Structure of Mg$_{50}$Ni$_{50}$ amorphous alloy studied by using X-ray diffraction and reverse Monte Carlo modelling

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Abstract. X-ray diffraction measurement was performed on an Mg$_{50}$Ni$_{50}$ amorphous alloy prepared by mechanical alloying under an Ar atmosphere. Reverse Monte Carlo (RMC) simulation based on the X-ray diffraction data was used to construct a three-dimensional atomic arrangement of the amorphous alloy. In addition, the local environments around the Mg and Ni atoms were investigated by using Voronoi polyhedral analysis on the RMC configuration. The results show that isosahedral structures are predominant around the Mg and Ni atoms in Mg$_{50}$Ni$_{50}$, although prismatic local structures are present around some of the Ni atoms.

1. Introduction

Amorphous alloys for hydrogen storage have attracted significant interest because their hydrogen absorption properties differ from those of the corresponding crystalline compounds. They are usually prepared by using a melt-quenching method. However, mechanical alloying has become recognized as a method to synthesize amorphous materials instead of conventional melt-quenching. It has been reported that Mg$_{50}$Ni$_{50}$ amorphous alloys can be synthesized by mechanical alloying [1], and their hydrogen absorption properties have been investigated by several researchers [2-5]. It is noteworthy that the electrochemical pressure-composition isotherm of Mg$_{50}$Ni$_{50}$ amorphous alloys show an obvious pressure plateau, which is not observed in conventional amorphous alloys, such as a Ni-Zr system [6, 7]. The site occupancy of hydrogen (deuterium) atoms in Mg$_{50}$Ni$_{50}$ amorphous alloys has been studied by using X-ray and neutron diffraction, and the results show that the hydrogen (deuterium) atoms prefer to occupy the 2Mg+2Ni tetrahedral sites [3]. However, the topological structure of Mg$_{50}$Ni$_{50}$ amorphous alloys has not been reported. In this work, the local structure of an Mg$_{50}$Ni$_{50}$ amorphous alloy was investigated by using high-energy X-ray diffraction and reverse Monte Carlo (RMC) simulation.

2. Experimental Procedure

Mg$_2$Ni powder (3 g, High Purity Chemistry Research Institute, 99.9%) and Ni powder were mixed in the appropriate ratio to obtain a composition of Mg$_{50}$Ni$_{50}$, and the mixture was put into a steel vial (80 cc volume) with 10 steel balls (10 mm diameter). After evacuating the vial for 6 h to a pressure below $10^{-4}$ Pa using a turbomolecular pump, high purity argon (99.9999%) was introduced into it. A planetary ball mill (Fritsch P-5) was used for milling at 150 rpm. The structural change in the powder
during the milling process was characterized by using X-ray diffraction (RIGAKU RINT-Ultima) with Mo Kα radiation. After 100 h of milling, the Mg₅₀Ni₅₀ amorphous alloy was used for detailed structural analysis by using high-energy X-ray diffraction.

The high-energy X-ray diffraction measurement was carried out using a photon energy of 61.7 keV (0.0201 nm) in the high-energy X-ray diffraction beamline BL04B2 at the SPring-8 facility. A flat container with a thickness of 3 mm and with 0.025 mm thick Kapton windows was used. After correcting for polarization, absorption [8], and Compton scattering [9], the scattering intensity was converted to the total structure factor, \( S(Q) \). The total pair distribution function, \( g(r) \), was derived from the Fourier transformation of \( S(Q) \).

RMC simulation [10] was carried out by fitting the X-ray \( S(Q) \). A starting configuration of 5,000 atoms (Mg, 2500 atoms; Ni, 2500 atoms) randomly distributed in a cube with a length of 4.254 nm was used. To ensure a physically realistic configuration, we used 0.26, 0.24, and 0.23 nm for the closest distances of the Mg-Mg, Mg-Ni, and Ni-Ni pair correlations, respectively.

![Figure 1](image1.png)

**Figure 1.** (a) Experimental total structure factor, \( S(Q) \), obtained by using X-ray diffraction (solid line) and RMC fit (broken line) for Mg₅₀Ni₅₀ amorphous alloy. (b) Partial structure factors, \( S_{\text{Mg-Mg}}(Q) \), \( S_{\text{Mg-Ni}}(Q) \) and \( S_{\text{Ni-Ni}}(Q) \), calculated from the RMC model.

![Figure 2](image2.png)

**Figure 2.** (a) Total pair distribution function, \( g(r) \), obtained by using X-ray diffraction on the Mg₅₀Ni₅₀ amorphous alloy. (b) Partial pair distribution functions, \( g_{\text{Mg-Mg}}(r) \), \( g_{\text{Mg-Ni}}(r) \) and \( g_{\text{Ni-Ni}}(r) \), calculated from the RMC model.

