly above T_g), which would have aided densification could not be applied because of the very long heating and cooling times of the mold in our process.

A consolidated Vit105-diamond composite is presented in Fig. 3.1.2. It can be seen that the densification process is far from ideal. In particular the top edge of the sample is crumbled which is most likely due to high pressure gradients during processing.
SEM investigation of the samples showed that the densification is not homogeneous at all. In the bulk of the sample shown in Fig. 3.1.3a, cohesion among the powder particles is very limited, whereas viscous flow seems to have taken place near the mold wall as can be seen in Fig. 3.1.3b.

The composite sample 6 was also investigated by SEM. The effect of consolidation is comparable to sample 1. Fig. 3.1.4a shows that a homogeneous diamond particle distribution was achieved in the composite. The diamond particles seem to be quite well embedded in the amorphous matrix as shown in Fig. 3.1.4b.
3.1.4 Discussion

Obviously the very low density of the consolidated samples reflects on the insufficient mechanical stability of the tested samples. The SEM images showed that much higher density was achieved close to the sample-mold interface. This gives hope that it might be possible to achieve higher density with the utilized powder by adjusting the pressing parameters.

It is shown in literature that the tensile strength of Zr-based cast samples is almost achieved by consolidating powder with an extrusion ratio of at least 3. This means that the initial diameter is reduced to a third during the densification process which implies higher shear forces. On the other hand common hot pressing at 1 GPa resulted in a much lower tensile strength of about 40 % of the cast material [9]. Obviously the applied pressure of about 600 MPa was much too low to achieve dense samples. We were, however, limited by the strength of the mold. Since consolidation takes place in the undercooled liquid region, it is based on viscous flow. It has been shown that an increased pressing time can improve the densification [2]. Increasing processing time and temperature is only possible in a system allowing exact temperature control. Unfortunately this was not the case in our preliminary consolidation setup.
3.1.5 Conclusion

As we have shown in Chapter 2.1 (see Ref [6]), amorphous Vit 105 powder with low levels of gas contamination can be achieved very fast by milling of crystalline pre-alloys. Investigation of the powder’s crystallization kinetics shows that there is a potential processing window for consolidation above the glass transition temperature. Unfortunately our very basic consolidation setup was not only limited by the strength of the mold, but also by long heating and cooling times. This only allowed for insufficient processing pressure and temperature leading to samples with relative densities below 75%. However, local densification was observed by SEM, giving evidence that the utilized powder could be consolidated under appropriate conditions.

Considering the obvious problems connected with the consolidation process, we believe that this processing route will continue to lose importance in the future as the glass-forming ability of today’s BMGs further increases. For this reason and because of the lack of a sufficient consolidation setup only BMG composites produced by melt processing are discussed in the following chapters.

3.1.6 References

3.2 Melt processing of diamond-reinforced bulk metallic glass composites

Abstract

A Zr_{52.5}Cu_{17.8}Ni_{14.6}Al_{10}Ti_{5} bulk metallic glass reinforced with 20-30 μm diamond particles was produced using two production routes: induction mixing and particle flotation. A homogeneous particle distribution was achieved by the particle flotation technique, while induction mixing produced millimeter-size agglomerates. A model for this behavior is proposed. The composites were characterized by scanning electron microscopy, differential scanning calorimetry, x-ray diffraction and hardness measurements. High particle-matrix adhesion was found, and even a very low reinforcement volume fraction generated a significant increase in hardness, making these composites potential candidates for a new cutting tool material.

3.2.1 Introduction

Many bulk metallic glasses (BMGs) displaying good glass-forming ability and very high yield strength have been developed over the past two decades (for overviews see [1,2,3]). More recently, composites have been developed with the aim of improving the plasticity of BMGs, which, as monolithic materials, tend to fail on one or a few highly-localized shear bands [4,5]. In-situ formed [6,7] and foreign-particle-reinforced [8,9,10,11] BMG composites have been shown, at least under compression,

---

to combine the high yield strength of BMGs with the plasticity of their crystalline counterparts.

In addition to possessing mechanical properties interesting for structural applications, BMGs display a self-sharpening effect, meaning that micro-scale fracture taking place during cutting leaves back sharp edges due to failure on shear bands, as for example demonstrated in Ref. [12]. This effect also makes BMGs a promising material for low-temperature cutting tools and surgical knives. Due to BMGs’ high strength and elastic limit these blades can be made thinner than those formed of conventional crystalline materials. To further improve BMG cutting properties we considered industrial diamond as a reinforcement particle. Diamond, the hardest material known to man, displays excellent cutting properties and is widely used as an abrasive for grinding wheels and cutting blades. Diamond-reinforced crystalline metal matrix composites have already been developed with the aim of improving the wear properties [13] or the thermal conductivity [14,15] of the matrix material.

In this contribution we present possible melt processing methods and a primary characterization of a novel diamond-reinforced Zr$_{52.5}$Cu$_{17.9}$Ni$_{14.6}$Al$_{10}$Ti$_{5}$ (Vit 105) composite. The feasibility of such a material for use as a low-temperature cutting tool is discussed.

3.2.2 Experimental

Pre-alloys with atomic composition Zr$_{52.5}$Cu$_{17.9}$Ni$_{14.6}$Al$_{10}$Ti$_{5}$ were prepared in a Bühler AM system by arc melting the high-purity elements (> 99.95%) in a 300 mbar Ar 6.0 atmosphere and casting the molten alloy ingot into a Cu mold of 13 mm in diameter and 40 mm in length. The subsequent composite preparation took place in a 1200 mbar Ar 6.0 atmosphere by mixing mono-crystalline, synthetic diamonds (MSY 20-30, Microdiamant AG, Switzerland) with a particle size of 20-30 μm into the matrix material. Two different mixing techniques were used: induction mixing in a silver boat, and particle floatation. Particle floatation was performed by melting the Vit 105 alloy on top of a diamond powder bed placed inside a silica tube, which was heated to 1000°C in a horizontal oven. The mixing step was followed by suction casting in a Bühler MAM1 arc melter or water quenching in a steel tube to achieve an
amorphous matrix. Samples with < 3 vol.% reinforcement content were cut with a BN blade, whereas samples with higher reinforcement content were cut by spark erosion.

X-ray diffraction (XRD) was carried out on polished discs with a diameter of 6 mm using a powder diffractometer in Bragg-Brentano geometry. Measurements were carried out with a PANalytical X'Pert instrument with a rotating sample holder and a X'cellerator multi-channel detector using Cu-Kα radiation. The data was analyzed using X'Pert Highscore Plus software. A Setaram Labsys differential scanning calorimeter (DSC) was used for calorimetric analysis. All calorimetric measurements were performed using a sample weight of approximately 50 mg at a heating rate of 20 K/min under an Ar 6.0 flow of 2 l/h. The DSC was also used to anneal the diamond powder to investigate its thermal stability. A Reichert-Jung Polyvar Met microscope combined with a Leica camera was used to create the optical microscopy images, and a high-resolution Zeiss Gemini 1530 FEG scanning electron microscope was used for further microstructure investigation. Hardness measurements were performed on a Gnehm Brickers 220 instrument at a setting of HV 30 with an impression time of 6 s.

3.2.3 Results

The mono-crystalline synthetic diamond powder used as reinforcement material in this work is shown in Fig. 3.2.1a. This so-called “micron-diamond powder” is obtained by crushing and sieving of synthetic diamond of type lb. The diamond particles display tight particle size distribution (20-30 μm) and have flat surfaces which produce a low interfacial surface in the composites, limiting nucleation during melt processing. To characterize its thermal stability, the diamond powder was annealed in the DSC at 800°C, 1000°C, 1200°C and 1400°C under Ar 6.0 flow. The powder annealed at 1000°C and higher displayed slight dark shading, probably due to a very thin amorphous carbon layer. However, as seen in Fig. 3.2.1b XRD revealed no structural changes even in the sample annealed at 1400°C.
Fig. 3.2.1  a) SEM image of monocrystalline industrial diamond used in this study. Particle size ranges from 20 to 30 $\mu$m. b) XRD scans of 20-30 $\mu$m diamond particles (i) in the as-delivered state and (ii) after annealing for 1 h at 1400°C under Ar 6.0 flow. A comparison of the scans shows that no structural transformation took place upon annealing.

Fig. 3.2.2 displays a cross-section of a composite ingot after induction mixing in a silver boat. An arc-shaped region with very high diamond concentration expanding all the way across the sample can be seen. This state is reached after only a few seconds of mixing. The inset on the bottom right shows that a reinforcement content of about 50 vol.% is present in this region. Outside of it a very homogeneous particle distribution with < 2 vol.% reinforcement is present.

Fig. 3.2.2  Cross-section of diamond-BMG pre-alloy after induction mixing. Arrows display areas of high and low diamond concentration. The inset shows an SEM image of an area with high diamond concentration.
One ingot was broken up and pieces of low volume content were collected and remelted in a 6 mm steel tube for rapid quenching in water. This method produced a relatively homogeneous particle distribution. A micrograph of one of these samples is shown in Fig. 3.2.3. It can be seen that crystallization of the amorphous matrix material has started from the diamond particles, which seem to act as heterogeneous nucleation sites.

![Optical micrograph of a diamond-Vit 105 composite (diamond content ≈ 2 vol.%) produced by rapid quenching in a 6 mm steel tube. It can be seen that the diamond particles act as crystal nucleation sites.](image)

XRD and DSC scans of the sample shown in Fig. 3.2.3 can be seen in Fig. 3.2.4a and b, respectively. The XRD scan shows a typical amorphous halo, but also some crystallization peaks due to the partial crystallization of the matrix material around the diamond particles. The DSC scan shows the same onset of crystallization temperature for both the composite and the monolithic matrix material. The crystallization enthalpy of the composite is $-20.5 \text{ J/g}$, as compared to $-32 \text{ J/g}$ for pure Vit 105. Samples with a diameter of less than 6 mm showed fully amorphous matrixes.
Fig. 3.2.4  a) XRD and b) DSC scans of the diamond-reinforced BMG composite (diamond content ≈ 2 vol.%) seen in Fig. 3.2.3. Also shown in b) is a DSC scan of monolithic Vit 105 for comparison. The crystallization enthalpies of the composite and the monolithic alloy are −32.5 J/g and −20.5 J/g, respectively.

