Bulk Metallic Glasses
Bulk Metallic Glasses

An Overview
In memory of
Prof. Raymond A. Buchanan
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PREFACE

Natural glass has existed from the early days of the Earth and was formed from the rapid solidification of molten rock produced during volcanic eruptions, lightning strikes, and meteorite impacts. Phoenician merchants were aware of its existence in Syria from around 5000 BCE. Man-made glass objects from Egypt and Eastern Mesopotamia are thought to date back to around 3500 BCE.

In comparison, amorphous metals or metallic glasses are newcomers to the field of amorphous materials. Prior to the 1960s, some amorphous thin films were fabricated by metal deposition onto very cold substrates. In 1960 Klement, Willens, and Duwez at the California Institute of Technology reported the synthesis of an amorphous metal by rapidly quenching a Au-Si alloy from ~1,300 °C to room temperature. A high cooling rate of ~10^6 K/s was required to bypass crystallization and this restricted the thickness of the sample to the micrometer range. In the 1960s, Chen and Turnbull developed amorphous alloys of Pd-Si-Ag, Pd-Si-Cu, and Pd-Si-Au. Chen also fabricated an amorphous Pd-Cu-Si alloy with a diameter of up to 1 mm that could be considered to be a bulk metallic glass. In 1974, Chen made systematic investigations on Pd-Si-, Pd-P-, and Pt-P-based alloys and obtained a critical casting diameter of 1-3 mm by quenching the melt, contained in a drawn fused quartz capillary, into water. In the early 1980s, Turnbull’s group studied Pd-Ni-P alloys and they were able to produce glassy ingots of Pd$_{40}$Ni$_{40}$P$_{20}$ with diameters of 5 mm. In 1984, they extended the critical casting diameter to 10 mm by processing the Pd-Ni-P melt in a boron oxide flux. From the late 1980s, Inoue’s group has discovered many new bulk metallic glasses in a variety of multicomponent alloy systems including the rare-earth-based systems that have cooling rates less than 100 K/s and thicknesses reaching several centimeters. These systems are discussed in detail in Chapter 1. In 1992, Johnson and Peker developed a pentary Zr$_{41.2}$Cu$_{12.5}$Ni$_{10}$Ti$_{13.8}$Be$_{22.5}$ metallic glass with a critical cooling rate of 1 K/s. This alloy became the first commercial bulk metallic glass and is known as Vitreloy 1. Over the last four decades, the critical casting thickness has been increased by more than three orders of magnitudes and amorphous components weighing several kilograms can be fabricated. To date, more than a thousand different bulk metallic glasses have been produced in Zr-, Fe-, Pd-, Ni-, Cu-, Mg-, and Ti-based systems.

Bulk metallic glasses are a new emerging field of materials with many desirable and unique properties, such as high strength, good hardness, good wear resistance, and high corrosion resistance that can be produced in near net shape components. These amorphous materials have many diverse applications from structural applications to microcomponents. Some unique
applications of these novel materials such as pressure sensors, microgears for motors, magnetic cores for power supplies, and nano-dies for replicating next generation DVDs are documented in Chapter 1. An atomistic theory of local topological fluctuations is introduced in Chapter 2 to describe the atomistic movements in glasses and liquids. In this theory, topological fluctuations are represented by the atomic level stresses, and evolution of their distribution with temperature determines various thermal properties. This theory describes the glass transition, structural relaxation, glass formation and mechanical deformation, and the importance of Poisson’s ratio. This theory promises to replace the free volume theory in elucidating the complex behaviors of metallic glasses. Atomistic simulations, including empirical potentials and \textit{ab initio} calculations, are presented in Chapter 3. The application of classical nucleation theory and role of Molecular Dynamics simulations to bulk metallic glasses are discussed. In Chapter 4, glass formation, glass forming ability, and the underlying mechanisms and physical insights of these criteria are presented. The unique microstructures of these amorphous materials are discussed in Chapter 5. The state-of-the-art techniques (XRD, SEM, HREM, FEM, FIM, APT, SANS/SAXS, and PAS) that have been used to characterize the microstructures of these bulk metallic glasses from the as-produced to the crystallized material are described. The mechanical deformation of bulk metallic glasses including the topics of strength, plasticity (Poisson’s ratio and solidity index), homogenous deformation, dynamic deformation, strain rate effects, strain hardening, and shear band nucleation and propagation, and the yielding criterion of metallic glasses are reviewed in Chapter 6. The structure of the shear band and the temperature associated with the propagation of a shear band are also reviewed. The fatigue, fracture and corrosion behaviors of these materials are also reviewed in Chapters 7 and 8.

