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

$$Q = (4\pi/\lambda)\sin\theta = (4\pi m/h)(L/t)\sin\theta \qquad (1)$$

where λ 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:

$$I_a(Q) = \langle f^2\rangle+(c_1f_1)^2[I_{11}(Q)-1]+(c_2f_2)^2[I_{22}(Q)-1]+2c_1f_1c_2f_2[I_{12}(Q)-1] \qquad (2)$$

$$I_a(Q) = \langle f^2\rangle+\langle f\rangle^2[S_{nn}(Q)-1]+2\Delta f\langle f\rangle S_{nc}(Q)+c_1c_2(\Delta f)^2\{[S_{cc}(Q)/(c_1c_2)]-1\} \qquad (3)$$

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 $S_{n-c}(Q)$ are related [1].

The total structure factors I(Q) and S(Q) are defined as follows:

$$I(Q)-1 = [I_a(Q)-\langle f^2\rangle]/\langle f\rangle^2 = \Sigma\Sigma W_{ik}(Q)[I_{ik}(Q)-1] \quad (4)$$

$$S(Q)-1 = [I_a(Q)-\langle f^2\rangle]/\langle f^2\rangle = \Sigma\Sigma W_{ik}(Q)[\langle f\rangle^2/\langle f^2\rangle][I_{ik}(Q)-1] \quad (5)$$

where $W_{ik}(Q) = c_i f_i(Q) c_k f_k(Q)/\langle f(Q)\rangle^2$ (6)

The Fourier transforms of Q[I(Q)-1] and Q[S(Q)-1] yield the total, reduced atomic distribution functions $G_I(r)$ and $G_S(r)$, respectively. It can be readily shown that the total correlation function T(r) is given by:

$$T(r) = \langle f(0)\rangle^2 G_I(r) + 4\pi r\rho_0\langle f(0)\rangle^2 = \langle [f(0)]^2\rangle G_S(r) + 4\pi r\rho_0\langle f(0)\rangle^2 \quad (7)$$

where ρ_0 is the average atomic density of the amorphous alloy. T(r) is related to the partial correlation functions $T_{ik}(r)$, i.e.,

$$T(r) = \Sigma\Sigma c_i f_i(0) c_k f_k(0) T_{ik}(r) \quad (8)$$

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 $I_{ik}(Q)$:

$$G_{ik}(r) = (2/\pi)\int Q[I_{ik}(Q)-1]\sin Qr\, dQ \quad (10)$$

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 2θ 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 λ technique.

III.- RESULTS AND DISCUSSION.

The total structure factors I(Q) [equation (4)] of the $(Ni\text{-}Co\text{-}Fe)_x Zr_{1-x}$ 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.

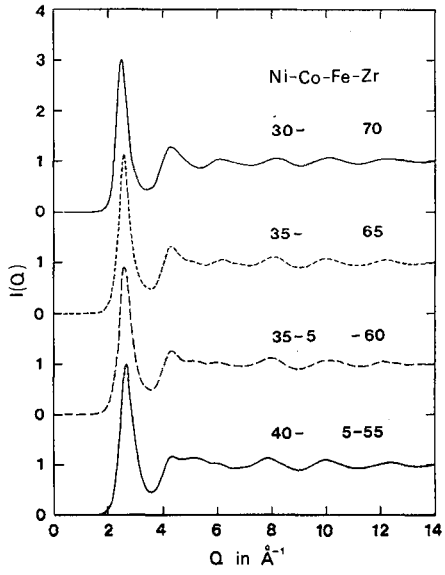

Fig. 1 Total structure factors I(Q) of amorphous (Ni-Co-Fe)-Zr, measured with x-rays.

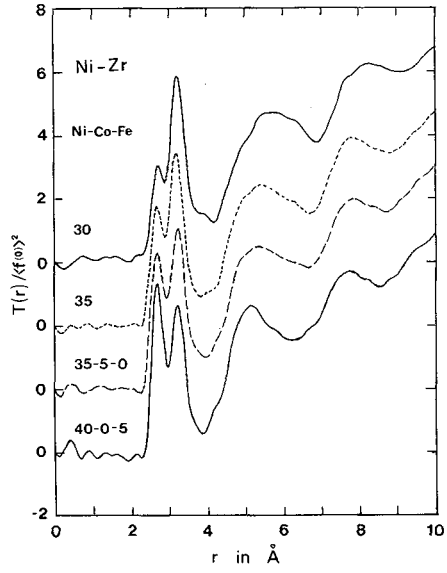

Fig. 2 Total correlation functions T(r) of amorphous (Ni-Co-Fe)-Zr alloys.

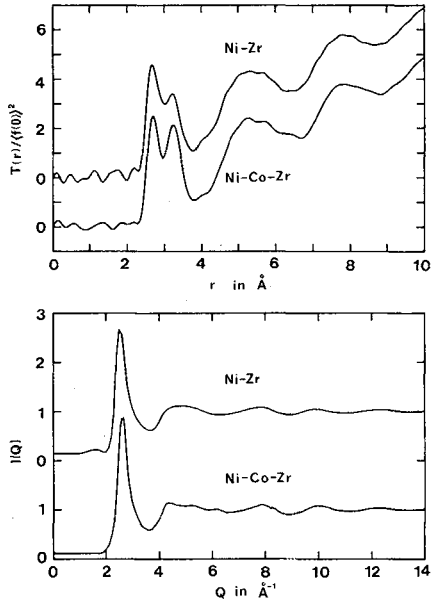

Fig. 3 Neutron structure factors I(Q) and correlation functions T(r) of amorphous (Ni-Co-Fe)-Zr.