SEM micrographs after mechanical tests are shown in Fig. 3.2.5. for a diamond-reinforced sample cast to a diameter of 4 mm. Hardness testing tended to show a large scattering of values because of the unevenly- and widely-spaced diamond particles in the composite compared to the size of the indenter (~200 μm). If two or three diamond particles were present under the indent this led to an increase in hardness to about 535 HV, compared to 468 HV for the amorphous matrix material. Local areas with higher diamond particle concentration, as seen in Fig. 3.2.5a, even showed a hardness of up to 700 HV. Breaking of samples with a diameter smaller than 6 mm leads to vein patterns in the matrix material as seen in Fig. 3.2.5b. These patterns show that the matrix is fully amorphous.
Particle floatation was also considered as a processing route for achieving a more homogeneous particle distribution. The matrix material was melted on a diamond bed at 1000°C for various lengths of time, as described in the experimental section. The cross-section of the sample melted for 30 min is shown in Fig. 3.2.6a. It was seen that particles diffused into the matrix material, while a diamond coating of the material remained at the bottom of the sample. Fig. 3.2.6b gives an overview of the particle distribution in samples of this type melted for 0.5, 2 and 4 h, respectively. These samples were cut perpendicular to the diamond bed and their particle densities were determined by counting particles on the micrographs in regions of 200 μm × 1500 μm. It is seen that in all samples the highest particle density is found 0.2-1.6 mm from the bottom of the sample. As expected, longer floatation times generated higher particle densities. Average particle densities of 26, 36, and 44 mm⁻² were found for 0.5, 2 and 4 h floatation times, respectively. The highest particle density achieved corresponds to about 2.2 vol.% of diamond in the BMG sample.
Fig. 3.2.6  a) SEM image near the bottom of a sample produced by particle floatation. A thin diamond layer was formed at the bottom. b) Diamond-particle distribution as a function of distance from the bottom of the sample after various floatation times (the dashed lines are a parabolic fit to the data). The inset shows the average particle density in the 2 mm layer as a function of time.

3.2.4 Discussion

As our annealing experiment (Fig. 3.2.1b) showed, mono-crystalline industrial diamond is stable enough for processing at temperatures of up to 1400°C in an Ar 6.0 atmosphere. It was demonstrated in Ref. [16] that the degeneration temperature is highly dependent on the atmosphere. As the Vit 105 alloy melts at about 800°C and all processing is conducted in Ar 6.0, the diamond powder is expected to not undergo any structural transformation. If graphitization took place at the surface this would most likely improve the wetting behavior of the particles, considering that graphite particles do not agglomerate in a Vit 105 matrix [11].

Homogeneous particle distribution is essential to generating good mechanical properties in BMG composites. Even though this was easily achieved by consolidating a mixture of amorphous Vit 105 powder [17] and diamond powder, we propose here a melt processing route, because by SEM of fracture surfaces we observed much better particle-matrix adhesion in melt-processed samples. Such particle-matrix adhesion is essential for cutting tools.

Because preparation of samples by machining is very difficult, a net-shape melt process would be of great value. Unfortunately, the induction mixing process which has been successfully applied to graphite-reinforced BMGs [11] does not produce a homogeneous particle distribution with the diamond particles. We believe this to be
due to the insufficient wetting of the melt on these particles. The state shown in Fig. 3.2.2 is reached very quickly, and further induction heating simply makes the area of high diamond concentration larger. Obviously the viscosity of the composite volumes with high diamond concentration will be higher than that of the remaining melt. During mixing these volumes will not show much motion, in contrast to the volumes with lower viscosity (low diamond concentration), which will be spun around the agglomerates. Under the assumption that the wetting of Vit 105 on diamond is not sufficient, more and more diamond particles will be stripped out of the volume in motion and attached to the arc-shaped agglomerates. If the sample is turned over in the silver boat, with the arc facing downwards, and remelted, the arc regains its original form. For this reason the arc shape is thought to be induced by the temperature gradient present in the sample during processing in the water-cooled silver boat. Even though the induction mixing process does not lead to fully homogeneous particle distribution in this system, as seen in Fig. 3.2.2, melt processing of the composite is still possible on the laboratory scale by breaking up the ingots and separating out the pieces of very high diamond concentration before the final melting step.

As a processing method generating a more homogeneous particle distribution, the flotation technique, also presented in this study, seems to be more promising because of the large difference in specific density between the diamond particles (~3.5 g/cm³) and the matrix material (~6 g/cm³). The disadvantage of such a method is that it is slow and limited to producing materials in small dimensions and with low reinforcement volume fractions. We believe that higher reinforcement fractions cannot be achieved for reasons to do with the time-dependent infiltration of the powder network below the melt. Before a diamond powder particle can float, it has to be taken up into the melt. Even though the wetting of diamond by Vit 105 is considered unsatisfactory, the melt nevertheless begins infiltrating the powder network via gravitational force. As long as only one powder layer is infiltrated the particles are free to float upwards. However, once more powder layers are infiltrated the whole layer attempts to ascend at the same time and the particles begin to hinder each other, which slows the floatation process and leads to the formation of a thin diamond coating at the bottom of the sample (Fig. 3.2.6a). In other words, if the powder network is infiltrated
faster than the particles can float away, the process slows down. This accords with the
data plotted in the inset to Fig. 3.2.6b. During the first half hour many particles float
into the melt, and afterwards the process slows significantly.

Nevertheless, the particle floatation method produces quite a homogeneous
particle distribution, and the formation of a thin diamond coating on the bottom of the
sample (Fig. 3.2.6a) is an advantage: for many cutting applications a bulk diamond-
reinforced composite is unnecessary, while a surface coating is adequate and it
minimizes the volume of costly diamond.

The critical casting thickness of the diamond-reinforced composite is
approximately 6 mm. The micrograph in Fig. 3.2.3 showing crystallization of the
matrix around the diamond particles accords with the XRD and DSC results in Fig.
3.2.4. Calculation of the crystallization enthalpies show that about 65% of the matrix
remains amorphous. The numerous peaks found in XRD could not all be identified,
but they provide evidence of multiple crystallization events. In contrast to what we
observed in graphite-reinforced Vit 105 [11] no carbides (resulting from interfacial
reactions) were detected. The fact that according to DSC the crystallization behavior
of the composite is the same as in the monolithic alloy is evidence that the matrix
composition does not change by local crystallization around the graphite particles.
This can be easily understood, because the cooling rate during processing is too high
for long diffusion paths.

Performing tensile tests on the composite is very difficult. Due to the high
hardness of the reinforcement particles it cannot be machined by conventional
methods. Cutting with BN blades is only possible if the reinforcement content is low
enough for the blade to be deflected by the diamond particles and to cut between them,
because these particles are not ripped out of the matrix during cutting. This, together
with the fact that grinding and polishing also do not tear out the particles, is evidence
of good adhesion between the particles and the matrix material. Because of this good
adhesion Vit 105 is a promising material for a substrate in diamond-populated saw
blades. As expected, diamond particles generate a significant increase in hardness even
at very low reinforcement fractions.
3.2.5 Conclusions

We have developed a novel diamond-reinforced BMG composite which displays a very good particle-matrix adhesion essential for cutting tool applications. Annealing experiments on the diamond powder gave no indications of structural transformation in the processing environment. Homogeneous particle distribution and a maximal reinforcement content of 2.2 vol.% were achieved using a particle floatation method. This method also produced a diamond coating on the sample which could be adequate for many cutting tool applications. We found that a very low reinforcement volume fraction significantly increased the hardness of the matrix material.

3.2.6 References


Seite Leer / Blank leaf
Graphite-reinforced BMGs were produced by a melt processing route. Graphite reinforcement of BMG leads to a significant increase in plastic strain under compression, as is shown in Chapter 4.1. Chapter 4.2 discusses the possibility of tailoring the mechanical properties of these composites by initiating an interfacial carbide layer between the graphite particles and the matrix by adjusting the processing parameters. The tribological properties of two different types of graphite-reinforced BMGs in comparison to the monolithic matrix material as well as commercial bearing steel are presented in Chapter 4.3.
4.1 Ductile bulk metallic glass-graphite composites

Abstract

Bulk metallic glasses (BMGs) are a new class of amorphous alloys which display very high yield strength, but, unfortunately, very little plastic strain before fracture. Here we present a novel graphite-particle-reinforced BMG composite with a fully amorphous Zr_{52.5}Cu_{17.9}Al_{10}Ni_{14.6}Ti_{5} (Vit 105) matrix which possesses a greatly improved combination of yield strength and plastic strain. The best results are seen in samples containing 3-10 vol.% graphite, where a plastic strain of up to 18.5% has been reached without sacrificing the high yield strength of 1.85 GPa of the matrix material.

4.1.1 Introduction

Bulk metallic glasses (BMGs) are a new class of amorphous alloys which display very high yield strength, but, unfortunately, very little plastic strain before fracture. Here we present a novel graphite-particle-reinforced BMG composite with a fully amorphous Zr_{52.5}Cu_{17.9}Al_{10}Ni_{14.6}Ti_{5} (Vit 105) matrix which possesses a greatly improved combination of yield strength and plastic strain. The best results are seen in samples containing 3-10 vol.% graphite, where a plastic strain of up to 18.5% has been reached without sacrificing the high yield strength of 1.85 GPa of the matrix material.

Many amorphous metallic alloys with good glass-forming ability have been developed over the last few years (see Refs. [1,2,3] for reviews). These bulk metallic

3 M. E. Siegrist, J. F. Löffler; Scripta Materialia 2007 (in print)
glasses (BMGs) usually display double the fracture strength and up to four times the elastic limit of crystalline alloys, which make them potentially interesting as a novel structural material. Unfortunately, however, these alloys also display very little plastic strain: due to the lack of a crystalline structure, their deformation does not proceed via dislocations but along one or a few highly-localized shear bands [4,5,6,7,8].

Increasing plastic strain in BMGs is a very timely topic and several approaches have produced favorable high levels of plastic deformation: for example, *in-situ* forming of BMG composites [9,10,11,12]; work with porous Pd-based BMGs [13,14]; monolithic Pt-based BMGs displaying a high Poisson ratio [15]; and foreign-particle reinforcement [16,17]. These approaches have in common the intention to increase shear-band density such that fracture energy is distributed over a larger volume of the sample, and all have shown great potential for increasing plastic strain. However, with the exception of foreign-particle reinforcement they are either very expensive or the microstructures in question are difficult to reproduce. Monolithic BMGs with high Poisson ratios, for example, appear promising [18], but the elements with the highest Poisson ratios (e.g., $\nu = 0.39$ for Pt and $\nu = 0.42$ for Au) tend to be precious ones (indeed, enhanced plastic strain has only been observed once in a costly Pt-based alloy [15]). In porous BMGs, it is relatively difficult to achieve a homogeneous pore size distribution. The *in-situ* method does generate a homogeneous crystal distribution, but there the microstructure of the two-phase composite is very sensitive to casting conditions [19].