This book is based on a short course that was organized by Peter Liaw and taught by several of the contributing authors at the Department of Materials Science and Engineering, The University of Tennessee in 2005 and 2006.

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Chapter 1

DEVELOPMENT AND APPLICATIONS OF LATE TRANSITION METAL BULK METALLIC GLASSES

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1.1 INTRODUCTION

Bulk metallic glasses (BMGs) in metal–metal systems such as La-, Mg-, and Zr-based alloys were first prepared in the early 1990s by the stabilization of supercooled liquid. Since then much effort has been devoted to the development of BMGs for both fundamental scientific research and for industrial applications. As a result, many unique and useful properties of BMGs have been found. In particular, research at the Institute for Materials Research has been concentrated primarily on early transition metal (Zr-, Ti-, and Hf-based) systems, lanthanide metal (Ln-based) systems, simple metal (Mg- and Ca-based) systems, and noble metal (Pd- and Pt-based) systems. Because of their excellent properties, BMGs are expected to emerge as a new type of industrial or engineering material. The development of late transition metal (LTM)-based BMGs is strongly encouraged due to material costs and the availability of raw material deposits. Therefore, an Fe-based BMG in the Fe–Al–Ga–P–C–B alloy system was successfully developed in 1995. Also at that time, three empirical component rules for the stabilization of a supercooled metallic liquid were proposed. These rules stated that (1) the multicomponent system should consist of three or more elements, (2) there should be a significant difference (greater than ~12%) in the atomic sizes of the main constituent elements, and (3) the elements should have
negative heats of mixing. A variety of Fe-based,\textsuperscript{10–14} Co-based,\textsuperscript{15–17} Ni-based,\textsuperscript{18–20} and Cu-based\textsuperscript{21–25} BMGs have been synthesized in accordance with these rules and other topological and chemical criteria. As a result, various unique properties of LTM-based BMGs have been obtained. These properties have not been obtained in any crystalline alloys. Therefore, it should be possible to extend the range of applications. This chapter reviews recent results on the formation, properties, thermal stability, workability, and applications of LTM-based BMGs.

### 1.2 FEATURES OF ALLOY COMPONENTS IN LTM-BASED BMGS

Since the first synthesis of LTM-based BMG containing more than 50% LTM in the Fe–(Al,Ga)–(P,C,B)\textsuperscript{9}, other systems including Co–Ga–(Cr,Mo)–(B,C,P),\textsuperscript{15} Ni–Nb–(Zr,Ti,Hf)–(Co,Fe,Cu,Pd),\textsuperscript{26} and Cu–(Zr,Hf)–Ti\textsuperscript{21} BMGs were developed between 1996 and 2001. It is important to note that the research for LTM-based BMGs began just over a decade ago in 1995.

The typical BMG-forming systems containing more than 50% LTM as a main constituent element are summarized in Table 1.1. The systems can be classified into two different groups: metal–metalloid and metal–metal systems. The metal–metalloid group systems are primarily in Fe-, Co-, Ni-, Pd-, and Pt-based alloys, and metal–metal group systems are primarily in Ni- and Cu-based alloys. Only Ni-based alloys belong to both groups. For engineering applications, low-cost LTM-based BMGs with simplified composition that are easy to process should be preferred. To fit these requirements, metal–metal type BMGs such as Ni–Nb–(Ti,Zr,Hf), Cu–Ti–(Zr,Hf), and Cu–Al–(Zr,Hf) systems are more applicable than metal–metalloid types such as Fe–(Al,Ga)–metalloid, Fe–(Cr,Mo)–(C,B), Fe–(early transition metal)–B, Fe–Ln–B, and Fe–(B,Si)–Nb. Unfortunately, these metal–metal type BMGs generally exhibit lower glass-forming abilities than the metal–metalloid type. The critical diameter, $D_{\text{max}}$, for metal–metal type alloy systems is typically limited to 1.5 mm. To extend the range of applications, it will be necessary to optimize the composition and further to develop the metal–metal type BMGs.

