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THE STRUCTURE OF AMORPHOUS Ni-Zr ALLOYS

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Resume: Les structures des alliages Ni-Zr avec 55, 60, 65 et 70 at% Zr, et avec des additions mineures de Co et Fe ont été déterminées en employant la technique de l'angle 2θ variable pour les rayons X et de la longueur d'onde variable pour les neutrons. Les facteurs partiels de structures (fonctions partielles d'interférence) I_{ik}(Q) et S_{n-c}(Q) ont été reévalués, et leurs transformations de Fourier indiquent qu'il y a peu de voisins NiNi dans l'alliage amorphe Ni_{35}Zr_{65}.

Abstract: The structures of amorphous Ni-Zr alloys with 55, 60, 65 and 70 at% Zr, and small additions of Co and Fe, have been determined employing the variable 2θ x-ray and the variable wavelength neutron techniques. The partial structure factors (partial interference functions) I_{ik}(Q) and S_{n-c}(Q) have been reevaluated and their Fourier transforms indicate that there are few NiNi neighbors in the amorphous Ni_{35}Zr_{65} alloy.

I. - INTRODUCTION

The structure of multi-component, non-crystalline materials is still not well understood. The problem lies in the diffuse nature of the scattering patterns which permit us to determine only a weighted average of the partial atomic distribution functions [1]. The weight factors in this average depend on the scattering of the individual components in the non-crystalline materials. They can be changed by using different radiation probes (e.g. x-rays and neutrons), and by isomorphous and isotopic substitution of one or both alloying elements in binary systems.

The total, coherently scattered intensity per atom I_a(Q) can be expressed in terms of the atomic pair partial structure factors I_{ik}(Q) or the number-concentration structure factors S_{n-c}(Q) as a function of the length of the diffraction vector Q, i.e.

\[ Q = (4\pi/\lambda)\sin\theta = (4\pi m/\hbar) (L/\tau) \sin\theta \]  

where \( \lambda \) is the wavelength, \( m \) is the mass of the neutron, \( \hbar \) is Planck's constant, \( L \) is the total path traveled by the neutrons in the time \( \tau \). For binary alloys, we can write:

\[ I_a(Q) = \langle f^2 \rangle + (c_1 f_1)^2[I_{i1}(Q)-1] + (c_2 f_2)^2[I_{i2}(Q)-1] + 2c_1 c_2 f_1 f_2[I_{i12}(Q)-1] \]  

\[ I_a(Q) = \langle f^2 \rangle + \langle f^2 \rangle S_{n-c}(Q) + 2\Delta f \langle f \rangle S_{n-c}(Q) + c_1 c_2 (\Delta f)^2 [S_{n-c}(Q)/(c_1 c_2)]-1 \]

where \( f_1(Q) \) and \( c_1 \) are the coherent scattering amplitude and atomic concentration, respectively, of element 1, \( \langle f \rangle = \Sigma c_i f_i(Q), \langle f^2 \rangle = \Sigma c_i [f_i(Q)]^2 \) and \( \Delta f = f_1(Q)-f_2(Q) \). It can be readily shown that the factors I_{ik}(Q) and S_{n-c}(Q) are related [1].

The total structure factors I(Q) and S(Q) are defined as follows:
The Fourier transforms of $\mathbb{Q}[I(\mathbb{Q})-I]$ and $\mathbb{Q}[S(\mathbb{Q})-I]$ yield the total, reduced atomic distribution functions $G_1(r)$ and $G_S(r)$, respectively. It can be readily shown that the total correlation function $T(r)$ is given by:

$$T(r) = \langle f(0) \rangle^2 G_1(r) + 4\pi r \rho_0 \langle f(0) \rangle^2$$

(7)

where $\rho_0$ is the average atomic density of the amorphous alloy. $T(r)$ is related to the partial correlation functions $T_{ik}(r)$, i.e.,

$$T(r) = \Sigma \Sigma c_{i} f_{1}(0) c_{k} f_{k}(0) T_{ik}(r)$$

(8)

$$\rho_{ik}(r) = 4\pi r \rho_{ik}(r) / c_{k} = G_{ik}(r) + 4\pi r \rho_0$$

(9)

$G_{ik}(r)$ is the Fourier transform of the partial structure factor $I_{ik}(Q)$:

$$G_{ik}(r) = (2/\pi) \int Q[I_{ik}(Q)-1] \sin Qr dQ$$

(10)

II.- EXPERIMENTAL TECHNIQUES.