These problems do not apply to the foreign-particle-reinforcement procedure. Using this method, microstructure and mechanical properties can be easily tailored via adjustments in the type, shape, size and volume fraction of the reinforcement particles (this is already state-of-the-art for crystalline metal-matrix composites [20]). What has up to now held this method back is that high plastic strain in foreign-particle-reinforced BMGs has been accompanied by poor yield strength due to the high levels of reinforcement content required [17].

Here we present a new class of foreign-particle-reinforced BMGs in which a fully amorphous Zr$_{52.5}$Cu$_{17.9}$Al$_{10}$Ni$_{14.6}$Ti$_{5}$ (Vit 105) matrix has been reinforced with 25-44 \(\mu\)m and, in one case, with 44-75 \(\mu\)m graphite particles with the aim of improving
the plastic strain of the matrix material. A compressive plastic strain of up to 18.5% has been achieved without sacrificing the high yield strength (1.85 GPa) of the metallic glass. This novel composite displays the highest combination of yield strength and compressive plastic strain so far reported in foreign-particle-reinforced BMGs, and its mechanical properties are favorable even compared to those of amorphous alloys or composites produced by the other methods discussed above. In this way, the enhancement of combined plastic strain and yield strength in particle-reinforced BMGs, together with the straightforward reproducibility of their microstructure, may lead to an interesting new material for structural and functional applications.

4.1.2 Experimental

Pre-alloys with the atomic composition Zr\textsubscript{52.3}Cu\textsubscript{17.9}Ni\textsubscript{14.6}Al\textsubscript{10}Ti\textsubscript{5} (Vit 105) were prepared in a Bühler AM system by arc melting high-purity elements (> 99.95%) in a 300 mbar Ar 6.0 atmosphere. The subsequent composite preparation took place in a 1200 mbar Ar 6.0 atmosphere. 3-20 vol.% conducting-grade graphite with a particle size of 25-44 \textmu{}m (in one case, 44-75 \textmu{}m) was mixed with the matrix material by induction-melting of the alloy on top of the graphite powder in a water-cooled silver boat. After the powder was incorporated into the alloy the sample was re-melted in the boat to achieve a homogeneous particle distribution. The crystalline composites were then suction-cast in a Bühler MAM1 arc melter into 3 mm rods with a length of 30 mm. 5-mm-long slices were cut for compression testing.

The composites were characterized by x-ray diffraction (XRD) using a PANalytical X'Pert diffractometer with Cu-K\textsubscript{a} radiation; differential scanning calorimetry (DSC) using a Seiko DSC 220CU; energy dispersive x-ray spectrometry (EDX) with a CamScan scanning electron microscope equipped with a Noran EDX detector; and optical microscopy (OM) using a Reichert-Jung Polyvar Met microscope. The mechanical properties of the 5 mm-rod segments were investigated by hardness (Gnehm Brickers 220) and compression testing (Schenk Trebel tensile tester at a strain rate of $10^{-3}$ s\textsuperscript{-1}). A high-resolution Zeiss Gemini 1530 FEG scanning electron microscope (SEM) was also used for microstructure investigation.
4.1.3 Results

Fig. 4.1.1 shows the graphite particle distribution in the Vit 105 matrix for the composite containing 5 vol.% graphite, as obtained by induction mixing. The particles are uniformly distributed in the matrix and have shapes ranging from rectangular to circular.
Fig. 4.1.1  Optical microscopy image of graphite-reinforced BMG composite with 5 vol.% graphite. The graphite particles are homogeneously distributed within the glassy Vit 105 matrix.

Fig. 4.1.2 shows DSC scans of monolithic Vit 105 and of the composites with various reinforcement volume fractions ranging from 5 to 20 vol.%. A comparison of these composites' crystallization enthalpy with that of monolithic Vit 105 shows that their matrix material is fully amorphous. Using particles in the 25-75 micrometer range apparently minimizes the heterogeneous nucleation surface, such that the high critical casting thickness of Vit105 is maintained. Adding graphite, however, shifts the onset of crystallization to a higher temperature, i.e. the composite has a higher thermal stability than the monolithic metallic glass, and the crystallization behavior changes. The first crystallization peak increases with increasing graphite content at the expense of the second crystallization event.
Fig. 4.1.2 DSC scans of monolithic Vit 105 and BMG-graphite composites at 20 K/min with varying graphite particle volume content. The composites show a higher onset temperature of crystallization and modified crystallization behavior compared to the monolithic BMG.

The fully amorphous structure of the matrix was also confirmed by XRD. Small carbide peaks were detected which result from an interfacial carbide layer in the submicrometer range surrounding the graphite particles. EDX showed that no graphite particles had fully transformed into carbides and that the content of Zr and Ti in the matrix was within 0.5% of the nominal composition.

Compression tests indicate a large improvement in plastic strain, with only a slight decrease in yield strength compared to monolithic Vit 105. Fig. 4.1.3 shows that the plastic region has strongly increased, from 3% for monolithic Vit 105 to about 7% for 3.5 vol.% graphite, 13% for 5 vol.% graphite, and 15% for 10 vol.% graphite, whereas yield strength has decreased only slightly from 1.85 GPa for the monolithic alloy to 1.7 GPa for 3.5 vol.% graphite, 1.6 GPa for 5 vol.% graphite, and 1.5 GPa for 10 vol.% graphite reinforcement. Our most recent experiments have shown that even higher compressive strains with only a slight reduction in yield strength can be achieved by varying particle size. For 3 vol.% of 44-75 µm particles we managed a maximal plastic strain of 18.5% in combination with a yield strength of 1.85 GPa, and expect further optimization of these values.
The composites also display decreasing hardness with increasing graphite volume content, as seen in the inset to Fig. 4.1.3. Even small reinforcement volume fractions of 5% lead to significant softening of the material, and hardness decreases by about 25% for graphite contents of ≥ 10 vol.%. This softening with increasing reinforcement volume fraction (inset to Fig. 4.1.3) also suggests that only a very small fraction of the graphite reacted to carbide, in contrast to other studies where ZrC particles formed in-situ (e.g., Ref. [21]).

Fig. 4.1.4 shows the yield strength and plastic strains of 5 vol.%, 10 vol.% and optimized (3 vol.%, 45-75 μm) graphite-reinforced BMG composites compared with those of other documented Zr-based particle-reinforced BMG composites [17,18]. The graphite-reinforced BMG composites developed in this study seem to represent a step forward in their combination of yield strength and plastic strain.
Fig. 4.1.4 Yield strength and plastic strain of our 5 vol.%, 10 vol.% and optimized graphite-reinforced BMGs (solid triangles) in comparison to those of other melt-processed Zr-based foreign-particle-reinforced BMGs (open triangles) found in literature [16,17] (accuracy of literature values: ± 10%). The optimized composite has a graphite volume fraction of 3% with sizes ranging from 44-75 μm, while in all other cases 25-44 μm particles were used.

Fig. 4.1.5 shows SEM images of fracture surfaces and particle-shear band interactions for these graphite-BMG composites. Fig. 4.1.5a shows how the graphite particle obstructs the flow of the matrix material from the top left to the bottom right (direction of arrow) during deformation, and Fig. 4.1.5b displays shear bands and steps on the outer surface of the compression samples after failure (the fracture surface is on the left side of the image). As may be concluded from Fig. 4.1.5b, the primary shear-band spacing around the particles is in the range of 1-5 μm.
4.1.4 Discussion

In discussing our results we wish first to emphasize that a uniform particle distribution, as shown in Fig. 4.1.1, was only achievable because of the good wetting behavior between graphite and Vit 105. Our preliminary attempts to produce composites with non-wetting particles in fact led to particle agglomerations. As to the DSC results (Fig. 4.1.2), the addition of graphite apparently improved the thermal stability of our composites compared to that of the monolithic alloy. The phenomenon of improved thermal stability was also observed for SiC reinforcement particles in a Zr-based BMG composite [17]. This effect may be due either to the change in thermal conductivity compared to the monolithic BMG or to a slight shift in matrix composition resulting from the interfacial carbide reaction. The latter may also be responsible for the slight change in crystallization behavior [22].

The combination of fracture strength and plastic strain found in the composites developed is the highest recorded up to now for foreign-particle-reinforced BMGs, as shown in Fig. 4.1.4. While similar plastic strain has been seen in 50% Nb-reinforced Zr-based BMGs [15], their yield strength dropped drastically to 30% of the strength of the monolithic alloy due to the high reinforcement volume fraction deployed. Our key to success was that we used “soft” reinforcement particles, i.e. a reinforcement material with a much lower Young’s modulus (ca. 15 GPa in graphite) than that of the Vit 105 matrix (Young’s modulus, $E \approx 100$ GPa). In contrast, all the other reinforcement materials shown in Fig. 4.1.4 have a higher Young’s modulus than the
matrix material: for the refractory metals Nb, Ta, and Mo, for example, $E$ ranges from 105 to 327 GPa.

In the following, the graphite particles are treated as pores for the description of the stress concentrations in the composites. Treatment as a pore is justified if one considers that this particle will deform willingly under stress due to the low stiffness, strength and density of graphite.

A simulation of stress fields for arrays of pores under uniaxial compression in two dimensions [23, 24] shows that regions of local tensile stress run diagonally between the particles (with respect to the loading direction). Considering the Mohr-Coulomb criterion, which is often used to describe stress states in BMGs [25], shear bands frequently propagate in such tensile stress fields, especially since these fields run, on average, 45° to the loading axis. Thus, because of these stress fields a shear band which has been initiated due to local stress concentration in the particle-matrix interface will be guided in the direction of the neighboring graphite particle. This makes it very improbable that a shear band will propagate unhindered through the material. In contrast, if reinforcement particles with a higher than the matrix were used the stress fields are expected to be opposite, guiding the shear bands around the particles letting shear bands run through the materials without being arrested.

Thus, graphite may act as a typical reinforcement particle, splitting shear bands [26] (such splitting and the particle-shear band interaction is shown in Fig. 4.1.5(b)); however, we expect the graphite particles to halt the propagation of shear bands by reducing the stress at their tips when they run onto the soft material. This is actually seen in Fig. 4.1.5(a), where the reinforcement particle clearly hinders the matrix flow during deformation.

New shear bands are initiated at sites of local stress concentration. In this respect graphite particles may act in a way similar to the pores in amorphous alloys described in Refs. [13] and [14]. During compression testing the first shear band may be initiated as soon as the stress in the "soft" particle (or pore) reaches a critical value. After initiation of this shear band the stress around the particle decreases, while other shear bands are initiated at the particles which reach critical stress concentrations. Thus multiple shear bands nucleate, run through the material and are either blocked by
neighboring graphite particles or cross, and thus hinder, each other – further enhancing plastic strain.

