X-Ray Diffraction Study on the Structure of the Metallic Glasses $Mg_{84}Ni_{16}$ and $Mg_{30}Ca_{70}$

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The total structure factors as well as the total pair correlation functions of amorphous $Mg_{84}Ni_{16}$ and $Mg_{30}Ca_{70}$ were determined by X-ray diffraction. The Mg-Ni glass shows rather strong chemical short range ordering. By Gaussian fit of the total pair correlation function partial coordination numbers and atomic distances were obtained. Similar surrounding of the Ni atoms in the amorphous phase and in crystalline Mg_2Ni was found. The structural features of the Mg-Ca glass differ from those of the Mg-Ni glass.

Introduction

In recent structural investigations on the metal-metal glasses $Mg_{85.5}Cu_{14.5}$ and $Mg_{70}Zn_{30}$ [1] chemical short range order (CSRO) and correspondence of the coordination of the Cu atoms in the Mg-Cu glass with that in crystalline Mg_2Cu was found. The present paper is a continuation of these investigations. The first subject was the question whether Mg-Ni glasses also exhibit a CSRO effect and whether it resembles to the structure of crystalline Mg_2Ni. This research was stimulated by thermodynamic studies on Mg-Cu- and Mg-Ni-glasses [2], where evidence for a chemical ordering effect for both glasses has been given.

The second subject was the examination of the structure of a metal-metal glass, namely $Mg_{30}Ca_{70}$, where both constituents belong to the same group of the periodic table. As CSRO was concluded from the thermodynamic data [3] of this glass, it was of interest to investigate whether such an effect is also found by X-ray diffraction.

Experimental and Data Reduction

The preparation of the melt spun samples, the diffraction experiments and the evaluation of the structural data were essentially done as reported previously [1]. The Ca-Mg samples had to be alloyed in a glove-box and melt spun immediately after alloying.

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The density of amorphous $Mg_{84}Ni_{16}$ was measured by the same technique as used in [1] yielding $D = 2.6$ g/cm^3. This value, however, is regarded to be not very exact due to the small amount of the amorphous material available. But it corresponds to an excess volume of about -10 pct, which was measured also with amorphous $Mg_{85.5}Cu_{14.5}$. For the $Mg_{30}Ca_{70}$ the density could not be measured, and therefore the value $D = 1.6$ g/cm^3 according to ideal mixing of the components was used. The real value is expected to be somewhat larger.

Results and Discussion

$Mg_{84}Ni_{16}$

From the coherently scattered intensity per atom $I_C(Q)$ the total structure factor $S(Q)$ was obtained according to:

$$S(Q) = I_C(Q)/\langle f^2(Q)\rangle, \qquad (1)$$

where

$$\langle f^2(Q)\rangle = c_1 f_1^2(Q) + c_2 f_2^2(Q),$$

c_1, c_2 = molar fractions,

$f_1(Q), f_2(Q)$ = scattering factors,

Q = $(4\pi \sin \Theta)/\lambda$,

2Θ = scattering angle,

λ = wavelength of the X-rays.

The structure factor is plotted in Fig. 1 together with that of amorphous $Mg_{85.5}Cu_{14.5}$ taken from [1]. Comparison shows that the general run of both curves is quite similar. The most remarkable feature is the occurence of a strong prepeak in front of the sharp main maximum, which gives evidence for chemical short range order in the Mg-Ni glass, too. Both curves show a splitting up of the second
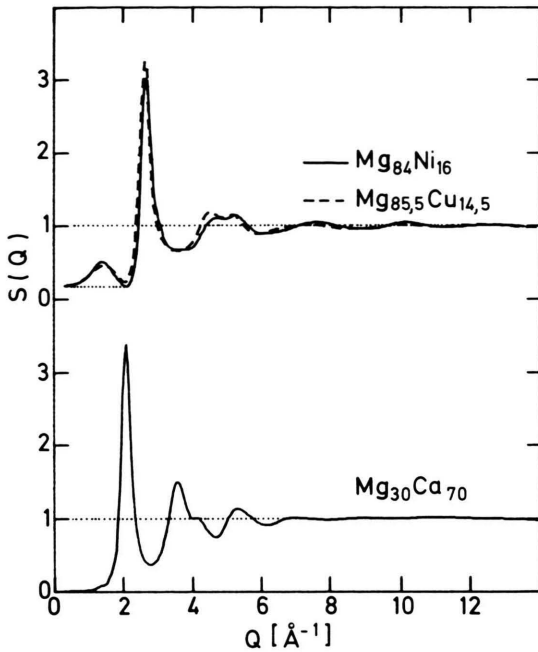
Fig. 1. Total structure factors $S(Q)$ of the metallic glasses $Mg_{84}Ni_{16}$, $Mg_{85.5}Cu_{14.5}$, and $Mg_{30}Ca_{70}$.