The amorphous alloys of Ni-Zr with 55, 60, 65, and 70 at% Zr, and 5 and 18 at% Co or 5 at% Fe, were produced by the melt-spinning process. The x-ray specimens were prepared by mounting several small ribbons next to each other over the opening in a sample holder. The neutron samples consisted of about 5 of ribbons for each composition. The ribbons were wound in such a way as to produce cylindrical specimens, 60 mm in height and 5 mm in diameter. The x-ray measurements were carried out with the variable $2\theta$ technique using Ag-Kα radiation and a Si solid state detector. The neutron measurements were performed on the pulsed spallation source at Argonne National Laboratory, using the variable $\lambda$ technique.

III.- RESULTS AND DISCUSSION.

The total structure factors $I(Q)$ [equation (4)] of the (Ni-Co-Fe)$_x$Zr$_{1-x}$ glasses, measured with x-rays, are shown in Fig. 1, and the corresponding total correlation functions $T(r)/\langle f(0) \rangle^2$ [equation (6)] are presented in Fig. 2. The equivalent neutron data are shown in Fig. 3. Although the structure factors $I(Q)$ are rather similar for the concentration range studied, the corresponding correlation function $T(r)$ clearly show the effect of the different Zr concentrations. The first peak in $T(r)$ is split into two maxima, one positioned at $r_1=2.69$Å, and the other at $r_2=3.15$Å. The latter peak changes in height with varying Zr content in the same way as the values of the weight factor $[c_{Zr} f_{Zr}(0)]^2/\langle f(0) \rangle^2$ do [see equations (6) and (8)].

Thus, it is reasonable to assume that the peak at $r_2=3.15$Å is due to the Zr-Zr first neighbors in the metallic glass [2].

Substitution of Co (up to 25 at%) or Fe (5 at%) for Ni did not change the x-ray scattering patterns of the Ni$_{53}$Zr$_{65}$ glasses. The x-ray total $I(Q)$ shown in Fig. 1 is the composite curve of the data taken with specimens containing 5 and 18 at% Co and 5 at% Fe, respectively. Since the x-ray weight factors $W_{ik}(Q)$ [equation (6)] are little affected by the substitution of Fe or Co for Ni, it is reasonable to assume that Co can be readily substituted for Ni, and that 5 at% Fe substitution did not change the structure within the accuracy of the experiment.
Fig. 1 Total structure factors $I(Q)$ of amorphous (Ni-Co-Fe)-Zr, measured with x-rays.

Fig. 2 Total correlation functions $T(r)$ of amorphous (Ni-Co-Fe)-Zr alloys.

Fig. 3 Neutron structure factors $I(Q)$ and correlation functions $T(r)$ of amorphous (Ni-Co-Fe)-Zr.

Fig. 4 Partial atomic pair structure factors $I_{ik}(Q)$ of amorphous Ni$_{35}$Zr$_{65}$. 

Ni-Co-Fe-Zr

30 - 70

35 - 65

35 - 5 - 60

40 - 5 - 55

Ni-Zr

Ni-Co-Fe

Zr - Zr

Ni$_{35}$Zr$_{65}$

Zr - Ni

Ni - Ni

Ni-Co-Zr

Ni-Zr

0 2 4 6 8 10 12 14

Q in Å⁻¹

0 2 4 6 8 10

r in Å

0 2 4 6 8 10 12 14

Q in Å⁻¹

0 2 4 6 8 10

r in Å

0 2 4 6 8 10 12 14

Q in Å⁻¹

0 2 4 6 8 10

r in Å

0 2 4 6 8 10 12 14

Q in Å⁻¹
The neutron measurements on the Ni$_{35}$Zr$_{65}$ were recently repeated at Argonne National Laboratory, and showed a lower background than the previous data [3,4]. Therefore, it was felt that a reevaluation of the partial structure factors would be desirable. We used the x-ray data of the Ni$_{35}$Zr$_{65}$ and Ni$_{35}$Zr$_{35}$Hf$_{50}$ alloys and the neutron data of the Ni$_{35}$Zr$_{65}$ and Ni$_{17}$Co$_{18}$Zr$_{65}$ alloys in the recalculation. The atomic pair partial structure factors $I_{11}(Q)$, $I_{12}(Q)$ and $I_{13}(Q)$ are shown in Fig. 4. These data are in very good agreement with those published previously [4], but their weighted sum [equation (4)] produced a much better fit with the total structure factor $I(Q)$, measured with neutrons.