Apparently the combination of the above-mentioned effects (shear-band splitting, impairment of propagation, and shear-band initiation) generates a great increase in plastic strain at very low graphite content, which in turn leads to a merely minimal decrease in yield strength compared to the monolithic alloy. The regions around the particles display a very small shear-band spacing in the micrometer or even sub-micrometer range (Fig. 4.1.5), in contrast to what has been reported for monolithic Zr-based BMGs [27]. As can be seen in Fig. 4.1.3, there is no significant benefit if the graphite content is increased from 5 to 10 vol.%. Once the inter-particle distance is small enough to generate a homogeneous high shear-band density in the matrix during deformation, adding reinforcement particles will not further improve plastic strain in any significant way: doubling the reinforcement concentration will in fact reduce the inter-particle distance by only about 1/3.

4.1.5 Conclusion

In conclusion, the BMG-graphite composites developed in this study may constitute a very promising material for structural applications due to their high compressive plastic strains (comparable to that of crystalline alloys) and high yield strength (typical of metallic glasses). Additionally, their microstructure can be tailored and easily reproduced for specific applications. We are thus confident that these results will have a great impact on research efforts in the field of amorphous structural materials.

4.1.6 References


4.2 Tailoring the mechanical properties of graphite-reinforced bulk metallic glass composites

Abstract

Graphite-reinforced bulk metallic glasses have been shown to display high plasticity under compression without sacrificing the high yield strength of the monolithic matrix material. In this contribution, we present the effect of particle size and the thickness of the interfacial carbide layer on the mechanical properties of these composites.

4.2.1 Introduction

Even though many amorphous metallic alloys with good glass-forming ability have been developed over the last few years [1,2,3] the high strength of these materials cannot be fully exploited due to the alloys' brittle fracture behavior. Unlike crystalline alloys, deformation does not take place in dislocation movement but in formation and propagation of one or a few highly-localized shear bands [4,5,6,7,8]. A drastic enhancement of the plasticity of bulk metallic glasses (BMGs) would lead to a new material with improved properties to be used in structural applications.

All the approaches of increasing the plasticity of BMGs are based on increasing the shear band density during deformation. In addition to two very new approaches, namely porous Pd-based BMGs [9,10] and monolithic Pt-based BMGs displaying a high Poisson’s ratio [11], in-situ-formed BMG composites [12,13,14,15,16,17,18] and foreign-particle-reinforced BMGs [19,20,21,22,23,24], have been shown to exhibit high levels of plastic deformation. Foreign-particle-reinforced BMGs have the major advantage that they allow direct tailoring of the mechanical properties by adjusting
particle shape, size and volume content, as is standard procedure in crystalline metal matrix composites (MMCs) [25]. They also display high reproducibility because they can be processed by standard MMC processing techniques [26] followed by a rapid quenching step, and their morphology is not dependent on the cooling rate as in in-situ-formed BMGs. In Ref. [19] (see also Chapter 4.1) we have shown that graphite-reinforced BMGs display mechanical properties superior to other foreign-particle-reinforced BMGs due to their very soft reinforcement particles.

In this contribution, we present the effect of particle size and the thickness of the interfacial ZrC layer formed at the matrix-particle interface of graphite-reinforced BMG composites on mechanical properties. By adjusting the processing parameters, the thickness of the interfacial layer can be varied. By increasing the thickness of the layer the hardness of the composite was increased, while the plasticity was decreased. By minimizing ZrC formation and increasing particle size, a maximal plasticity of 18.5% was achieved without sacrificing the high yield strength of the metallic glass (see Chapter 4.1). Thus, this novel composite displays exceptional mechanical properties which can even be tailored by adjusting the microstructure.

4.2.2 Experimental

Pre-alloys with the atomic composition Zr\textsubscript{52.5}Cu\textsubscript{17.9}Ni\textsubscript{14.6}Al\textsubscript{10}Ti\textsubscript{5} (Vit 105) were prepared in a Bühler AM system by arc melting the high-purity elements (> 99.95%) in a 300 mbar Ar 6.0 atmosphere. The subsequent composite preparation took place in a 1200 mbar Ar 6.0 atmosphere. 3-10 vol.% conducting-grade graphite with a particle size of 25-44 μm or 45-75 μm was mixed into the metallic glass by induction melting in a water-cooled silver boat. The crystalline composites were then suction-cast into 3 mm rods with a length of 30 mm in a Bühler MAM1 arc melting system. Interfacial ZrC formation was initiated by overheating the molten samples in the arc melter before casting. The arc power was varied from 0.35 kW (no overheating, leading to standard graphite composites) to 2.1 kW (large overheating, leading to an interfacial ZrC layer).

The composites were characterized by x-ray diffraction (with a PANalytical X’Pert diffractometer using Cu-K\textsubscript{α} radiation), differential scanning calorimetry (using
a Setaram Labsys instrument), energy dispersive x-ray diffraction (with a CamScan scanning electron microscope equipped with a Noran Energy Dispersive X-ray detector), and optical microscopy (Reichert-Jung Polyvar Met microscope). The mechanical properties of 5 mm rod segments were investigated by hardness (using a Gnehm Brickers 220 instrument) and compression testing (using a Schenk Trebel tensile tester combined with Merlin software at a strain rate of $1 \times 10^{-3}$ s$^{-1}$). High-resolution scanning electron microscopy (Zeiss Gemini 1530 FEG) was also used for microstructure investigation.

4.2.3 Results

By adjusting the power input in the final arc-melting step it is possible to vary the carbide content of the BMG composites. Fig. 4.2.1 shows XRD scans for the Vit 105 composite with 3.5 vol.% graphite heated at 0.35 kW, 0.9 kW, and 2.1 kW. The two clearly seen amorphous humps result from the glassy Vit 105 matrix, while the Bragg peaks can be attributed to crystalline ZrC. DSC also confirmed the glassy structure of the matrix.
Fig. 4.2.1 XRD scans of BMG-graphite composites with 3.5 vol.% graphite reinforcement produced at different casting temperatures. Crystalline ZrC peaks in addition to the amorphous humps of the glassy Vit105 matrix are clearly visible. The ZrC content increases with increasing casting temperature; power settings 1 (corresponding to 0.35 kW power input), 2.5 (0.9 kW) and 4 (2.1 kW) in the Bühler MAM1 system.

While only traces of ZrC are observed in the lower scan (standard graphite composite), the ZrC content increases significantly with increasing casting temperature. The graphite peaks are not visible in the XRD scans because carbon is too light to be detected compared to the other elements present. We found by energy-dispersive x-ray diffraction (EDX), however, that no graphite particles had fully transformed into carbides and that the content of Zr and Ti in the matrix were within 1% of the nominal composition. Thus, the carbides observed in XRD must be due to interfacial reaction between the matrix material and the reinforcement particles as is shown in Fig. 4.2.2. The sample in Fig. 4.2.2a was processed at a very low power input of 0.35 kW and displays only a very thin interfacial carbide layer, which is not visible in optical microscopy. The sample in Fig. 4.2.2b was processed at a high power setting of 2.1 kW leading to a reaction layer with a thickness of about 1.5 μm and was herewith thick enough to also be identified as ZrC by EDX. The thicker carbide layer in Fig. 4.2.2b is still mostly intact after polishing.
Fig. 4.2.2 Optical microscopy images of graphite particles in amorphous Vit 105 matrix. The sample shown in a) was heated at a setting of 1 in the Bühler MAM1 system (corresponding to 0.35 kW power input). No obvious reaction is visible. The sample shown in b) was heated at a setting of 4 (corresponding to 2.1 kW power input). A distinctive reaction layer of about 1.5 \( \mu m \) can be seen in the graphite-matrix interface. The reaction layer in b) was thick enough to be identified as ZrC by EDX.

We also investigated the effect of interfacial carbide formation on the mechanical properties. The effect of the composites' carbide layer on hardness is shown in Fig. 4.2.3. Graphite-BMG composites processed at low power setting (0.35 kW) resulting in minimal carbide formation display strong softening with increasing graphite volume fraction. Samples processed at high power setting (2.1 kW), and thus, with a thicker carbide layer, display significantly higher hardness than composites with minimal carbide formation. At volume contents up to 5\% the composites processed at 2.1 kW display even higher hardness than the pure matrix material.
Fig. 4.2.3 Hardness of composites processed at 0.35 kW and 2.1 kW power input compared to the monolithic matrix material.

Fig. 4.2.4 shows compression test results conducted on three samples with 5 vol.% graphite and various amounts of interfacial carbides, induced by casting the composites at different energy settings. The change in carbide content with increasing casting temperature is seen in the XRD scans shown as an inset to Fig. 4.2.4. Sample 1, with the lowest carbide content, displays the highest plasticity, whereas sample 3, where the thickest carbide layer has formed, displays very brittle fracture behavior. Sample 3, for example, displayed a hardness of 476 HV, while sample 1 showed a hardness of 432 HV.
Fig. 4.2.4 Effect of interfacial carbide formation on the stress-strain behavior of BMG-graphite composites. (a) Stress-strain curves of samples with 5 vol.% graphite reinforcement as a function of increasing interfacial carbide formation from samples 1 to 3 (power input 0.35 kW, 0.9 kW, and 2.1 kW). The inset shows the corresponding XRD scans for the composites containing 5 vol.% carbon.

Samples with 45-75 μm particles displayed higher plasticity than with the smaller 25-44 μm particles. Fig. 4.2.5 shows stress-strain curves of a composite containing 3.5 vol.% of the large graphite particles compared to monolithic Vit 105. Care was given to inhibit carbide formation. A plasticity of 18.5% and a yield strength of 1.85 GPa was achieved compared to a plasticity of about 7% with the 25-44 μm particles reported in [19] for the same reinforcement content. This is in agreement with the high shear band density found on the outer surface of the compression samples, as shown in the inset of Fig. 4.2.5.
Fig. 4.2.5  Stress-strain curves of composite containing 3.5 vol.% of graphite particles with a particle size of 45-75 μm compared to the monolithic Vit 105 alloy. Care was given to minimize the thickness of the interfacial carbide layer. The inset shows the high shear band density in the matrix achieved for this composite.