Table 1. D = density, d_i = atomic diameter [9]. Q^P, Q^I = position of the prepeak and the main peak, respectively, of the X-ray structure factor. ΔQ^P, ΔQ^I = width of the peaks. ξ^C, ξ^T = correlation lengths for chemical and topological ordering. I^P = amplitude of the prepeak measured from the dotted baseline in Figure 1. R^I, N^I = atomic distance and total coordination number, respectively, calculated from the main peak of the total pair correlation function. R_{ij}, Z_{ij} = atomic distance and partial coordination number of j-type atoms around an i-type atom.

	$Mg_{85.5}Cu_{14.5}$	$Mg_{84}Ni_{16}$
D [g/cm³]	2.54	~ 2.6
excess volume	−10%	~−10%
d_{Mg}/d_{Cu}; d_{Mg}/d_{Ni}	3.20/2.56	3.20/2.48
	= 1.25	= 1.29
Q^P [Å⁻¹]	1.48	1.41
Q^I [Å⁻¹]	2.65	2.68
ΔQ^P [Å⁻¹]	0.83	0.70
ΔQ^I [Å⁻¹]	0.34	0.37
I^P	0.28	0.33
Q^P/Q^I	0.56	0.53
$\xi^C = \dfrac{2\pi}{\Delta Q^P}$ [Å]	7.6	9.0
$\xi^T = \dfrac{2\pi}{\Delta Q^I}$ [Å]	18.5	17.5
R^I [Å]	2.75	2.70
N^I	10.2	11.8
R_{MgMg} [Å]; R_{MgCu} [Å];	3.10; 2.71	
R_{MgMg} [Å]; R_{MgNi} [Å];		3.09; 2.65
Z_{MgMg}; Z_{MgCu}; Z_{CuMg};	9.6; 1.4; 8.3	
Z_{MgMg}; Z_{MgNi}; Z_{NiMg};		11.1; 1.7; 8.5

maximum where, however, the subpeak height ratio for $Mg_{84}Ni_{16}$ is reversed as compared with that of $Mg_{85.5}Cu_{14.5}$. The wavelength of the oscillation at $Q \approx 7$ Å⁻¹ is rather large compared to the following oscillation in both cases.

In Table 1 structural parameters obtained from $S(Q)$ of the Mg-Ni glass are compared with those of the Mg-Cu glass, which again reflect the similarities of the structure of both glasses. However, slight differences can be observed: the prepeak I^P is somewhat higher in the case of $Mg_{84}Ni_{16}$. Whereas the correlation lengths of the topological ordering ξ^T, calculated from the width of the main maxima, are about the same, the correlation length of the chemical short range ordering ξ^C, following from the width of the prepeak, is larger in the Mg-Ni glass than in Mg-Cu.

The total structure factor can be written in terms of the three Bhatia Thornton partial structure factors $S_{NN}(Q)$, $S_{CC}(Q)$, and $S_{NC}(Q)$ [4]:

$$S(Q) = 0.860\, S_{NN}(Q) + 0.140\, S_{CC}(Q) + 1.89\, S_{NC}(Q). \tag{2}$$

On the basis of the assumption that the prepeak of $S(Q)$ is contributed by the partial structure factor $S_{CC}(Q)$, which describes the CSRO, from its

amplitude I^P the value of $S_{CC}(Q^P)$ can be evaluated by dividing I^P by the weighting factor of S_{CC} in (2) (see [1]). Comparison between Mg-Ni and Mg-Cu yields

$$S_{CC}^{MgNi}(Q^P)/S_{CC}^{MgCu}(Q^P) = 1.24.$$

This suggests that the CSRO is somewhat stronger in amorphous $Mg_{84}Ni_{16}$ than in amorphous $Mg_{85.5}Cu_{14.5}$, which is supported by the larger correlation length ξ^C in the former one. In this respect, however, it must be noted that these considerations are based on the assumption that the partial structure factor $S_{NC}(Q)$ shows negligible oscillations in the region of the prepeak. Up to now no experimental data on $S_{NC}(Q)$ of this type of metal-metal glasses have been determined; rather this function was simulated by hard sphere models [5] or even neglected [6]. In [7], however, evidence is given that the influence of $S_{NC}(Q)$ in the low Q-range may be

significant. Further experimental work is needed to clarify this question.

