

Chapter 2

Metallic Glasses

Metallic glasses, which exhibit many fascinating properties, have been developed during the past half century. The atomic structure has been basically understood by using a dense random packing scheme. However, it is not easy to determine the local atomic environments experimentally.

2.1 Introduction

Glass matter and materials are ubiquitous in everyday life. The most popular application is probably windows. However, glasses are not always transparent; even metals can exhibit glassy states. Figure 2.1 shows pictures of a window glass and a metallic glass. The metallic glass exhibits metallic luster as does most crystalline metals. It is not possible to distinguish metallic glasses from crystalline metals by eye. A metallic glass, in the Au–Si system, was first fabricated at the California Institute of Technology (Caltech) in 1959 [1]. Following the success of this study, several kinds of metallic glasses (e.g., Pd and Fe based) were also found in the 1960s and 1970s. At that time, a rapid cooling technique was necessary to form the glass, because crystallization had to be suppressed during the cooling from the melts in the glass-forming alloys found in the early stage. A bulk-form glass with a dimension of one centimeter was obtained first for a Pd-based system [2]. Around 1990, various large-scaled bulk metallic glasses were successfully synthesized by using a simple mold-casting method by Tohoku and Caltech groups [3, 4]. Three empirical rules for the formation of bulk metallic glasses were proposed [3]:

1. The atomic size difference must be $>12\%$ between constituents,
2. there must be a negative mixing enthalpy between constituents, and
3. the alloy composition must include more than three elements.

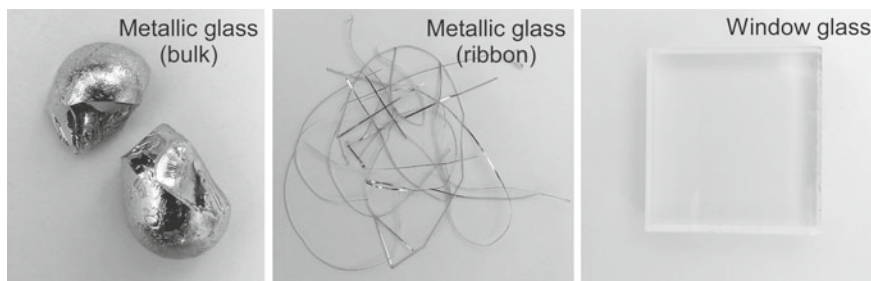


Fig. 2.1 Bulk metallic glass (*left*), ribbon metallic glass (*middle*), and window glass (*right*)

Through these guiding principles, nowadays we have a wide variety of centimeter-sized bulk metallic glasses (Zr, Pd, Mg, Fe, CuZr based, etc.) with multicomponent chemical compositions. Owing to their remarkable development, industrial applications of bulk metallic glasses have been deployed using their excellent structural, magnetic, and chemical properties [5, 6].

2.2 Structure Models

The central topic in this book is the characterization of atomic structures in metallic glasses. Here we briefly introduce some efforts to understand the atomic structures, which are basically inaccessible experimentally, through modeling processes. Crystal structures of metals are known to be simple and densely packed. Figure 2.2 shows typical crystal structures of pure metals: face-centered cubic (fcc), hexagonal closed packed (hcp), and body-centered cubic (bcc) structures. In particular, fcc and hcp structures have the highest packing density ($\sim 74\%$) where hard spherical-shaped atoms with equal radii are assumed. Using an analogy from crystals, Bernal attempted to build a hand-made atomic model of a metallic melt in the 1960s [7]. He assembled equal-sized spherical balls to form the dense packing but prevented them from forming a periodic crystal. Thus a dense random packing (DRP) model was successfully obtained by hand.

A two-dimensional schematic of the DRP model is shown in Fig. 2.3. In addition to metallic melts, the DRP model also provides fruitful insight into the packing scheme of three-dimensional atomic configurations for metallic glasses without any translational periodicity. The DRP model also reproduces the overall feature of experimental pair distribution functions, which are a kind of density functions for atomic environments, obtained from metallic glasses. However, the distribution for the DRP nearest-neighbor environment is largely different from that observed experimentally. The nearest atomic distances are always $>2R$ (where R is the atomic radii) in DRP, whereas the atomic distances could be both shorter and longer than $2R$ in real metallic glasses. This implies that real atoms would rather be soft spheres than hard ones