4.2.4 Discussion

In addition to the common methods of tailoring the mechanical properties of metal matrix composites [25] such as varying particle size, shape, hardness and volume fraction we have found a way of adjusting the mechanical properties of these BMG composites by merely varying the processing parameters. The formation of the interfacial carbide layer shown in Fig. 4.2.2 is of course temperature dependent, as is shown by the XRD scans in Fig. 4.2.1. Since Zr is the element in the matrix with the most negative enthalpy of formation with graphite [27] (H_{fo}=-106 kJ/mol followed by -77 kJ/mol for Ti), ZrC is formed. Smaller graphite particles of 10 μm can lead to complete transformation of the graphite particles into ZrC, as has been reported in Refs. [14,17,18]. We did not observe complete transformation of any graphite particles. In our case the carbides start growing in the matrix-particle interface forming a hard shell around the graphite particles. Interfacial carbide formation is favored because of the short diffusion paths necessary. The few ZrC particles that appear to be growing in the matrix in Fig. 4.2.2 are expected to be growing on graphite particles.
lying below the polished surface. The formed ZrC layer acts as a diffusion barrier and slows the carbide formation in the interface controlling the reaction. It is expected that strong stirring of the melt could lead to complete reaction of graphite to ZrC because the evolving ZrC would be separated from the graphite allowing further carbide reaction in the interface. This will indeed be shown in Chapter 4.3.

The thin interfacial carbide layer leads to a significant increase in hardness compared to the standard graphite composites. If we consider the graphite particles as spheres of 35 μm and the graphite layer as an interfacial layer of 1.5 μm, composites containing 5 vol.% graphite contain less than 0.7 vol.% ZrC. Due to this layer we observe an increase in hardness of about 16% compared to the composite with 5 vol.% graphite and minimal carbide formation. This phenomenon cannot be explained by Ashby's rules of mixing [28] because of the geometrical particularities of the carbide surrounding the graphite particles. If we consider the graphite particle with the hard carbide shell around it as a monolithic reinforcement particle, it will display similar mechanical properties like a hard-boiled egg. At low stress, it will be very stiff. If higher stress is applied, the shell will break and it will act like a soft particle. The stress value necessary to "crack the shell" is of course determined by the thickness of the carbide layer but also by the shape and size of the graphite particle. At very low reinforcement, graphite leads to a strong decrease in hardness whereas the composites with the carbide layers show a slight increase, as we would expect for a matrix reinforced with hard particles. At higher reinforcement contents, the hardness of the composites with an interfacial carbide layer also starts to decrease and the soft graphite seems to become dominant. It is expected that when hardness testing is conducted on samples with low graphite volume content the hard particles are pushed into the soft matrix relieving stress on the particles, whereas at high volume contents they hinder each other and are exposed to enough stress to crack the carbide shells and the graphite becomes dominant.

The thickness of the interfacial carbide layer also has a significant influence on the stress-strain behavior of the composites, as can be seen in Fig. 4.2.4. As we have shown in Ref. [19], soft graphite particles with a low Young's modulus are favorable in achieving high plasticity in compression. However, if the interfacial carbide layer
around the particle becomes thicker, the hard layer will make the particle act like a hard ceramic particle instead of a soft graphite particle. The carbide layer that has a Young’s modulus of about 400 GPa compared to 100 GPa of the matrix material leads to tensile stress concentration in the particle matrix interface which hinders splitting up of shear bands. In addition, the high hardness of the carbide layer (about 2500 HV compared to 15 HV of graphite) hinders the absorption of approaching shear bands but deflects them, leading to fracture on one or a few bands.

In order to maximize plasticity, it is obvious that the carbide layer must be kept as thin as possible. Even in samples processed at the lowest possible energy input where casting is still possible some ZrC was detected in XRD. Not being able to fully eliminate the carbide layer it is still possible to weaken the strength of a carbide shell by increasing the particle size. If we once again approximate the particles as a soft sphere with a hard shell around it, a shell of the same thickness will carry less load if the sphere is larger. As can be seen in Fig. 4.2.5 larger graphite particles lead to very high plasticity at low reinforcement volume fractions. Samples with 3.5 vol.% particles of 25-44 μm display only about 7% plasticity [19] compared to up to 18.5% with 45-75 μm particles. This low volume content of graphite leads to only a slight reduction of yield strength compared to the monolithic alloy.

4.2.5 Conclusions

We have shown that the mechanical properties of BMG-graphite composites can be tailored elegantly by adjusting the energy input before casting. A higher energy input leads to a thicker reaction layer in the matrix-particle interface. The very hard interfacial ZrC layer leads to higher hardness of the composite but also to more brittle fracture behavior. By minimizing the thickness of the carbide layer and using larger graphite particles 18.5% plasticity and a yield strength of 1.85 GPa were achieved.

4.2.6 References


4.3 Micro-tribological properties of graphite- / ZrC-reinforced bulk metallic glass composites

Abstract

The influence of second-phase reinforcement on the micro-tribological properties of Zr_{52.5}Cu_{17.6}Ni_{14.5}Al_{10}Ti_{5} (Vit 105) was investigated by ball-on-disc tests. It was found that monolithic amorphous Vit 105 displays a coefficient of friction (COF) similar to that of 100Cr6 bearing steel. Further, it was seen that a low volume content of graphite and especially of ZrC leads to a significant decrease in the COF, of up to 50%. Amorphous Vit 105 and its graphite-/ZrC-reinforced composites typically display two regimes of COF. After 100-500 revolutions it drops to about 2/3 of the starting value; jumps back up to the initial COF are also observed. These transitions take place within the space of about 10 revolutions and are accompanied by a significant change in wear track depth. Investigation of the wear rate indicated that the graphite-/ZrC-reinforced bulk metallic glass composites display an even lower wear rate than 100Cr6 bearing steel.

4.3.1 Introduction

Many amorphous metallic alloys with good glass-forming ability have been developed over the last few years (for reviews see [1,2,3]). Unfortunately, the high

---

5 M. E. Siegrist, E. D. Amstad, J. F. Löfler; submitted to Intermetallics
strength of these bulk metallic glasses (BMGs) cannot be fully exploited due to the alloys' brittle fracture behavior: they tend to deform along one or more highly-localized shear bands [4,5,6,7,8]. This has stimulated the development of many in-situ [9,10,11,12,13] and ex-situ [14,15,16,17,18] BMG composites, which have been shown to significantly improve plasticity of BMGs. The mechanical properties of such BMG composites have been thoroughly investigated; however, very little attention has so far been paid to their tribological properties. Even those of monolithic amorphous alloys are not yet fully understood (for an overview see [19]).

Due to the lack of plasticity in amorphous alloys, micro-cracking is considered to be their main wear mechanism [20]. Micro-cracking is more prevalent if crystals are present in the amorphous matrix, because they may act as crack nucleation sites. This is especially relevant because conventional metallic glasses have been shown to display local crystallization of the wear surface [21] and debris [22] due to frictional heat. BMGs have been put forward as displaying either worse [23] (especially under lubricated conditions) or better [24] wear resistance than commercial steel.

One way of altering the tribological properties of a system is to change the contact surface on a microscopic scale. In metallic glasses, the contact surface can be significantly influenced by adding second-phase particles which possess a different hardness than the amorphous matrix. We have chosen graphite as a reinforcement phase because of its superlubricity [25] and the possibility of in-situ formation of very hard ZrC particles in Zr-based BMGs [11]. In addition, graphite reinforcement of crystalline Al-Si alloys has been shown to significantly decrease both the coefficient of friction (COF) and the wear rate of the alloy at low contact loads [26].

In this contribution we compare the tribological properties of two different BMG composites (a Zr52.5Cu17.9Ni14.6Al10Ti5 (Vit 105)-graphite composite [18] and a novel three-phase composite with graphite and ZrC in a Vit 105 matrix) with those of the monolithic BMG and 100Cr6 bearing steel. We show that the COF of the metallic glass can be significantly decreased by adding the (graphite and ZrC) reinforcement phases. The low COF and the very high compressive yield strength (~1.8 GPa) of these composites make them potential candidates for self-lubricating friction-bearing materials.
4.3.2 Experimental

4.3.2.1 Processing

Pre-alloys with atomic composition $\text{Zr}_{52.5}\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}\text{Ti}_5$ (Vit 105) were prepared in a Bühler AM system by arc melting the high-purity elements (> 99.95%) in a 300 mbar Ar 6.0 atmosphere. The subsequent composite preparation took place in a 1200 mbar Ar 6.0 atmosphere. 2-13 vol.% conducting-grade graphite with a particle size of 25–44 μm was induction-mixed with the pre-alloy in a water-cooled “silver boat”. The crystalline composites were then suction-cast into 2 mm × 7 mm × 30 mm platelets in a Bühler MAM1 arc melter at a setting of 1 (0.35 kW) producing Vit 105-graphite composites, or at a setting of 2 to 3 (0.65 kW to 1.4 kW) producing Vit 105-graphite-ZrC composites (with the ZrC being present at the interface). Multiple remelting and suction-casting of these Vit 105-graphite-ZrC composites led to three-phase composites with graphite and ZrC present as particles in a Vit 105 matrix. Monolithic BMG samples were prepared without the induction mixing step, and one sample was fully crystallized by annealing at 430°C for 75 min. Hardened 100Cr6 bearing steel (846 HV) was used as a reference sample.

4.3.2.2 Tribological characterization

The tribological properties of the material were investigated on a CETR microtribometer, where the sample was paired against a bearing steel ball with a diameter of 2 mm at a constant sliding speed of 100 mm/min without lubrication. Before measurement all samples were ground and polished with a 0.05 μm Al$_2$O$_3$ dispersion.

The vertical force of the ball on the sample ($F_z$) was held constant during the test and the frictional force ($F_x$) and the change in track depth were recorded (see schematic in Fig. 4.3.1a).
Fig. 4.3.1  a) Schematic of the ball-on-disc tribometer used for micro-tribological investigation. A fixed bearing steel ball with a diameter of 2 mm is pressed on top of a rotating sample using a constant force (Fz). The frictional force (Fx) and the change in ball height were recorded. b) SEM images giving an overview of the various wear tracks made on a Vit 105-graphite composite containing 8 vol.% graphite using different parameters.

The COF was obtained by dividing the frictional force (Fx) by the vertical force (Fz). All tests were run at room temperature at a relative humidity of about 40%. First, the ball was run in for 100 revolutions at a 5 N load. The test runs were performed with 100 revolutions at a 5 N load and 10, 100 and 1000 revolutions at a 1 N load. The steel ball was run in at a radius of 2.9 mm and the radius was reduced by 0.4 mm for each of the following tests, as can be seen in Fig. 4.3.1b. The high COF regime was determined by approximating the force data obtained in the 100-revolution tests with an exponential relaxation function. In the steel sample the 1000-revolution data was used because the COF was not yet in equilibrium after 100 revolutions due to the steel sample’s oxide layer. In samples displaying two COF regimes in the 1000-revolution tests, the lower was determined by averaging the values of the lower shelves.