From the total structure factor the pair correlation function $G(R)$ was calculated by Fourier transformation:

$$G(R) = \frac{2}{\pi} \int_0^{Q_m} Q \frac{\langle f^2(Q)\rangle}{\langle f(Q)\rangle^2} [S(Q)-1] \sin(QR)\, dQ, \quad (3)$$

where $Q_m = 13.4\ \text{Å}^{-1}$.

Figure 2 shows the $G(R)$ function together with that of amorphous $Mg_{85.5}Cu_{14.5}$. Again agreement of the general features is observed. The double peak structure of the first maximum is more pronounced in the case of Mg-Ni than in the case of Mg-Cu, which is explained by the larger difference of the atomic diameters of both constituents in the former alloy (see Table 1).

The total $G(R)$ is a weighted sum of the three partial pair correlation functions $G_{NiNi}(R)$, $G_{MgNi}(R)$, and $G_{MgMg}(R)$:

$$G(R) = 0.095\, G_{NiNi}(R) + 0.426\, G_{MgNi}(R)$$
$$+ 0.479\, G_{MgMg}(R). \quad (4)$$

From the values of the weighting factors and from the atomic diameters we conclude that the first sub-peak belongs to the Mg-Ni correlation and the second subpeak to the Mg-Mg correlation, whereas the contribution of the Ni-Ni correlation is rather small. This has led to the concept of deriving partial coordination numbers by fitting the first maximum of $G(R)$ with two Gaussian curves for $G_{MgNi}(R)$ and $G_{MgMg}(R)$, respectively. The details of this procedure were described previously [1]. Figure 3 shows the fitting curve (dashed line) together with the experimental $G(R)$ in the region of the first coordination sphere.

The resulting distances R_{MgNi} and R_{MgMg} as well as the partial coordination numbers Z_{MgNi}, Z_{NiMg}, and Z_{MgMg} are listed in Table 1 together with the corresponding values for amorphous $Mg_{85.5}Cu_{14.5}$. The distance between unlike atoms $R_{MgNi} = 2.65\ \text{Å}$ is distinctly smaller than the sum of the Goldschmidt radii of Mg and Ni ($2.84\ \text{Å}$). This reflects the chemical interaction between unlike atoms in the amorphous phase. However, the distance between the Mg atoms $R_{MgMg} = 3.09\ \text{Å}$ is also somewhat smaller than the Goldschmidt diameter of Mg ($3.2\ \text{Å}$).

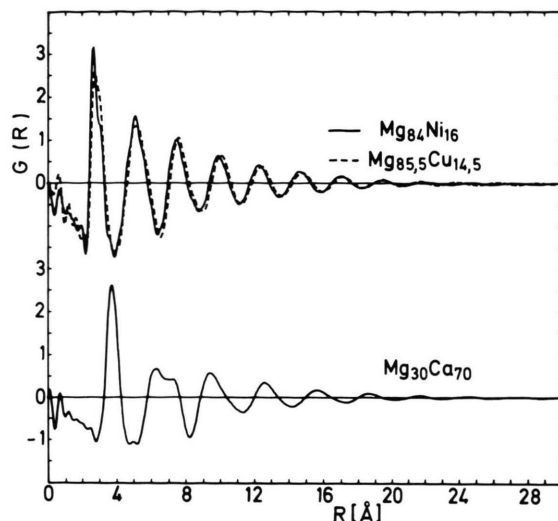The values of the partial coordination numbers Z_{MMg} (M = Ni, Cu) are the same within the

Fig. 2. Total pair correlation functions $G(R)$ of the metallic glasses $Mg_{84}Ni_{16}$, $Mg_{85.5}Cu_{14.5}$, and $Mg_{30}Ca_{70}$.
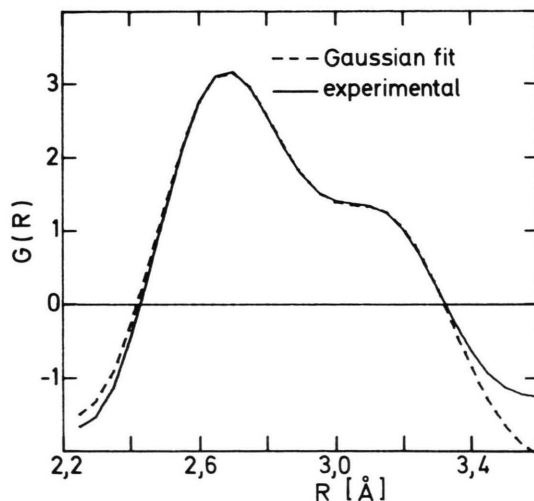

Fig. 3. Main peak of $G(R)$ of amorphous $Mg_{84}Ni_{16}$. —— experimental as in Fig. 2; – – – by Gaussian fitting.

