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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 $S_{nc}(Q)$ 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 $S_{nc}(Q)$ 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 $S_{nc}(Q)$ as a function of the length of the diffraction vector $Q$, i.e.

$$Q = (4\pi/\lambda)\sin\theta = (4\pi m/h)(L/t)\sin\theta$$

where $\lambda$ is the wavelength, $m$ is the mass of the neutron, $h$ is Planck's constant, $L$ is the total path traveled by the neutrons in the time $t$. For binary alloys, we can write:

$$I_a(Q) = \langle f^2 \rangle + (c_1f_1)^2[I_{11}(Q)-1] + (c_2f_2)^2[I_{22}(Q)-1] + 2c_1c_2f_1f_2[I_{12}(Q)-1]$$

$$I_a(Q) = \langle f^2 \rangle + \Delta f \langle f \rangle S_{nc}(Q) + c_1c_2(\Delta f)^2[S_{cc}(Q)/(c_1c_2)]-1$$

where $f_i(Q)$ and $c_i$ are the coherent scattering amplitude and atomic concentration, respectively, of element $i$, $\langle f \rangle = \Sigma c_i f_i(Q)$, $\langle f^2 \rangle = \Sigma c_i [f_i(Q)]^2$ and $\Delta f = f_1(Q)-f_2(Q)$. It can be readily shown that the factors $I_{ik}(Q)$ and $S_{nc}(Q)$ are related [1]. The total structure factors $I(Q)$ and $S(Q)$ are defined as follows:
The Fourier transforms of $Q[I(Q)-I]$ and $Q[S(Q)-I]$ 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:

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

(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.,

$$T(r) = \sum_{i,k} c_i f_i(0) c_k f_k(0) T_{ik}(r)$$

(8)

where $T_{ik}(r) = 4\pi r \rho_{ik}(r)/c_k = G_{ik}(r) + 4\pi r \rho_0$

(9)

$\rho_{ik}(r)$ is the partial atomic distribution function which represents the number of $k$-atoms per unit volume at the distance $r$ from an $i$-type atom, and $G_{ik}(r)$ is the Fourier transform of the partial structure factor $I_{ik}(Q)$:

$$G_{ik}(r) = \frac{2}{\pi} \int Q[I_{ik}(Q)-1] \sin qr \, dq$$

(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 Al sample holders. The neutron samples consisted of about 5 g 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-K$\alpha$ 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$_{35}$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$_{65}$. 
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$_{30}$ 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 \( I_{12}(Q) \) 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.

\[ I(Q) = \sum \frac{\rho_1 \rho_2}{\rho_1 + \rho_2} \frac{4}{\pi} \int_0^\infty \! r^2 \sin(Qr) \rho_1(r) \rho_2(r) \, dr \]

Fig. 5 Partial pair correlation functions \( T_{ik}(r) \) of amorphous Ni$_{35}$Zr$_{65}$.

The partial atomic pair correlation functions \( T_{11}(r), T_{22}(r) \) 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 \( T_{2}(r) = c_1 T_{21}(r) + c_2 T_{22}(r) \) 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 \( r T_{ik}(r) \), centered at \( (r_i)_k \). The following values were obtained: \( (r_i)_\text{NiNi}=2.66\,\text{Å}, \ (r_i)_\text{NiZr}=2.69\,\text{Å}, \ (r_i)_\text{ZrZr}=3.15\,\text{Å}, \)

\( N_{\text{NiNi}}=2.3, \ N_{\text{NiZr}}=7.9, \) and \( N_{\text{ZrZr}}=9.1. \) 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]:

\[ \alpha_1 = 1 - \frac{N_{12}}{c_2 N_w} \quad (11) \]

where \( N_w = c_2 N_1 + c_1 N_2 = 11.3 \quad (12) \)

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 \( r T_{n-c}(r) \), we can define the CSRO parameter \( \alpha_1(r) \) as follows:

\[
\alpha_1(r) = \frac{N_{cc}(r)}{N_w(r)} = 1 - \frac{N_{12}(r)}{c_2_n_1 N_1(r) + c_1 N_2(r)}
\]

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 \( \text{Ni}_{35}\text{Zr}_{65} \)

<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>N-NiNi(r)</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>N-NiZr(r)</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>N-ZrZr(r)</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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