The other classification is summarized in Table 1.2. All ternary or pseudo-ternary glass-forming systems can be divided into five groups. Group I consists of LTM, simple metal, and early transition metal as exemplified by Cu–Zr–Al and Cu–Hf–Al systems. Group II includes LTM, metalloid, and early transition metal or Ln such as Fe–(B,Si)–Nb, Fe–(Zr, Hf, Nb)–B, Fe–Ln–B, and Fe–(Cr,Mo)–(C,B) systems. Group III is composed of Fe,
metalloid, and Al or Ga. Group IV is exemplified by Ni–Nb–Ti and Cu–(Zr,Hf)–Ti systems. Group V consists of Ni–Pd–P and Cu–Pt–P systems. As evident in Table 1.2, all the glass-forming systems classified into different groups belong to ternary or pseudoternary alloys, which are composed of three types of elements with different atomic radii. From this, it is concluded that the stabilization of supercooled liquid is dominated by the atomic size mismatch rather than the negative heat of mixing between the constituent elements.

Table 1.1. Typical bulk metallic glass systems in late transition metal (LTM) base containing more than 50 at.% LTM reported to date

<table>
<thead>
<tr>
<th>Base metal</th>
<th>Metal–metalloid</th>
<th>Metal–metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Fe–(Al,Ga)–(P,C,B,Si)</td>
<td>Fe–Nd–Al</td>
</tr>
<tr>
<td></td>
<td>Fe–Ga–(P,C,B,Si)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe–Ga–(Nb,Cr,Mo)–(P,C,B) (Los Alamos)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe–(Cr,Mo)–(B,C)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe–Ln–B, Fe–(Zr,Hf,Nb,Ta)–B, Fe–(B,Si)–Nb</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>Co–Ga–(Cr,Mo)–(P,C,B)</td>
<td>Co–Sm–Al</td>
</tr>
<tr>
<td></td>
<td>Co–(Zr,Hf,Nb,Ta)–B</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>Ni–(Nb,Cr,Mo)–(P,B)</td>
<td>Ni–Nb–Ti, Ni–Nb–Zr, Ni–Nb–Hf</td>
</tr>
<tr>
<td></td>
<td>Ni–(Ta,Cr,Mo)–(P,B)</td>
<td>Ni–Nb–Zr–Ti</td>
</tr>
<tr>
<td></td>
<td>Ni–Zr–Ti–Sn–Si (Yonsei University)</td>
<td>Ni–Nb–Zr–Ti–M (M = Fe, Co, Cu)</td>
</tr>
<tr>
<td></td>
<td>Ni–Pd–P</td>
<td>Ni–Nb–Hf–Ti</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni–Nb–Hf–Ti–M</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni–Nb–Sn (Cal Tech)</td>
</tr>
<tr>
<td>Cu</td>
<td>Cu–Pd–P</td>
<td>Cu–Zr–Ti, Cu–Hf–Ti</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu–Zr–Ti–Be, Cu–Hf–Ti–Be</td>
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<tr>
<td></td>
<td></td>
<td>Cu–Zr–Al, Cu–Hf–Al</td>
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<tr>
<td></td>
<td></td>
<td>Cu–Zr–Al–M, Cu–Hf–Al–M (M = Ni, Co, Pd, Ag)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu–Zr–Ga, Cu–Hf–Ga</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu–Zr–Ga–M, Cu–Hf–Ga–M</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu–Zr–Al–Y (Cal Tech)</td>
</tr>
<tr>
<td>Pt</td>
<td>Pt–Cu–P</td>
<td>Cu–Zr–Ti, Cu–Hf–Ti</td>
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<td></td>
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<td>Cu–Zr–Ti–Be, Cu–Hf–Ti–Be</td>
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<td>Cu–Zr–Al, Cu–Hf–Al</td>
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<td>Cu–Zr–Al–M, Cu–Hf–Al–M (M = Ni, Co, Pd, Ag)</td>
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<td>Cu–Zr–Ga, Cu–Hf–Ga</td>
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<td>Cu–Zr–Ga–M, Cu–Hf–Ga–M</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu–Zr–Al–Y (Cal Tech)</td>
</tr>
<tr>
<td>Pd</td>
<td>Pd–Cu–Ni–P</td>
<td>Cu–Zr–Ti, Cu–Hf–Ti</td>
</tr>
</tbody>
</table>