4.3.2.3 Thermophysical and optical characterization

The samples were further characterized by X-ray diffraction (PANalytical X’Pert diffractometer with Cu-Kα radiation), energy dispersive x-ray diffraction (CamScan scanning electron microscope equipped with a Noran Energy Dispersive X-ray detector), high-resolution scanning electron microscopy (SEM) (Zeiss Gemini 1530 FEG); and optical microscopy (Reichert-Jung Polyvar Met microscope). The graphite
volume content of the tribology surfaces was determined by analyzing the optical micrographs (Leica QWin software).

4.3.3 Results

4.3.3.1 Thermophysical properties of various composite types

The microstructure of graphite-reinforced BMG composites can be tailored by adjusting the processing parameters. As seen in Fig. 4.3.2a-c, we have produced three types of BMG composites: (a) Vit 105-graphite composites as described in Ref. [18], which show a clean graphite-matrix interface; (b) Vit 105-graphite-ZrC composites with an interfacial ZrC layer of about 2 µm (obtained by increasing the processing temperature in the final casting step); and (c) three-phase composites with graphite and ZrC particles in the Vit 105 matrix (obtained by multiple remelting and casting of Vit 105-graphite-ZrC composites). All the composites display a homogeneous particle distribution, as seen for example in Fig. 4.3.1b.

Fig. 4.3.2 Optical micrographs of (a) Vit 105-graphite composite; (b) Vit 105-graphite-ZrC composite (with only interfacial ZrC); and (c) three-phase composite (graphite and ZrC particles in a Vit 105 matrix).

Fig. 4.3.3 shows XRD scans of the three types of composites, all with 7 vol.% graphite. The Vit 105-graphite-ZrC composite and the three-phase composite display ZrC peaks of similar intensity, while the Vit 105-graphite composite displays almost no carbide formation. All composites show a significant amorphous background. The Vit 105-graphite composites and the three-phase composites were used further for tribological testing.
Fig. 4.3.3 XRD scans of the three composite types shown in Fig. 4.3.2: Vit 105-graphite composite; Vit 105-graphite-ZrC composite (with only interfacial ZrC formation); and three-phase composite (graphite and ZrC particles in a Vit 105 matrix) with 7 vol.% reinforcement.

Fig. 4.3.4 shows XRD scans before and after tribology tests of a three-phase composite, and a Vit 105-graphite composite with 3 and 4 vol.% graphite, respectively. A comparison of XRD scans performed on the sample plates of both BMG composite types before and after tribological testing shows no significant changes, suggesting that no crystallization of the wear track or debris took place.
Fig. 4.3.5a-e show a comparison of the COF (black data) and wear trace depth (grey data) in 1000-revolution tests conducted with a 1 N load on (a) amorphous Vit 105; (b) crystalline Vit 105; (c,d) three-phase composites with 3 and 7 vol.% graphite; and (e) 100Cr6. All the samples tested for 1000 revolutions showed an increase in wear track depth, with the exception of amorphous Vit 105 (Fig. 4.3.5a), which showed a decrease in track depth due to debris agglomerating between the steel ball and the wear track (pin-lifting phenomenon). Crystalline Vit 105 (Fig. 4.3.5b) and the three-phase composites (Fig. 4.3.5c and Fig. 4.3.5d) showed a more or less linear increase in track depth (with a similar increase of about 5 μm after 1000 revolutions), whereas the bearing steel (Fig. 4.3.5e) displayed a faster increase in track depth during the first 200 revolutions than during the remainder of the test. In contrast to the three-phase composites and crystalline Vit 105, the 100Cr6 steel showed a track depth of about 13 μm after 1000 revolutions. The fluctuations in wear track depth seen in 100Cr6 and crystallized Vit 105 in particular are due to the non-parallel installation of
the samples in the testing rig, and are of no tribological significance, whereas the jumps in amorphous Vit 105 are related to the pin-lifting phenomenon.

Fig. 4.3.5 COF (black) and pin height (grey) during 1000-revolution tests at 1 N load on (a) monolithic amorphous Vit 105; (b) monolithic fully crystalline Vit 105; (c) three-phase composites with 3 vol.%; (d) three-phase composite with 7 vol.% graphite; and (e) 100Cr6 hardened bearing steel.

It took about 200 revolutions at a load of 1N for the 100Cr6 bearing steel sample to reach a steady COF state (see black data in Fig. 4.3.5e). This did not apply to the other tested materials, which all reached a steady state within < 20 revolutions. The
amorphous Vit 105 (Fig. 4.3.5a) and the three-phase composites (Fig. 4.3.5c and Fig. 4.3.5d) display two significant COF regimes. This is not the case for crystalline Vit 105 (Fig. 4.3.5b) or 100Cr6 (Fig. 4.3.5e). The samples showing two COF regimes are in the high regime at the beginning of the test and drop to the lower one after 100-400 revolutions. Jumps from the lower regime of COF to the higher regime were observed in the three-phase composites with more than 3 vol.% graphite, as shown in Fig. 4.3.5d.

The three-phase composites show smaller COF fluctuations in the lower regime than in the higher, whereas amorphous Vit 105 displays very high fluctuations in both regimes. Crystalline Vit 105 and 100Cr6 both display small fluctuations in COF. In general, it was found that the Vit 105-graphite composite and especially the three-phase composites showed smaller COF fluctuations with increasing graphite content.

Sections with jumps from high to low and low to high regimes of the COF are shown in Figs. 7a and 7b, respectively, for the three-phase composite with 7 vol.% graphite (Fig. 6d). The jump from the high to low COF regime takes place within the space of about 10 revolutions, whereas the jump back up takes place within about 2 revolutions. In both cases the jumps are accompanied by a significant change in track depth, of about 2 μm. The track depth decreases when the COF drops and increases when the COF rises.

Fig. 4.3.6 Graph showing transition from (a) high to low regime and (b) from low to high regime of COF (black) and the associated change in track depth (grey) for the three-phase composite with 7 vol.% graphite shown in Fig. 4.3.5d.
Fig. 4.3.7 shows the COF measured in 100-revolution tests using a load of 1 N for (a) amorphous Vit 105; (b) crystalline Vit 105; (c) Vit 105-graphite composite with 8 vol.% graphite; and (d) three-phase composite with 8 vol.% graphite. The raw data (black) was approximated by an exponential relaxation function (grey). It can be seen that amorphous Vit 105 (Fig. 4.3.7a) displays the highest COF, followed by crystalline Vit 105 (Fig. 4.3.7b) and the Vit 105-graphite composite (Fig. 4.3.7c), which display similar values, and the three-phase composite (Fig. 4.3.7d), which has the lowest COF. As in the 1000-revolution tests, amorphous Vit 105 displays large fluctuations in the COF compared to crystalline Vit 105 and the three-phase composite. The Vit 105-graphite composite displays fluctuations similar to those of monolithic amorphous Vit 105.

Fig. 4.3.7 COF during 100-revolution tests for (a) monolithic amorphous Vit 105; (b) monolithic crystalline Vit 105; (c) Vit 105-graphite composite with 8 vol.% graphite; and (d) three-phase composite with 8 vol.% graphite. The raw data was approximated with an exponential relaxation function (grey curve) to determine the COF.
Fig. 4.3.8 gives an overview of the COF-graphite content relationship for Vit 105-graphite composites and three-phase composites at a load of 1 N. The high and low regimes of friction were determined from the 100 and 1000 revolutions tests, respectively. In the high COF regime the amorphous monolithic alloy shows a COF of about 0.8, which is comparable to that measured for the 100Cr6 bearing steel (0.78). As seen in Fig. 4.3.8, the reinforcement of the monolithic glass with very low volume contents of graphite generates a significant decrease in COF, especially in the case of the three-phase composites, which show about twice the decrease in COF than that seen in the Vit 105-graphite composites for the same reinforcement fraction. In the lower regime of friction, monolithic Vit 105 displays a COF of about 0.48. A reinforcement content of only 3 vol.% graphite generates a decrease of COF to about 0.15 in the three-phase composite, while the three-phase composites with 7, 8 and 9 vol.% graphite show a slightly higher COF of about 0.23. In the tests conducted with a 5 N load (not shown), only the higher regime of friction was investigated, because no 1000-revolution tests were performed; no significant difference in the effect of graphite reinforcement was found compared to the tests run at a 1 N load.

![Fig. 4.3.8 COF as a function of graphite content for Vit 105-graphite composites and three-phase composites. The upper and lower regimes of COF are shown for monolithic Vit 105 and three-phase composites.](image-url)
Fig. 4.3.9 shows SEM images of the three-phase composites after the tribology tests. A few shear bands were found at the edge of the wear traces after 1000 revolutions at a 1 N load, as can be seen in Fig. 4.3.9a. The shear bands, which give evidence of high stress leading to inhomogeneous flow, run about 25° to the sliding direction. In some of the composite samples smeared matrix material was found in the wear trace, as shown in Fig. 4.3.9b. This probably comes from deformation in the undercooled liquid region caused by local frictional heating and shear in the wear tracks. No micro-cracking was observed in the wear tracks of any of the tested materials.

In general, very little smearing of graphite was observed in the composite samples. We found by SEM investigation of 1 N wear tracks that entire graphite particles were ripped out of the 1000-revolution tracks but not from the 100-revolution track, meaning that the first particles came out after > 100 revolutions. Fig. 4.3.10a shows the hole left by a graphite particle torn from a composite sample after 1000 revolutions at a 1 N load. A lot of debris is visible in the hole. The three-phase composite samples show several channels in their wear tracks, as seen in Fig. 4.3.10b. Fig. 4.3.10c shows the surface of the steel ball after a complete test on a three-phase composite. Several small particles with a size of between 50 and 500 nm were found on the surface of the steel ball, and are thought to be ZrC debris because they were only observed after tribology tests on the three-phase composites.
Fig. 4.3.10 SEM images showing (a) holes left by ripped-out graphite particles found in all three-phase composites after 1000 revolutions at a 1 N load; (b) channels in the wear traces of three-phase composites; and (c) small ZrC particles found on the steel ball used for the wear tests of the three-phase composites.

A comparison of the width and depth of the wear tracks provides a qualitative approximation of the wear rate. The narrowest wear track, with about 50 μm after 1000 revolutions at a 1 N load, was seen for crystalline Vit 105, and the widest, with about 200 μm, for the hardened steel. No significant difference was detected between those of amorphous Vit 105 and its composites, which all displayed trace widths of about 120 μm. The depths of the wear tracks are difficult to compare because of the observed pin-lifting phenomena in amorphous Vit 105. However, we found that the wear tracks of the three-phase composites after 1000 revolutions at a load of 1 N are less deep than those of the bearing steel, as shown in Fig. 4.3.5c,d and e and confirmed by SEM analysis. The depths and widths of the wear tracks do not correlate with the hardness values of the monolithic materials, which are 846 HV, 547 HV and 478 HV for the bearing steel and crystalline and amorphous Vit 105, respectively.