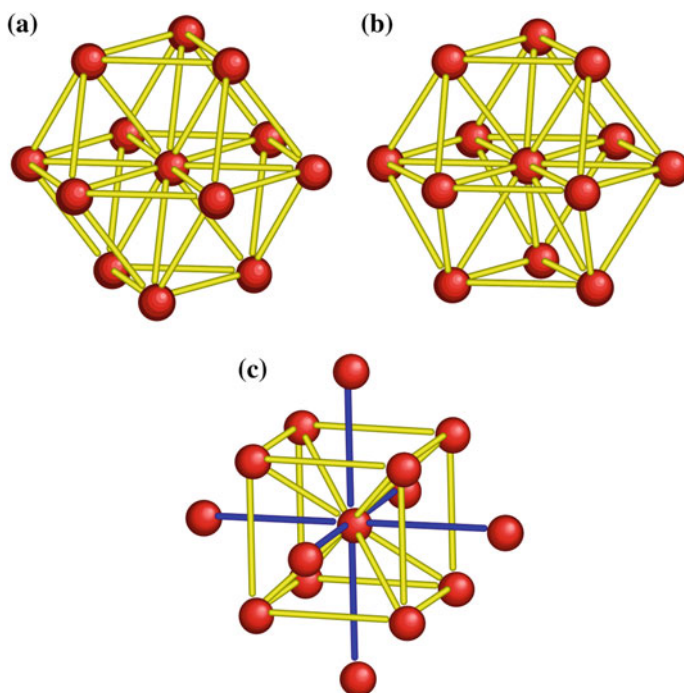
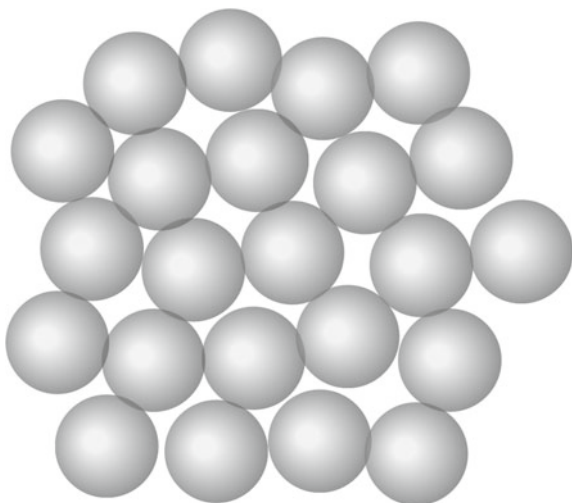


Fig. 2.2 Atomic coordinates in **a** face-centered cubic, **b** hexagonal close packed, and **c** body-centered cubic structures (ball-and-stick style)

in DRP. In fact, more realistic interatomic potentials have been developed to reproduce experimental pair distribution functions where atomic distances are distributed over a range >0.1 nm (see Fig. 2.4b) [8]. It is thus not easy to understand the nearest-neighbor atomic environment called short-range order (SRO) in metallic glasses because of the wide distribution. As also mentioned earlier, the meaning of “order” is still not clear for SRO in metallic glasses. The situation is fundamentally different from the case of oxide glasses in which a clear SRO such as a SiO_4 tetrahedron is formed. However, it is hard to observe the real three-dimensional SROs experimentally, as discussed in the next section. Recently, modeling of metallic glasses has been extended to the medium-range scale ($\sim 1\text{--}2$ nm) [9, 10]. Consideration of this scale is, however, beyond our scope in this book, although we should investigate it in the future. The structure–property relationship [11] and structural origin of the glass dynamics [12] are also important subjects to be mentioned.

Fig. 2.3 Two-dimensional picture of the dense random packing model



2.3 Experimental Difficulty in Determining Structures

In this section, we discuss the difficulty in experimentally determining the atomic structures of metallic glasses. A well-known procedure for determining the atomic configuration of materials, whether crystalline or amorphous, is by diffraction using some kind of radiation source. It should be noted that it is currently not possible to identify atomic configurations in a straightforward way. Atomic configurations found in the literature are more or less plausible atomic models that are consistent with the experimental diffraction data. In the case of crystals, the reliability of models is generally high owing to the periodicity of the atomic configurations. We only have to determine the arrangement of a limited number of atoms in a unit cell. However, if periodicity is completely lacking, it becomes extremely difficult to resolve the structures.