(49) courtesy Japan Institute of Metals
Table 1.2. Features of three metallic components in ternary base systems where bulk metallic glasses are formed by the copper mold casting method\(^4\) (courtesy Japan Institute of Metals)

<table>
<thead>
<tr>
<th>ETM</th>
<th>LTM</th>
<th>Ln</th>
<th>Cu–Zr–Al, Cu–Hf–Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>II</td>
<td>III</td>
<td>Fe–(B,Si)–Nb, Fe–Nb–B</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fe–Zr–B, (Fe,Co)–Ln–B</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Co,Fe)–Ta–B</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fe–(Cr,Mo)–(C,B)</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td></td>
<td>Fe–(Al,Ga)–(P,C,B)</td>
</tr>
<tr>
<td></td>
<td>IV</td>
<td></td>
<td>Ni–Nb–Ti</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cu–Zr–Ti, Cu–Hf–Ti</td>
</tr>
<tr>
<td></td>
<td>V</td>
<td></td>
<td>Ni–Pd–P, Cu–Pt–P</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pd–(Ni,Cu)–P, (Pd,Pt)–Cu–P</td>
</tr>
</tbody>
</table>

The tendency of glass-forming ability (GFA), temperature interval of supercooled liquid region \((\Delta T_x)\), and reduced glass transition temperature \((T_g/T_l)^2\)\(^7\) for all LTM-based BMGs reported to date are summarized in Table 1.3. The highest GFA can be obtained for Pd- and Pt-based alloys,

Table 1.3. Features of glass-forming ability, temperature interval of supercooled liquid, and reduced glass transition temperature for late transition metal-based bulk metallic glasses (base metals > 50 at.\%)\(^9\) (courtesy Japan Institute of Metals)

<table>
<thead>
<tr>
<th>Glass-Forming Ability</th>
<th>Base Metal &gt; 50 at%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy Type</td>
<td>Fe</td>
</tr>
<tr>
<td>Metal-Metalloid</td>
<td>◘</td>
</tr>
<tr>
<td>Metal-Metal</td>
<td>-</td>
</tr>
</tbody>
</table>

GFA: Pd >> Cu >> Ni >> Fe >> Co

<table>
<thead>
<tr>
<th>Temperature Interval of Supercooled Liquid ((\Delta T_x))</th>
<th>Base Metal &gt; 50 at%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy Type</td>
<td>Fe</td>
</tr>
<tr>
<td>Metal-Metalloid</td>
<td>◘</td>
</tr>
<tr>
<td>Metal-Metal</td>
<td>-</td>
</tr>
</tbody>
</table>

\(\Delta T_x\): Cu >> Fe >> Ni >> Pd >> Pt >> Co

<table>
<thead>
<tr>
<th>Reduced Glass Transition Temperature ((T_g/T_l))</th>
<th>Base Metal &gt; 50 at%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy Type</td>
<td>Fe</td>
</tr>
<tr>
<td>Metal-Metalloid</td>
<td>◘</td>
</tr>
<tr>
<td>Metal-Metal</td>
<td>-</td>
</tr>
</tbody>
</table>

\(T_g/T_l\): Cu >> Fe >> Ni >> Pd >> Pt >> Co

\(\Delta T_x\): Cu >> Fe >> Ni >> Pd >> Pt >> Co
followed by Cu-, Ni-, Fe-, and then Co-based alloys. Generally, the GFA of ternary alloys is enhanced with decreasing liquidus temperature. In fact, it can be seen that there is a relationship between GFA and $\Delta T_x$ or $T_g/T_l$.