The partial atomic pair correlation functions $T_{1k}(r)$, $T_{2k}(r)$ and $T_{12}(r)$ are shown in Fig. 5, and the corresponding pair correlation functions $T_{1}(r) = c_{1}T_{11}(r) + c_{2}T_{12}(r)$ and $T_{2}(r) = c_{1}T_{12}(r) + c_{2}T_{22}(r)$ are presented in Fig. 6. It is clear from this figure that the distribution of atoms about a Ni atom is quite different from atomic distribution about a Zr atom. The individual partial coordination numbers $N_{ik}$ were evaluated from the area under the first peak in $rT_{ik}(r)$, centered at $(r)_{ik}$. The following values were obtained: $(r)_{NiNi}=2.66\AA$, $(r)_{NiZr}=2.69\AA$, $(r)_{ZrZr}=3.15\AA$, $N_{NiNi}=2.3$, $N_{NiZr}=7.9$, and $N_{ZrZr}=9.1$. It is possible to calculate the partial coordination numbers $N_{11}=N_{11}+N_{12}$ from these data, i.e., $N_{1}=10.2$ and $N_{2}=13.4$. These numbers are in reasonable agreement with those calculated directly from Fig. 6.

In order to see the effect of chemical ordering in this amorphous alloy, the chemical short-range order (CSRO) parameter $\alpha_1$ was calculated using the relation [5]:

$$\alpha_1 = 1 - N_{12}/c_2N_w$$  \hspace{1cm} (11)

where $N_w = c_2N_1 + c_1N_2 = 11.3$  \hspace{1cm} (12)

Equation (11) yields a value of $\alpha_1 = -0.08$. However, it is also possible to evaluate
the CSRO parameter directly from the number-concentration correlation functions $T_{n-c}(r)$ which are the Fourier transforms of the number-concentration structure factors $S_{n-c}(Q)$, which are shown in Figs. 8 and 7, respectively.

If we define the number-concentration coordination numbers $N_{n-c}(r)$ as a function of the upper limit of integration of the correlation functions $rT_{n-c}(r)$, we can define the CSRO parameter $\alpha_{1}(r)$ as follows:

$$\alpha_{1}(r) = N_{n-c}(r)/N_{w}(r) = 1 - N_{12}(r)/(c_{2}[c_{2}N_{1}(r)+c_{1}N_{2}(r)])$$

The values of the coordination numbers $N_{ik}(r)$ are given in Table 1 as a function of the upper limit of integration $r$, together with the CSRO parameter $\alpha_{1}(r)$.

Table 1. Partial coordination numbers $N_{ik}(r)$ and CSRO parameter $\alpha_{1}(r)$ in Ni$_{35}$Zr$_{65}$

<table>
<thead>
<tr>
<th>$r$ (Å)</th>
<th>3.0</th>
<th>3.2</th>
<th>3.4</th>
<th>3.6</th>
<th>3.8</th>
<th>4.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-NiNi</td>
<td>2.2</td>
<td>2.3</td>
<td>2.2</td>
<td>2.2</td>
<td>2.3</td>
<td>2.8</td>
</tr>
<tr>
<td>Ni-NiZr</td>
<td>4.9</td>
<td>5.6</td>
<td>6.7</td>
<td>7.7</td>
<td>8.6</td>
<td>9.2</td>
</tr>
<tr>
<td>Zr-ZrZr</td>
<td>2.1</td>
<td>5.0</td>
<td>7.5</td>
<td>8.7</td>
<td>9.1</td>
<td>9.1</td>
</tr>
<tr>
<td>$\alpha_{1}(r)$</td>
<td>-0.20</td>
<td>-0.09</td>
<td>-0.07</td>
<td>-0.09</td>
<td>-0.11</td>
<td>-0.11</td>
</tr>
</tbody>
</table>

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