### 3. Results and discussion

The total structure factor, \( S(Q) \), and partial structure factors, \( S_{\text{Mg-Mg}}(Q) \), \( S_{\text{Mg-Ni}}(Q) \) and \( S_{\text{Ni-Ni}}(Q) \), calculated from the RMC model for the Mg₅₀Ni₅₀ amorphous alloy are shown in Fig. 1 together with the experimental \( S(Q) \) determined by using X-ray diffraction. An excellent fit of the experimental \( S(Q) \) was obtained. The \( S(Q) \) had a small peak at around \( Q = 15 \text{ nm}^{-1} \). This pre-peak originated from the Ni-Ni correlations because only the \( S_{\text{Ni-Ni}}(Q) \) had a peak at around \( Q = 15 \text{ nm}^{-1} \).
Table 1. Nearest neighbour coordination numbers of atomic pair i-j, $N_{i-j}$, and interatomic distances, $r_1$, for the Mg$_{50}$Ni$_{50}$ amorphous alloy calculated from the RMC model. The first coordination shell distances for the Mg-Mg, Mg-Ni, and Ni-Ni pair correlations were 0.36, 0.34, and 0.33 nm, respectively.

| atomic pair i-j     | $N_{i-j}$ | $r_1$ (nm) |
|---------------------|-----------|------------|
| Mg-Mg               | 6.4       | 0.28       |
| Mg-Ni (Ni-Mg)       | 5.9       | 0.26       |
| Ni-Ni               | 5.3       | 0.24       |

Figure 4. Fractions of Voronoi polyhedra around Mg and Ni atoms, respectively, obtained from the RMC configuration of the Mg$_{50}$Ni$_{50}$ amorphous alloy.

Figure 2 shows the partial pair distribution functions, $g_{Mg-Mg}(r)$, $g_{Mg-Ni}(r)$ and $g_{Ni-Ni}(r)$, calculated from the RMC model of the Mg$_{50}$Ni$_{50}$ amorphous alloy together with the experimental $g(r)$. The nearest neighbor coordination numbers of atomic pair i-j, $N_{i-j}$, calculated from the RMC model are summarized in Table 1, where the first coordination shell distances for the Mg-Mg, Mg-Ni, and Ni-Ni pair correlations were determined to be 0.36, 0.34, and 0.33 nm, respectively, from the minimum positions in the $g_{Mg-Mg}(r)$, $g_{Mg-Ni}(r)$ and $g_{Ni-Ni}(r)$. The interatomic distances estimated from the first peaks in the $g_{Mg-Mg}(r)$, $g_{Mg-Ni}(r)$ and $g_{Ni-Ni}(r)$ are also listed in Table 1. The total coordination numbers of Mg ($N_{Mg-Mg} + N_{Mg-Ni}$) and Ni ($N_{Ni-Mg} + N_{Ni-Ni}$) were slightly above and below 12, respectively. In addition, the Ni-Mg interatomic distance was approximately equal to the mean value of the Ni-Ni and Mg-Mg interatomic distances. These results suggest that the Mg and Ni atoms are randomly distributed in the Mg$_{50}$Ni$_{50}$ amorphous alloy.

In order to determine the local environments around the Mg and Ni atoms in detail, Voronoi polyhedral analysis was performed on the RMC configuration of the Mg$_{50}$Ni$_{50}$ amorphous alloy. Figure 3 shows the fractions of the Voronoi polyhedra around the Mg and Ni atoms, respectively. A Voronoi polyhedron is denoted by a set of indices $(n_3 \ n_4 \ n_5 \ n_6 \ n_7 \ n_8)$, where $n$ is the number of faces and the number of vertices indicated by the subscript. It has been reported that prismatic structures,
such as Archimedean antiprisms and trigonal prisms, are mainly located around the Ni atoms in Ni-containing metallic glasses, such as Ni-Zr [11] and Ni$_{80}$P$_{20}$ glasses [12]. Indeed, as shown in Fig. 3, Archimedean antiprisms, denoted by the index (028000), and trigonal prisms, denoted by the index (036000), were observed around the Ni atoms in the Mg$_{50}$Ni$_{50}$ amorphous alloy. However, the fraction of these polyhedra was only about 10%. In contrast, a large number of icosahedral and isosahedron-like polyhedra, corresponding to the indices (00 12 000), (028100), (028200), and (01 10 200), were observed. The results indicate that icosahedron-like polyhedra basically form the structure of the Mg$_{50}$Ni$_{50}$ amorphous alloy.

On the basis of Ni-j of the Mg and Ni atoms and the results of Voronoi polyhedral analysis, we concluded that the Mg and Ni atoms were randomly distributed in the Mg$_{50}$Ni$_{50}$ amorphous alloy from both chemical and topological structural viewpoints. This means that 2Mg+2Ni tetrahedral units predominantly form the structure of the Mg$_{50}$Ni$_{50}$ amorphous alloy, and thus, several 2Mg+2Ni tetrahedral sites are available for hydrogen occupation.

4. Conclusions

An X-ray diffraction measurement was carried out on an Mg$_{50}$Ni$_{50}$ amorphous alloy prepared by mechanical alloying under an Ar gas atmosphere. The three-dimensional atomic configuration of the Mg$_{50}$Ni$_{50}$ amorphous alloy was obtained by using reverse Monte Carlo (RMC) modelling of the X-ray diffraction data. The RMC model showed that icosahedral structures were the main structures around the Mg and Ni atoms in the Mg$_{50}$Ni$_{50}$ amorphous alloy, although there were a small number of prismatic local structures around the Ni atoms. Therefore, we concluded that the random distribution of Mg and Ni atoms resulted in the formation of several 2Mg+2Ni tetrahedral sites in the Mg$_{50}$Ni$_{50}$ amorphous alloy.

Acknowledgements

This work was supported in part by a Grant-in-Aid for Young Scientists (B) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

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