The mechanical fracture strength, $\sigma_f$, and fracture elongation, $\epsilon_f$, under compressive load for the LTM-based BMGs are summarized in Table 1.4. All the BMGs exhibit high $\sigma_f$, exceeding 1,000 MPa. In addition to their elastic elongations of 2%, Fe-, Ni-, Cu-, Pd-, and Pt-based metal–metalloid BMGs also have good ductility as evident from the achievement of plastic elongation. Conversely, Co-based metal–metalloid and metal–metal BMGs and Fe-based metal–metal BMGs exhibit no plastic elongation. The 2% elastic elongation property has been recognized for other BMGs such as Zr-, Mg-, and Ln (lanthanide metal)-based alloy systems. The elastic limit of a crystalline alloy is typically less than 0.65% due to the presence of dislocations. BMGs do not contain dislocations and ideally should exhibit an elastic limit of 2%. However, some BMGs do not achieve this 2% elastic limit due to cast defects. Therefore, the 2% elastic limit reflects the random atomic configuration of an ideal glass and is an essential factor for the achievement of high fracture strength.

The development of Fe- and Co-based BMG alloys has not been as rapid as the other systems. However, BMGs in (Fe,Co,Ni)–Nb–(B,Si) and Co–Fe–Ta–B alloy systems were developed over the last 3 years. Therefore, the formation and fundamental properties of these new Fe- and Co-based BMGs are described in Sect. 1.3.

Table 1.4. Features of static mechanical strength and compressive ductility for late transition metal-based bulk glassy alloys$^{49}$ (courtesy Japan Institute of Metals)

<table>
<thead>
<tr>
<th>Static Mechanic Strength</th>
<th>Compressive Ductility</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alloy Type</strong></td>
<td><strong>Fe</strong></td>
</tr>
<tr>
<td>Metal-Metalloid</td>
<td>☀</td>
</tr>
<tr>
<td>Metal-Metal</td>
<td>△</td>
</tr>
</tbody>
</table>

Strength ($\sigma_f$): Co > Fe > Ni > Cu > Pd > Pt

<table>
<thead>
<tr>
<th><strong>Alloy Type</strong></th>
<th><strong>Fe</strong></th>
<th><strong>Co</strong></th>
<th><strong>Ni</strong></th>
<th><strong>Cu</strong></th>
<th><strong>Pd</strong></th>
<th><strong>Pt</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal-Metalloid</td>
<td>☀*</td>
<td>☀</td>
<td>☀*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Metal-Metal</td>
<td>△</td>
<td>△</td>
<td>☀*</td>
<td>☀*</td>
<td></td>
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</tr>
</tbody>
</table>

Ductility: Cu >> Ni > Pd > Pt > Fe > Co

- ☀*; $\sigma_f$ = 0.02 ± plastic strain
- ☀; $\epsilon_f$ = 0.02
- ○; $\epsilon_f$ = 0.017–0.02
- △; $\epsilon_f$ < 0.017

Base Metal ≥ 50 at% (○; $\sigma_f$ ≥ 5000 MPa, ☀; $\sigma_f$ ≥ 3000 MPa, ○; $\epsilon_f$ ≥ 2000 MPa, △; $\epsilon_f$ < 2000 MPa)
1.3 FORMATION AND FUNDAMENTAL PROPERTIES OF Fe- AND Co-BASED BMGS IN (Fe,Co,Ni)–(B,Si)–Nb SYSTEMS

Small Nb additions were found to increase the stability of supercooled liquid and enhance the GFA in amorphous (Fe,Co,Ni)–(B,Si) alloys. The compositional dependence of $T_g$ in (Fe,Co,Ni)–B–Si–4%Nb BMG alloys is shown in Fig. 1.1. The glass transition phenomenon can be observed over the entire composition range in \([(Fe_{1-x-y}Co_xNi_y)_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4\) alloys. The glass transition temperature, $T_g$, shows a significant change with Ni content and decreases almost linearly with increasing Ni content from 810 to 760 K. There is no distinct change in $T_g$ with the Co:Fe concentration ratio.