4.3.4 Discussion

4.3.4.1 Tailoring of composite microstructure

We have shown that the microstructure of the graphite-reinforced BMG composites can be tailored by adjusting their processing parameters. The literature documents that ZrC can be formed by adding small graphite particles to a Zr-based BMG, leading to in-situ composite formation [11,27,28]. By using larger graphite particles (> 25 μm instead of typically < 10 μm for in-situ composite formation) and adjusting the processing temperature we can develop Vit 105-graphite composites.
(Fig. 4.3.2a) without an interfacial reaction, or Vit 105-graphite-ZrC composites (Fig. 4.3.2b) with interfacial carbide formation.

The three-phase composites shown in Fig. 4.3.2c are produced by multiple remelting and suction-casting of the composites with interfacial carbides. We believe that part of the interfacial ZrC is torn from the graphite particles by the suction casting process due to the high flow rate of the melt through the small opening of the mold, and that it is distributed homogeneously within the melt. Multiple repetition of this procedure leads to a higher ZrC content in the matrix. Even though the ZrC formation causes depletion of Zr in the matrix, these composites still display an amorphous matrix at a casting thickness of 2 mm as shown in the XRD results of Fig. 4.3.3 and Fig. 4.3.4.

4.3.4.2 Frictional properties of Vit 105

In the high COF regime, amorphous Vit 105 displays a similar COF as 100Cr6 bearing steel (see Fig. 4.3.5a and e); however, the metallic glass shows much stronger fluctuations of COF. These fluctuations are due to stick-slip of the steel ball on the metallic glass. Stick-slip is common in materials where the static COF is significantly higher than the kinetic COF. We observed this in a Vit 105 sample by placing it on a steel plate and varying the incline. A very steep incline was needed to start the sliding of the sample; however, once it was in motion a much smaller incline was sufficient for it to continue. In amorphous Vit 105, the stick-slip observed may also be attributed to the special mechanical properties of the metallic glass. Because of the low stiffness and high elastic strain of metallic glasses, the glassy Vit 105 alloy is expected to have a higher surface roughness than bearing steel or crystalline Vit 105 after grinding and polishing. Additionally, in an elastic, high-strength material the steel ball may be increasingly hindered by edges in the wear track, whereas in materials displaying little elastic strain or low strength these edges will be worn off. Thus both effects support the observed stick-slip phenomenon.

There are two possible explanations for the pin-lifting phenomenon, observed especially in the high COF regime in amorphous Vit 105 (see Fig. 4.3.5a). First, debris
accumulated in the wear track may get stuck between the steel ball and the amorphous matrix, lifting the steel ball off the wear surface. Second, local material smearing may lead to the material pile-up observed mainly on the edges of the wear tracks (as shown in Fig. 4.3.9b for a composite sample). This material pile-up looks like a decrease in wear track depth on a macroscopic scale. Such smearing is expected to take place in the undercooled liquid region, which is extensive in the matrix material [29] and even larger than in the monolithic alloy [18]. Due to the very low sliding speed the smeared material is cooled by heat transfer to the bulk of the sample before the next revolution takes place. The cooling rate appears to be fast enough to hinder local crystallization: in contrast to work on conventional metallic glasses [21,22], we found no hint of crystallization in the wear track or debris for any of the samples tested (see XRD scans in Fig. 4.3.4).

The local stress on the sample during the tribology tests can be very large, even exceeding the yield stress of the matrix. This renders plausible the large amount of smearing of the matrix material. If we consider the contact surface to be a circle with the diameter of the wear track (120 μm), the global stress would be about 90 MPa at a 1 N load. If, however, we further consider that very small debris may lie between the ball and the sample, the contact surface will decrease significantly, generating very high local stress which could easily exceed the flow stress of the matrix material (about 1.9 GPa at room temperature). This further supports the possibility of deformation in the undercooled liquid region. Such high stresses also explain the shear banding observed next to the wear track, as shown for the three-phase composite in Fig. 4.3.9a. In this region inhomogeneous deformation (shear banding) is favored because no direct frictional heating takes place and the material temperature lies well below the glass transition temperature (Tg). Homogeneous deformation, in contrast, is more prevalent in the frictionally heated wear track, where the temperature is estimated to rise locally above Tg, allowing deformation at lower stresses (work softening). In contrast to the mechanism in metallic glasses, in 100Cr6 a decrease in the apparent wear track depth rate is observed after about 200 revolutions (see Fig. 4.3.5e). This is attributed to work hardening of the steel, leading to a more wear-resistant surface.
The two regimes of COF observed in the 1000-revolution tests for amorphous Vit 105 are clear evidence of two different sliding mechanisms. They may be attributed to the geometrical particularities of the sliding contact between the steel ball and the metallic glass in the micro-tribology experiments, as shown in Fig. 4.3.11. Within our model the ball plows through debris and rough edges in the wear track in the high COF regime, whereas in the low COF regime the ball is lifted onto the smeared material piled up on the edges of the track. This leads to a smaller contact area, reducing plowing and the adhesive component of friction (see also Ref. [30]). This model can also explain the apparent decrease in wear track depth associated with the drop in the COF. The COF in the low regime of friction is slightly lower than what we observed for crystalline Vit 105, which, like 100Cr6, displays no COF jumps.

Fig. 4.3.11 Schematic of steel ball on wear sample during tribological testing for the high and low COF regimes.

4.3.4.3 Influence of reinforcement phases on frictional properties

As we have shown, reinforcement of Vit 105 leads to a significant change in tribological behavior. Graphite reinforcement generates a significant decrease in COF (see Fig. 4.3.8). Graphite is known to lower the COF of tribological partners in metallic [26] and polymer-based [31] materials. In metallic systems, graphite sticks especially well to oxidized surfaces [25] (present on the surface of Zr-based BMGs...
[32] and steel). If graphite sticks to the surfaces of both tribological partners, graphite actually slides on graphite on a microscopic scale, which produces a very low COF. We also observed that debris were pushed into the soft graphite particles or the holes left by ripped-out particles (see Fig. 4.3.10a). This is expected to cause less abrasive wear and to additionally lower the COF.

The three-phase composites, which were also tested for 1000 revolutions at a 1 N load (see Fig. 4.3.5c and Fig. 4.3.5d), also display two regimes of COF as observed for amorphous Vit 105. Thus we expect a similar ball-lifting mechanism to take place. In comparison to the monolithic amorphous alloy we have shown that reinforcement of Vit 105 with graphite and ZrC (three-phase composites) leads to even further decrease of the COF in the high and low regimes (see Fig. 4.3.8). In the regime of high COF strong fluctuations are present. This was also observed for the monolithic matrix material and Vit 105-graphite composites, which indicates that the sliding mechanism is similar. However, once the COF drops to the lower regime the COF fluctuations decrease drastically, which does not happen in amorphous Vit 105. This may be because the hard ZrC debris produce a smoother wear surface here than in the monolithic alloy.

The channel-like morphology of the wear tracks observed in the three-phase composites shown in Fig. 4.3.10b stands in contrast to the relatively smooth wear tracks found in Vit 105-graphite composites or the monolithic matrix material (not shown). Due to the very high strain rates achieved on a microscopic scale during sliding (~10^5 s^-1) it is unlikely that the channels are formed by inhomogeneous deformation of the matrix material but rather by local abrasion of the matrix material by ZrC debris. Very small particles, probably ZrC debris, were found on the steel ball used for these tests (see Fig. 4.3.10c). It is expected that larger ones were also present but fell away due to their lower surface-to-weight ratio. Once a shallow channel has formed, debris will remain in the channel and cause local abrasion, deepening it. The lower COF observed in the three-phase composites compared to Vit 105-graphite composites is expected to be due to the special geometry of the wear tracks, which generates a less extensive contact surface between the steel ball and the composites. The smaller contact surface has two effects: first, it reduces the adhesive component of
friction between the steel ball and the composite; and second, it produces higher local stress in the sliding contact, which may cause a smoothing of the sliding surface. The COF in the three-phase composites may be further reduced by bearing-like behavior on the part of the small, round carbide debris particles (see Fig. 4.3.10c) in the wear track channels.

The fact that very low reinforcement contents are sufficient to lower the COF in both types of composite is further evidence that the mechanisms are not based on the bulk material pairing, but rather on the influence of second-phase debris on dynamic contact during sliding. In both composites graphite acts as a lubricant and a debris trap. In the three-phase composites, ZrC debris additionally leads to channel formation, drastically changing the sliding contact of the tribological system.

4.3.4.4 Wear rate

In contrast to Ref. [20], we observed no micro-cracking in the wear tracks of any of the amorphous materials. This supports the idea that the main wear mechanism in amorphous Vit 105 is the plowing of the amorphous material in the undercooled liquid region, and the additional tearing out of reinforcement particles in the Vit 105 composites.

Due to various wear mechanisms which lead to different wear track morphologies, it is very difficult to compare the wear rates of the materials investigated. However, an analysis of the data from the 1000-revolution tests and the SEM images taken thereafter show that the width of the wear tracks and the measured depths of the wear traces are smaller in the three-phase composites than in 100Cr6 bearing steel. This is evidence that the wear rate of the newly-developed three-phase composites is, in the micro-tribology testing setup used, lower than that of commercial bearing steel. This is due at least partially to the self-lubricating effect of graphite and the debris deposited in the holes left by torn-out graphite particles, both of which may lead to less abrasive wear.
4.3.5 Conclusion

The microstructure of graphite-reinforced Vit 105 can be tailored by adjusting the processing parameters. This procedure also led to the development of a novel three-phase composite with graphite and ZrC in a fully amorphous Vit 105 matrix (as confirmed by XRD).

It was found that amorphous Vit 105 and all of its composites display two regimes of COF, and that the COF in the lower regime drops to about 2/3 of its initial value. This phenomenon was not observed either in crystalline Vit 105 or in bearing steel. The presence of two COF regimes was explained by an alteration in the wear track geometry via smearing of the matrix material in the undercooled liquid region. We also found that graphite and especially ZrC reinforcement generate a significant decrease in the COF, of up to 50% compared to the monolithic alloy.

A qualitative comparison of the wear rate provides evidence that the graphite / ZrC composites developed in this study show even lower wear rates than commercial 100Cr6 bearing steel used as a reference material. These improved tribological properties and the high yield strength of the composites make them promising candidates for dry frictional bearing material.

