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Résumé - Une détermination précise des trois facteurs de structure partiels, pour la composition eutectique Ni₆₃,7^Zr₃₆,3 a été faite par diffraction des neutrons sur trois échantillons de composition isotopique différente. L'utilisation d'un "alliage zéro" fournit une détermination directe du facteur de structure partiel de Bhatia-Thornton S_{CC}. L'existence d'un fort ordre chimique à courte distance et d'un effet de taille très net est évidente. La présence de cet ordre chimique se traduit par des facteurs de structure partiels tout à fait incompatibles avec ceux calculés dans un modèle de sphères dures en utilisant l'équation de Percus-Yevick. A cause de l'effet de taille un paramètre d'ordre local du type Warren-Cowley ne peut pas être calculé. L'écart à la répartition statistique autour d'un atome de nickel est comparé aux résultats récemment publiés sur deux autres verres Ni-Zr, de compositions différentes.

Abstract - A precise determination of the three partial structure factors for the eutectic composition $Ni_{63.7}Zr_{36.3}$ has been carried out using neutron diffraction on three isotopically substituted glasses. The use of a "zero alloy" yields a direct determination of the Bhatia-Thornton structure factor S_{CC} . Evidence for the existence of strong chemical short-range order and a clear size effect is obtained. Due to this chemical order, the partial structure factors cannot be consistent with the ones calculated for a two components system of hard spheres using the Percus-Yevick equation. Due to the size effect, a short-range order Warren-Cowley parameter cannot be calculated. The deviation from a purely statistical distribution around a nickel is compared to the results recently published for two other Ni-Zr glasses.

Introduction

The stability and the ease of glass formation of amorphous alloys are thought to be related to the existence of chemical short range order. In the amorphous $2r_{1-x}Ni_x$ alloys the composition dependence of the activation energy for crystallization has been taken as reflecting the occurrence of CSRO, which would be a particularly important effect in the composition regions close to x = 0.38 and x = 0.64 /l/. Hence diffraction studies giving the change in CSRO with concentration are important. Recently, partial structure factors have been determined for Ni₃₆Zr₆₄ /2/, Ni₃₅Zr₆₅ /3/ and NiZr /4/. We present here the three partial structure factors (P.S.F.) for the eutectic composition Ni₆₃.7Zr₃₆.3, determined by neutron diffraction on isotopically substituted samples. A preliminary report of this study has been published elsevhere /5/.

Experiment

For binary amorphous alloys, at least three different experiments are required to obtain the three PSF's. The isotopic compositions we have chosen are $NatNi_{63.7}Zr_{36.3}$ $^{60}Ni_{63.7}Zr_{36.3}$ and $^{62}Ni_{39.2}c^{60}Ni_{24.5}Zr_{36.3}$. The amorphous ribbons were obtained by planar flow casting /6/ under a helium pressure of 375 Torr. The ribbons are typically 6 mm wide and 35 m thick.

The experiments have been carried out on the spectrometer 7C2 on the hot source of ORPHEE (wavelength 0.704 A) with a 640 cells position sensitive detector /7,8/. Data reduction consisted of correction for transmission, incoherent multiple scattering and inelastic scattering following classical procedures. The scattering lengths used are those compiled by Mughahghah et al. /9/.

The total structure factor S(q) may be defined by the relation

$$S(q) = I_{coh}(q) / \langle b^2 \rangle$$

which is particularly appropriate for alloy whose value might be zero, the so-called "zero alloy".

According to the Faber-Ziman formalism /10/ the total structure factor for a binary AB alloy is a sum of the three weighted partial structure factors $S_{ij}(q)$:

$$S(q) - 1 = \frac{C_A^2 b_A^2}{\langle b^2 \rangle} (S_{AA}(q) - 1) + \frac{C_B^2 b_B^2}{\langle b^2 \rangle} (S_{BB}(q) - 1) + \frac{2C_A C_B b_A b_B}{\langle b^2 \rangle} (S_{AB}(q) - 1)$$

The coefficient $w_{ij} = c_i c_j b_i b_j / \langle b^2 \rangle$ are given in table 1 for the three samples.

	W _{NINI}	WZrZr	W _{NiZr}	2/<b<sup>2 > 2Δb/<b<sup>2 > Δb²/<b<sup>2 ></b<sup></b<sup></b<sup>		
^{nat} Ni63.7 ^{Zr} 36.3	0.499	0.078	0.396	0.973	-0.6674	0.1169
⁶⁰ Ni _{63.7} ^{Zr} 36.3	0.136	0.285	0.394	0.815	1 614	0.8008
⁶² Ni _{39.2} ⁶⁰ Ni _{24.5} ^{2r} 36.3	0.231	0.231	-0.462	0	0	4.329

TABLE 1

TABLE 2

Very few precise determinations of PSF's of binary metal-metal amorphous alloys have been presented up to date. The three diffraction experiments provide a set of three equations from which the partials can be extracted.