As shown in Fig. 1.2, the $\Delta T_x$ shows a maximum value of approximately 65 K in the range of 0.50–0.65Fe, 0.35–0.45Co, and 0–0.15Ni and keeps relatively large values of over 60 K in the Ni content range up to approximately 0.35Ni. In addition, the large $T_g/T_l$ values above 0.61 can also be obtained, leading to the formation of BMGs with diameters up to at least 5 mm by copper mold casting, as shown in Fig. 1.3. Considering that the conventional Fe–Co–Ni–B–Si system does not show glass transition phenomenon, it is important to note that, as it is a pseudoternary system, the

![Fig. 1.1. Compositional dependence of glass transition temperature ($T_g$) for \([(Fe_{1-x-y}Co_xNi_y)_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4\) BMG alloys (courtesy Japan Institute of Metals)]
**Fig. 1.2.** Compositional dependence of supercooled liquid region ($\Delta T_x$) for $\left[(\text{Fe}_{1-x-y}\text{Co}_x\text{Ni}_y)_{0.75}\text{B}_{0.2}\text{Si}_{0.05}\right]_{96}\text{Nb}_{4}$ BMG alloys$^{49}$ (courtesy Japan Institute of Metals)

**Fig. 1.3.** Compositional dependence of maximum sample diameter ($D_{max}$) for $\left[(\text{Fe}_{1-x-y}\text{Co}_x\text{Ni}_y)_{0.75}\text{B}_{0.2}\text{Si}_{0.05}\right]_{96}\text{Nb}_{4}$ BMG alloys$^{49}$ (courtesy Japan Institute of Metals)
addition of Nb satisfies the three empirical component rules for stabilization of supercooled liquid. In other words, the satisfaction of the rules leads to the formation of BMG. As an example, the outer shape and surface appearance of the cast Fe–Co-based BMG rods with diameters of up to 5 mm are shown in Fig. 1.4. The rods exhibit good metallic luster with a smooth surface, and no crystalline peaks are recognized in X-ray diffraction (XRD) patterns even in the 5-mm-diameter rods.

Fig. 1.4. Outer shape and X-ray diffraction patterns of [(Fe_{1-x}Co_x)_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_{4} BMG alloy rods (courtesy Japan Institute of Metals)

The compositional dependence of compressive $\sigma_f$ for the cast Fe–Co–Ni–B–Si–Nb alloy rods is shown in Fig. 1.5. High strengths exceeding 4,000 MPa can be obtained in the wide composition range of 0–1.0Co and 0–0.7Ni. Further increasing the Ni content decreases the strength to $\sim$3,700 MPa. By fixing the B, Si, and Nb contents, the highest $\sigma_f$ can be obtained for the Fe-based alloy, followed by the Co-based alloy and then the Ni-based alloy. In addition to the high strength, the Fe–Co–Ni–B–Si–Nb alloy rods also exhibit distinct plastic elongation up to about 0.5% before final fracture as revealed in Fig. 1.6. The alloy rod subjected to the plastic elongation up to 0.3% shows a distinct shear band along the maximum shear stress plane. Traces of viscous flow deformation were also observed on the shear band, indicating a significant temperature rise in the shear band.