accuracy of the fitting method, while Z_{MgMg} is larger in the Mg-Ni glass than in the Mg-Cu glass. For the Mg-Ni system the crystalline phase Mg_2Ni is reported, whose structure is closely related to that of crystalline Mg_2Cu [8]: The Ni atoms are surrounded by 8 Mg neighbours at a mean distance of $2.7\ \text{Å}$ building a distorted hexahedron. The agreement of these figures with the values $R_{MgNi} = 2.65\ \text{Å}$ and $Z_{NiMg} = 8.5\ \text{Å}$ obtained with amorphous $Mg_{84}Ni_{16}$ suggests the neighbourhood of the Ni atoms to be very similar in the amorphous and in the crystalline phase. This behaviour was also observed with

respect to the surrounding of the Cu atoms, in amorphous $Mg_{85.5}Cu_{14.5}$ and in crystalline Mg_2Cu [1]. Concerning the fitting procedure it should be noted that the small contribution of the Ni-Ni pairs, which has been not taken into account by a separate Gaussian, is therefore included in $Z_{NiMg} = 8.5$, which thus may be somewhat too large. On the other hand, compared to a Gaussian curve the real $G_{NiMg}(R)$ function is certainly asymmetric, that means broader at its right hand side, which would imply a larger value for Z_{NiMg}.

The Mg atoms in crystalline Mg_2Ni are surrounded by 11 Mg neighbours, 3 at 3.0 Å, 8 at 3.3 Å, and 4 Ni neighbours at 2.7 Å. Whereas Z_{MgMg} in the amorphous and crystalline phase is the same, Z_{MgNi} is smaller in the amorphous phase. This smaller value is explained by the lower Ni concentration in the $Mg_{84}Ni_{16}$ glass compared to crystalline Mg_2Ni.

$Mg_{30}Ca_{70}$

The structure factor of amorphous $Mg_{30}Ca_{70}$ is plotted in Figure 1. Comparison with the curves of the Mg-Ni and Mg-Cu glasses shows significant differences: Instead of a prepeak the Mg-Ca curve only exhibits a small bump near $Q = 1.3$ Å^{-1}. The second maximum of $S(Q)$ of Mg-Ca is splitted up into a higher first subpeak and a lower second one. Also the further oscillations are different.

From the equation

$$S(Q) = 0.958\, S_{NN}(Q) + 0.042\, S_{CC}(Q)$$
$$- 0.871\, S_{NC}(Q) \qquad (5)$$

one can see that the weighting factor of S_{CC} is rather small. Therefore CSRO, if present in the Mg-Ca glass, hardly can be observed by X-ray diffraction. The small bump, however, can be regarded as an indication for a CSRO effect. In Table 2 structural parameters of $S(Q)$ are listed.

The Fourier transform of $S(Q)$ is plotted in Figure 2. We observe very extended topological

Table 2. d_i = atomic diameter [9]. Q^P, Q^I = position of the prepeak and the main peak, respectively, of the X-ray structure factor. ΔQ^I = width of the mean peak. ξ^T = correlation length for topological ordering. R^I, N^I = atomic distance and total coordination number, respectively, calculated from the main peak of the total pair correlation function.

	$Mg_{30}Ca_{70}$
d_{Ca}/d_{Mg}	$3.94/3.20 = 1.23$
Q^P [Å^{-1}]	~ 1.3
Q^I [Å^{-1}]	2.09
ΔQ^I [Å^{-1}]	0.33
Q^P/Q^I	0.62
$\dfrac{2\pi}{\Delta Q^I} = \xi^T$ [Å]	19.0
R^I [Å]	3.75
N^I	12.7

ordering up to nine coordination spheres. The main maximum shows no splitting up, although the atomic diameter ratio is almost as large as that of Mg-Cu (Table 2). The radius of the first coordination shell R^I and the total coordination number N^I, evaluated from $G(R)$, are listed in Table 2.

Writing $G(R)$ in terms of the partial pair correlation functions,

$$G(R) = 0.042\, G_{MgMg}(R) + 0.325\, G_{MgCa}(R)$$
$$+ 0.633\, G_{CaCa}(R), \qquad (6)$$

one can see that $G(R)$ is mainly determined by G_{MgCa} and G_{CaCa}. From the weighting factors it can be explained that $R^I = 3.75$ Å is closer to $d_{Ca} = 3.94$ Å than to $d_{Mg} = 3.20$ Å.

As conclusion one can state that the structural results for amorphous $Mg_{30}Ca_{70}$ derived in the present work do not show close relationship to the structure of Mg-Cu and Mg-Ni glasses.

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