4.3.6 References


Seite Leer / Blank leaf
This final chapter gives an general conclusion on the presented research. Further, the future of bulk metallic glasses as a structural material is discussed.
5.1 General conclusion

In conclusion we have developed several novel types of bulk metallic glass composites, namely diamond-reinforced and different types of graphite-reinforced composites. In the case of graphite-reinforced BMG composites we have shown that the microstructure and herewith the mechanical properties can be directly tailored by adjusting the processing parameters.

5.1.1 Diamond-reinforced bulk metallic glass composites

Diamond-reinforced metallic glass composites were produced by means of powder consolidation and melt processing. The first step in the consolidation route was the production of amorphous powder for the matrix material. We have shown that amorphous $\text{Zr}_{52.5}\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}\text{Ti}_5$ powder with very low oxygen content can be produced with a high yield when starting from crystalline pre-alloys. By thermophysical characterization of the powder we found that the amorphization rate follows an exponential relaxation function. Further, we were able to determine a processing window for consolidation in the undercooled liquid region. Even though we did not have adequate consolidation equipment, we attempted to consolidate the powders in order to see if they would bond at all. We did not succeed in densely consolidating the composite powder because our pressing set up did not allow sufficient temperature control and pressure. Local densification was found by SEM hinting that dense bulk consolidation may be possible with the achieved low oxygen content in an adequate press.

Bulk samples produced by melt processing displayed an amorphous matrix; however, they showed strong agglomeration of diamond particles. It is thought that this is due to insufficient wetting of the Zr-based melt on the diamond. Homogeneous composites could only be produced in very small dimensions, for instance by a particle floatation technique. We found that even a low volume content of diamond particles in the BMG led to a significant increase in hardness.
5.1.2 Graphite-reinforced bulk metallic glass composites

We have shown that graphite reinforcement of Zr$_{52.5}$Cu$_{17.3}$Ni$_{14.6}$Al$_{10}$Ti$_5$ BMG leads to a significant increase in plastic strain under compression. A maximal plastic strain of 18.5% in combination with a yield strength of 1.85 GPa was achieved with only 3.5 vol.% reinforcement content. To our knowledge this is the highest combination of yield strength and plasticity ever reported in foreign-particle-reinforced BMGs and one of the highest combinations reported in any type of BMG.

Further, we have tailored the microstructure of the composites by adjusting the processing parameters. Casting at a higher temperature leads to interfacial ZrC formation in the particle-matrix interface which results in higher hardness but lower plasticity compared to the composites without interfacial ZrC. This insight led to the development of a novel three-phase composite with graphite and in-situ formed ZrC in the amorphous matrix.

By studying the micro-tribological properties of the graphite-reinforced BMG composites we found that graphite and especially ZrC reinforcement lead to a significant decrease in the coefficient of friction and to a reduction of the wear rate compared to the monolithic alloy. With this new insight and because of their high yield strength, graphite-reinforced BMGs are thought to be a promising material for dry frictional bearings.
5.2 General outlook

It is clear that the only way to achieve the technological breakthrough of metallic glasses as a structural material is by conquering the obstacle of its intrinsic brittleness. Within this thesis we have presented a method of significantly improving the plastic strain of BMGs under compression by graphite-particle-reinforcement. Even though similar mechanical results have been presented before with other methods (apart from particle reinforcement), this contribution is of great value because of the good processibility and reproducibility of theses composites. However, the problem of limited tensile plastic strain remains and needs to be solved before metallic glasses will be accepted as a structural material for daily applications.

5.2.1 Diamond-reinforced bulk metallic glass composites

Even though we could not achieve a homogeneous particle distribution in bulk diamond-reinforced samples, we believe that such composites may have a very large potential as a cutting tool material due to the excellent adhesion of the diamond particles in the matrix. Possibly a more homogeneous particle distribution could be achieved by modifying the surface of the diamond particles and thus improving the wetting behavior. Since graphite particles have been shown to be distributed quite easily in the Zr-based melt, surface graphitization by annealing might improve the wetting properties and thus lead to a more homogeneous distribution of the diamond particles.

5.2.2 Graphite-reinforced bulk metallic glass composites

We have shown that graphite reinforcement is a promising approach for improving the plasticity of metallic glasses, at least in compression. Additionally graphite and especially ZrC reinforcement leads a lower coefficient of friction and wear rate compared to the monolithic alloy when paired against bearing steel. These interesting micro-tribological properties compared with the high yield strength predestine this composite for use in dry friction bearings. In a next step the results of
the micro-tribological test should be confirmed on the macro scale (for instance by pin on disc tests using larger samples) followed by testing of prototype bearings.

5.2.3 The question of tensile plasticity

After all the achievements in improving compressive plastic strain over the past five years, the problem of limited tensile plasticity still remains. The question which has to be asked is: "Can metallic glasses or metallic-glass-based composites ever display significant plastic strain under tensile loading, or is this not in agreement with the general deformation mechanism in metallic glasses?"

Shear bands are a lot more stable under compression than tension because under compression the compressive normal force on the shear band retards their propagation. In order to achieve plastic strain under tensile conditions, the tensile normal force opening the shear bands must be compensated. Two possible approaches are presented in the following subchapters.

5.2.3.1 Hindering shear band propagation under tensile stress by wire-reinforcement

One possibility of achieving tensile plasticity in BMG composites may be by hindering shear band propagation by wire reinforcement. If the bonding between the reinforcement wires and the matrix material is good, wires running across the shear band will hinder opening and offsetting of the band as is shown in Fig. 5.2.1 for one wire in a volume of metallic glass under tensile loading. If the wires are capable of arresting the propagation of a shear band, this could lead to an increase of the shear band density and herewith higher plastic strain.
This sounds promising, however, one must consider that the stress on a single wire in the vicinity of a shear band is enormous. Also, the schematic does not reflect the dimensions correctly; in reality the opening of the shear band (< 1 μm) is much smaller than the thickness of a typical reinforcement wire (> 10 μm), leading to shear and not tensile stress in the wire. Experiments with unidirectional tungsten and steel wire reinforced Vit 1 (wire diameter ~250 μm) led to very limited plastic strain under tensile conditions [1].

Nevertheless, the propagation of shear bands might be hindered under the following considerations. Perfect wire-matrix bonding is necessary so that the high stresses in the shear bands can be transformed into the matrix and the wires should display a Young’s modulus similar to that of the matrix material to avoid interfacial cracking and wire pull-out. Further, a high volume content of entangled reinforcement wires with various orientations might help overcome the problems of fiber fracture and pull-out. For this reason a metallic glass composite reinforced with a mesh-like wire structure is being developed in our lab.

5.2.3.2 Thought experiment: Hindering shear band propagation under tensile stress by initiating local compressive forces by volume change

It has been mentioned several times within this thesis that shear bands preferably propagate under tensile stress. If a metallic glass under tensile loading was to have local regions with compressive stresses, it is thought that the shear bands would avoid
these regions and propagate around them. However, if a mechanism was found that constantly generates compressive stress fields at the tip of a propagating shear band, its propagation would be arrested.

A similar mechanism is known for hindering of crack propagation in partially stabilized zirconia (PSZ) [2]. In this ceramic a stress-induced martensitic phase transformation takes place around the crack tip; namely, from the metastable tetragonal phase to the monoclinic structure. This phase transformation is associated with a volume increase of about 7% leading to a compressive stress field around the crack tip hindering its propagation. Unfortunately in the case of metallic glasses any transformation from the metastable amorphous phase to a more stable crystalline phase will be associated with a volume decrease, leading to tensile stress fields.

5.2.4 Metallic glass as a structural material?

The advantages of metallic glasses as a structural material in comparison to traditional crystalline alloys are evident due to their high strength and elasticity.

Will tensile plasticity ever be achieved in bulk metallic glasses? Considering the points mentioned in this thesis, it doesn’t look good as long as shear banding is the dominating deformation mechanism. Maybe we should just live with the properties of BMGs like they are, because many applications are possible. However, if we consider the development in the field of metallic glasses over the past 45 years, we are apt to be up for more surprises. Or do you think that Pol Duwez [3] thought that we would one day be playing golf with this stuff?

5.2.5 References

**Curriculum Vitae**

Marco Edwin Siegrist  
Born in Hanover NH, USA on Sept. 17, 1977  
Citizen of Fahrwangen, Switzerland and the United States of America

2007-present  
Project leader at awtec AG and president of Advanced Metal Technology AG

Nov. 2003-Dec. 2006  
PhD candidate at the Laboratory of Metal Physics and Technology, Department of Materials, ETH Zürich

2003  
Diploma Thesis “Singel chamber solid oxide fuel cells with integrated current collectors” at the Laboratory of Nonmetallic Inorganic Materials, Department of Materials, ETH Zürich

2002-2003  
1 semester studies in Materials Engineering at ETH Zürich

2002  
1 month internship at Leichtmetall Kompetenzzentrum Ranshofen, Ranshofen, Österreich

2001-2002  
8 month internship at ABB Corporate Research, Dättilwil, Switzerland

1998-2001  
6 semesters studies in Materials Engineering at ETH Zürich, Switzerland

1994-1998  
Wirtschaftsmatura Typus E, Kantonsschule Wohlen, Wohlen, AG, Switzerland
Publications

Journal publications during dissertation
Marco E. Siegrist, Michael Siegfried, Jörg F. Löffler; "High-purity amorphous Zr_{32.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_{5} powders via mechanical amorphization of crystalline pre-alloys" Materials Science and Engineering A 418 (2006) 236.


Marco E. Siegrist, Esther D. Amstad, Jörg F. Löffler; "Tribological properties of graphite- and ZrC-reinforced bulk metallic glass composites" submitted to Intermetallics.

Marco E. Siegrist, Jörg F. Löffler; "Tailoring the mechanical properties of graphite-reinforced bulk metallic glasses" submitted to Scripta Materialia.

Other journal publications

**Patent**

Bulk metallic glass-graphite composites; US 60/722,409

**Oral contributions at international conferences**


German Physical Society (DPG) Meeting 2006 Dresden; Marco E. Siegrist, Jörg F. Löffler; “Soft-particle-reinforced bulk metallic glass composites with high ductility”

Materials Research Society (MRS) Fall Meeting 2005, Boston; Marco E. Siegrist, Jörg F. Löffler; “Novel graphite-reinforced bulk metallic glass composites with high ductility”

European Congress on Advanced Materials and Processes (Euromat) 2005, Prague; Marco E. Siegrist, Jörg F. Löffler; “Synthesis and properties of carbon-reinforced bulk metallic glass composites”

**Poster conference contributions at international conferences**