Fe–Co-based BMG alloys also exhibit good soft magnetic properties. High saturation magnetizations, $J_s$, reaching 1.3 T were obtained in the Fe-rich composition range above 0.8 and low coercivities, $H_c$, of 1.0–2.5 A m$^{-1}$ in the wide composition range of 0.25–1.0Fe and 0–0.6Ni. Thus, the appearance of room temperature ferromagnetic properties is dependent on the Ni and Fe contents. The decrease of $H_c$ with increasing Co content has been recognized to originate from the reduction of saturation magnetostriction.28
Fig. 1.5. Compositional dependence of compressive fracture strength of [(Fe$_{1-x-y}$Co$_x$Ni$_y$)$_{0.75}$B$_{0.2}$Si$_{0.05}$]$_{96}$Nb$_4$ BMG rods produced by copper mold casting (courtesy Japan Institute of Metals)

Fig. 1.6. True stress–strain curves of [(Fe$_{0.8}$Co$_{0.1}$Ni$_{0.1}$)$_{0.75}$B$_{0.2}$Si$_{0.05}$]$_{96}$Nb$_4$ and [(Fe$_{0.8}$Co$_{0.2}$)$_{0.75}$B$_{0.2}$Si$_{0.05}$]$_{96}$Nb$_4$ BMG rods with a diameter of 2 mm (courtesy Japan Institute of Metals)
The relationship between $H_c$ and electrical resistivity, $\rho$, is shown in Fig. 1.7 for Fe-based BMGs in Fe–B–Si–Nb- and Fe–Ga–P–C–B-based systems, together with the data of amorphous and nanocrystalline alloys which require high cooling rates of over $10^5$ K s$^{-1}$ for preparation as well as Co$_{43}$Fe$_{20}$Ta$_{5.5}$B$_{31.5}$ BMG. The Fe- and Co-based BMG alloys have a better combination of lower $H_c$ and higher $\rho$ among all soft magnetic metallic alloys. The lower $H_c$ is presumably due to the smaller magnetic anisotropy and lower internal stress, $\sigma$. The contribution of $\sigma$ to $H_c$ has been examined in more detail. It has previously been reported that the $H_c$ is proportional to the ratio of saturation magnetostriction, $\lambda_s$, to $J_s$, i.e., $H_c \propto \rho_d (\lambda_s / J_s)^{29}$, and hence the slope is related to the volume and density of internal defects consisting mainly of free volumes in the glassy structure. Good linear relationships between $H_c$ and the ratio of $\lambda_s$ to $J_s$ for Fe-based BMGs and amorphous alloys are shown in Fig. 1.8. It is also evident that the slopes are clearly distinguished and are much smaller between the BMG alloys and the amorphous alloys. This difference indicates that the structure of the BMG alloys is distinguished from that of amorphous alloys and includes much lower volume and density of internal defects. The formation of a more homogenized disordered atomic configuration is concluded to be the origin for the lower $H_c$ for the BMG alloys as compared with the amorphous alloys including crystalline nuclei and density fluctuations.

**Fig. 1.7.** Relationship between coercivity and electrical resistivity for Fe- and Co-based bulk metallic glasses. The data of conventional amorphous and nanocrystalline alloys are also shown for comparison$^{29}$ (courtesy Japan Institute of Metals)
Development and Applications of LTM Bulk Metallic Glasses

Fig. 1.8. Relationship between coercivity and the ratio of saturation magnetostriction to saturation magnetization for Fe-based bulk metallic glasses. The data of amorphous type alloys are also shown for comparison\(^4\) (courtesy Japan Institute of Metals).