In this work the normalized determinant of the three linear equations to be solved to obtain the PSF's $S_{NiNi}(q)$, $S_{NiZr}(q)$ and $S_{ZrZr}(q)$ is exceptionally high (0,112), allowing a direct determination of the partials from the data without using constraints or inequality relations. A precision of 1% on each total structure factor leads

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to a precision of 3.85, 5.45 and 2.33% on the $S_{NiNi}(q)$, $S_{ZrZr}(q)$ and $S_{NiZr}(q)$ partials, respectively.

In the Bhatia-Thornton formalism /11/, PSF's are associated with the correlations between density fluctuations and concentration fluctuations. This formalism is therefore quite useful to study the local order phenomena. $S_{\rm NN}(q)$, $S_{\rm CC}(q)$, $S_{\rm NC}(q)$ describe the topological short-range order, the chemical short-range order and the correlation between number density and concentration, respectively. The different coefficients of $S_{\rm NN}(q)$, $S_{\rm CC}(q)$, $S_{\rm NC}(q)$, $S_{\rm CC}(q)$, $S_{\rm CC}($





<u>Fig.1</u>. Ni_{63.7}Zr_{36.3} Faber-Ziman partial structure factors

<u>Fig.2</u>. Ni_{63.7}Zr_{36.3} Bhatia-Thornton partial structure factors

Results

The Faber-Ziman and the Bhatia-Thornton P.S.F. are shown in Figures 1 and 2. They give evidence for the existence of a well defined chemical short-range order and an important size effect. Chemical short-range order produces, at small values of q, a sharp and intense peak or dip in the Faber-Ziman partials. A comparison of these with $S_{CC}(q)$, together with the calculations of the relations between the FZ partials and the BT ones show that this sharp feature is really due to the $S_{CC}(q)$ first peak. In analogy with the order phenomena in crystalline alloys, this is a "superstructure peak" corresponding to a new pseudoperiodicity with a longer range.

Negative values of $S_{CC}(o)-C_AC_B$ indicate a preference for unlike neighbours. The Fourier Transform of $S_{CC}(q)$ still confirms this preference (figure 3). Figure 3 also shows the Fourier Transforms of $S_{NC}(q)$ and $S_{NN}(q)$. An average coordination number of 13.12 atoms was calculated by integrating the first peak of $4\pi r^2 \rho_{OQ} g_{NN}(r)$.



<u>Fig.3</u>. Ni_{63.7}^{2r}36.3 Pair partial correlation functions



<u>Fig.4</u>. $Ni_{63.7}$ Zr_{36.3} Percus-Yevick hard spheres partial structure factors.

Percus-Yevick Hard Spheres $S_{\rm NN}$, $S_{\rm CC}$ and $S_{\rm NC}(q)$ curves have been calculated for a misfit ratio of $\sigma_{Ni}/\sigma_{Zr} = 2.07/2.68 = 0.775$ and a packing fraction of 0.43 (Figure 4). They are very different from the experimental curves. In particular, in this alloy the P.Y. $S_{\rm NC}(q)$ curves cannot be used instead of a third experiment to determine the partials as previously proposed by other authors /3,12/.

Table 3 gives the first neighbours distances r_1 and coordination numbers N1 calculated from the partial radial distribution functions 4 $r^2c_i\rho_{og_{ij}}(r)$. The two sets of values correspond to two experiments carried out on the same samples but separated by a time interval of six months. The reproducibility is very good as long as r_i or Ni are concerned.

	r _l		N ₁	Random	
	First Experiment	Second Experiment	First Experiment	Second Experiment	
NiNi	2.52	2.51	6.00	5.96	7
NiZr	2.67	2.67	5.00	5.18	4
ZrZr	3.28	3.27	5.84	5.91	
ZrNi	2.67	2.67	8.77	9.1	

TABLE 3 - First neighbours distances and partial coordination numbers

Owing to the strong size effect a Warren-Cowley parameter cannot be calculated. However the deviation from a purely statistical distribution is confirmed by the values of the partial coordination numbers. In Ni_{63.7}Zr_{36.3} a nickel atom has on average 5 nearest Zr neighbours instead of 4 for a random distribution. In Ni₂₇/4/ it has 6.7 nearest Zr neighbours instead of 5. In Ni₃₆Zr₆₄ /2/it has 8.56 nearest Zr neighbours instead of 7.59.

Thus the CSRO is of the same nature throughout this composition range. The deviation from a purely random distribution is typically one atom out of the eleven of the first coordination shell for the two compositions corresponding to the deep eutectics (Ni_{63.7} $z_{r_{36.3}}$ and Ni₃₆ $z_{r_{64}}$), and 1.7 out of 10 for the composition corresponding to the compound NiZr. Hence, the correlation suggested by Buschow /l/ between the maxima of the activation energy for crystallization and a stronger CSRO is not established.

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