Briefly, diffraction intensity from matter can be divided into two terms: a scattering term from each atom and a correlation term between atoms. Since diffraction patterns are normally taken from bulk samples including a huge number of atoms ($\sim 10^{23}$ atoms), numerous different correlations comprise the diffraction patterns from amorphous structures with random atomic arrangements. Figure 2.4 shows a typical reduced interference function $Qi(Q)$ and a pair distribution function $g(r)$ obtained from an amorphous material. A reduced interference function $Qi(Q)$ is a function in reciprocal space that is derived from a diffraction intensity profile by subtracting a background related to atomic scattering factors. A pair distribution function $g(r)$ is a real space density function, which is derived by Fourier transforming $Qi(Q)$ as shown in the inset. Since both $Qi(Q)$ and $g(r)$ include many atomic correlations, it is only possible to perform an average structure analysis using these functions. For example, we can discuss average atomic bond lengths and coordination

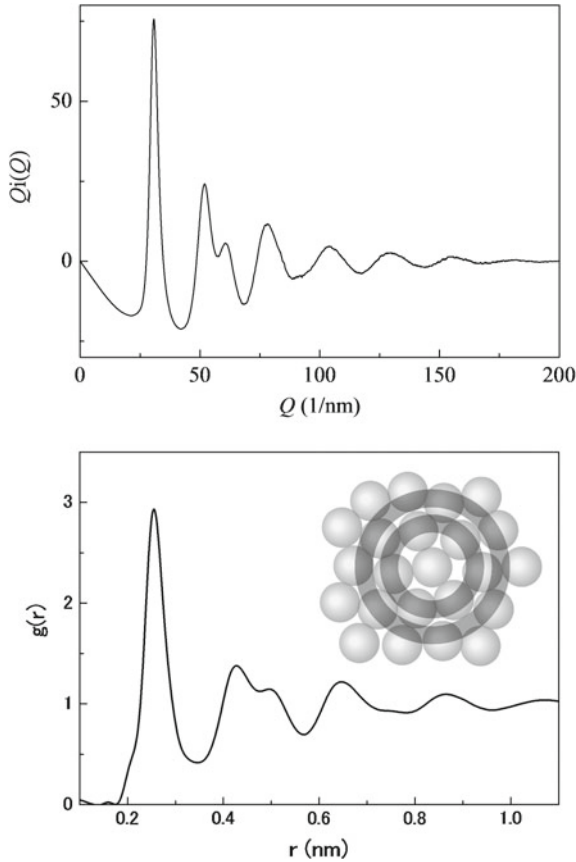


Fig. 2.4 Typical example of reduced interference function $Q_i(Q)$ (*upper*) and pair distribution function $g(r)$ (*lower*) obtained from a metallic glass

numbers based on the pair distribution function $g(r)$. Therefore some kind of direct experimental method is indispensable for a fundamental solution to the manner of distortion of individual SROs.

Recently, we have developed an angstrom-beam electron diffraction (ABED) method for detecting individual SROs in structurally disordered glass materials (Fig. 2.5) [13]. The nearly parallel electron beam is accurately focused down to 3–4 Å, comparable to the size scale of SROs in metallic glasses, by using custom-designed apertures. When the beam size is < 1 nm, distinct diffraction spots begin to appear in the diffraction patterns, as shown in the right panel. To understand the origin of the spots, we calculated ABED patterns from atomic clusters frequently found in the structure models obtained by using computational methods. By rotating the atomic clusters, we found several particular orientations giving symmetric ABED patterns with strong-intensity spots, just like crystals, even for amorphous materials. Using the ABED technique, we are now able to investigate the distortion of atomic clusters in metallic glasses by detecting diffraction from a single atomic cluster.

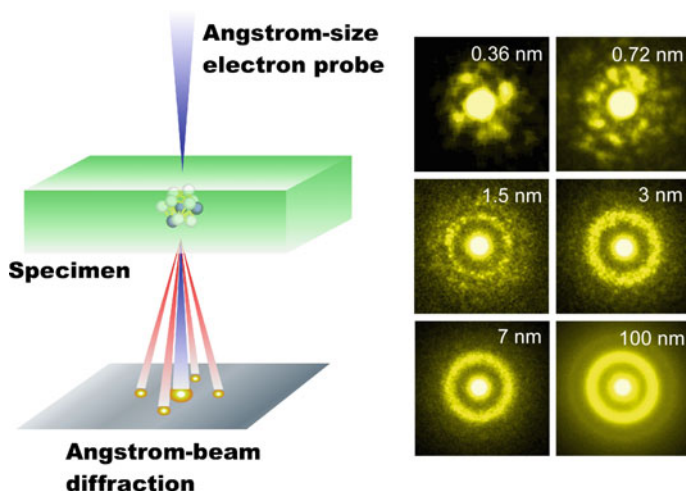


Fig. 2.5 Schematic of Angstrom beam electron diffraction method (*left*) and electron diffraction patterns obtained from a metallic glass with different beam sizes [13]

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