Co–Fe–Ta–B-based BMGs exhibit a large \(\Delta T_s\) above 70 K before crystallization. The large \(\Delta T_s\) value leads to the formation of BMG rods with diameters up to at least 2 mm.\(^1\) In addition, it has been reported that the Co–Fe–Ta–B BMG rods exhibit exceptionally high-yield strength of \(\sim 5,200\) MPa at room temperature as well as high elevated temperature strength of over 2,000 MPa in the wide temperature range up to 585°C, as shown in Fig. 1.9.\(^1\) Co-based BMGs exhibit not only an ultrahigh strength but also excellent soft magnetic properties. For instance, a Co-based BMG with a ring shape form of 1 mm in thickness, 10 mm outer, and 5 mm inner diameters exhibits an extremely high maximum permeability reaching 500,000 and low \(H_c\) of 0.26 A m\(^{-1}\). As these excellent soft magnetic properties are attributed to originate from a highly homogeneous magnetic domain structure in the cast ring, a soft magnetic amorphous thin film was fabricated by a sputtering technique that exhibited a unique soft magnetic property through the control of the structure-sensitive magnetic domain. A Co–Fe–Ta–B glassy alloy film with a thickness of 2.6 \(\mu\)m was deposited at 298 K and had a fine perpendicular-type domain structure with a spacing of \(\sim 1.7\) \(\mu\)m. The domain structure changed to an in-plane type for a film deposited at 473 K and was accompanied by a significant change in the magnetic properties, as shown in Fig. 1.10.\(^3\) The success of synthesizing these thin films with a fine perpendicular-type domain structure even at a
large thickness of 2.6 \( \mu \text{m} \) is promising for future development of new types of perpendicular-type data storage media, because the previous magnetic thin film thickness with the perpendicular domain structure is limited to less than several hundreds nanometers.\(^{31}\)

**Fig. 1.9.** Compressive true stress–true strain curves of Co\(_{43}\)Fe\(_{20}\)Ta\(_{5.5}\)B\(_{31.5}\) BMG rod deformed at various temperatures between room temperature and 873 K\(^{49}\) (courtesy Japan Institute of Metals)

**Fig. 1.10.** Spin reorientation from perpendicular to in-plane in Co–Fe–Ta–B thin films with increasing deposition temperature. Hysteric loops at 300 K for Co–Fe–Ta–B thin films deposited at different temperatures. *Insets* show the MFM images (area 20 \( \times \) 20 mm\(^2\)) for (a) film deposited at 25°C – in virgin state, (b) at 25°C – in remanence state, (c) at 100°C – in remanence state, (d) at 200°C – in remanence state, and (e) typical topography of Co–Fe–Ta–B thin films\(^{49}\) (courtesy Japan Institute of Metals)
Fe- and Co-based BMGs belonging to the metal–metalloid type have a unique network-like atomic configuration in which distorted trigonal prisms of Fe or Co and B are connected with each other in edge- or face-shared configuration modes through glue atoms of Ln, Zr, Hf, Nb, or Ta. The networked short-range ordered atomic configuration can effectively suppress the progress of crystallization due to the difficulty of long-range rearrangement of the constituent elements, leading to the stabilization of supercooled liquid. All Fe- and Co-based BMG alloys in metal–metalloid alloy systems have a unique primary crystallization phase of fcc-(Fe,Co)\textsubscript{2}B\textsubscript{6} that has a large lattice parameter of $\sim 1.2$ nm and a complicated structure with 96 atoms in the unit cell. This phase is different from the primary crystalline phase consisting of the mixture of $\alpha$-Fe, Fe\textsubscript{2}B, Fe\textsubscript{3}B, and Fe\textsubscript{3}Si equilibrium phases for Fe-based amorphous type alloys which require high cooling rates for amorphous phase formation.

### 1.4 Ni- AND Cu-BASED BMGS

Recent progress in Ni- and Cu-based BMGs is discussed in this section. The stress–strain curves of Ni-based bulk glassy alloys under tensile and compressive loads are shown in Fig. 1.11. The $\sigma_f$ under tensile load is as high as 2,700 MPa for the metal–metal type alloys, whereas metal–metalloid type alloys exhibit a high compressive $\sigma_f$ of 1,800 MPa as well as large compressive plastic elongation of 7.5%. The high $\sigma_f$ of the Ni-based metal–metal type BMG is believed to be the highest for all the BMGs. Much higher strength has been obtained under a compressive deformation mode. Therefore, metal–metal type Ni-based BMGs are appropriate for structural materials which require simultaneously high strength and good ductility.

![Fig. 1.11. Stress–strain curves of Ni-based bulk glassy alloys belonging to metal–metal and metal–metalloid types under tensile and compressive deformation model](courtesy Japan Institute of Metals)