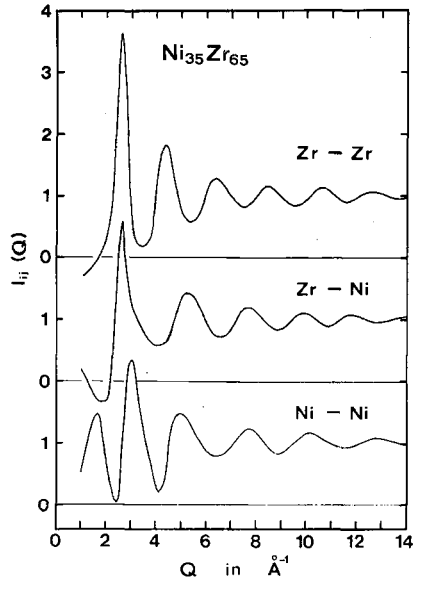

Fig. 4. Partial atomic pair structure factors $I_{ik}(Q)$ of amorphous $Ni_{35}Zr_{65}$.

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 $I_{11}(Q)$, $I_{22}(Q)$ 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.

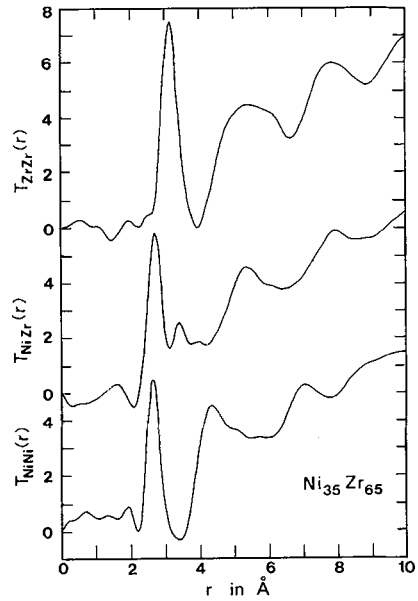

Fig.5 Partial pair correlation functions $T_{ik}(r)$ of amorphous $Ni_{35}Zr_{65}$.

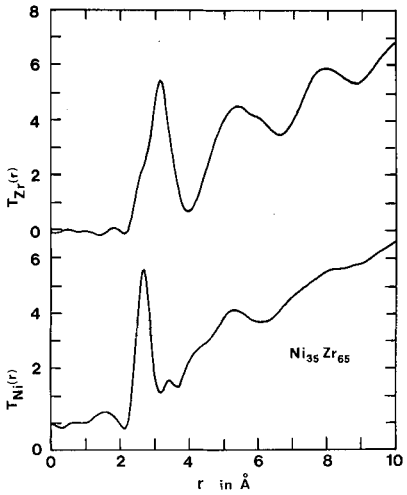

Fig. 6 Atomic pair correlation functions $T_i(r) = \Sigma c_k T_{ik}(r)$ of amorphous $Ni_{35}Zr_{65}$.

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 coorrelation functions $T_1(r) = c_1T_{11}(r)+c_2T_{12}(r)$ and $T_2(r) = c_1T_{21}(r)+c_2T_{22}(r)$ 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 $(r_1)_k$. The following values were obtained: $(r_1)_{NiNi}$=2.66Å, $(r_1)_{NiZr}$=2.69Å, $(r_1)_{ZrZr}$=3.15Å, N_{NiNi}=2.3, N_{NiZr}=7.9, and N_{ZrZr}=9.1. It is possible to calculate the partial coordination numbers $N_{i1}=N_{i1}+N_{i2}$ 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 α_1 was calculated using the relation [5]:

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

where $N_w = c_2N_1 + c_1N_2 = 11.3$ (12)

Equation (11) yields a value of α_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:

$$\alpha_1(r) = N_{cc}(r)/N_w(r) = 1 - N_{12}(r)/\{c_2[c_2N_1(r)+c_1N_2(r)]\} \quad (13)$$

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 coordiation numbers $N_{ik}(r)$ and CSRO parameter $\alpha_1(r)$ in $Ni_{35}Zr_{65}$

r (Å)	3.0	3.2	3.4	3.6	3.8	4.0
N-NiNi(r)	2.2	2.3	2.2	2.2	2.3	2.8
N-NiZr(r)	4.9	5.6	6.7	7.7	8.6	9.2
N-ZrZr(r)	2.1	5.0	7.5	8.7	9.1	9.1
$\alpha_1(r)$	-0.20	-0.09	-0.07	-0.09	-0.11	-0.11

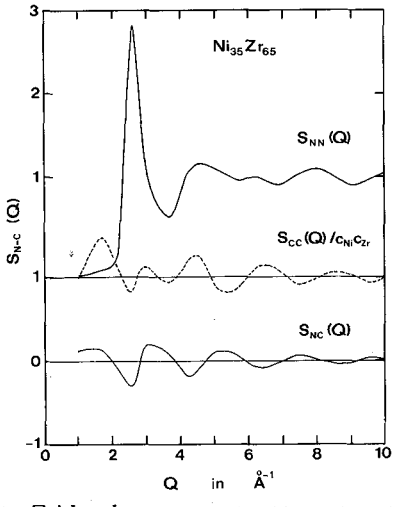

Fig 7 Number-concentration structure factors $S_{n-c}(Q)$ of $Ni_{35}Zr_{65}$.

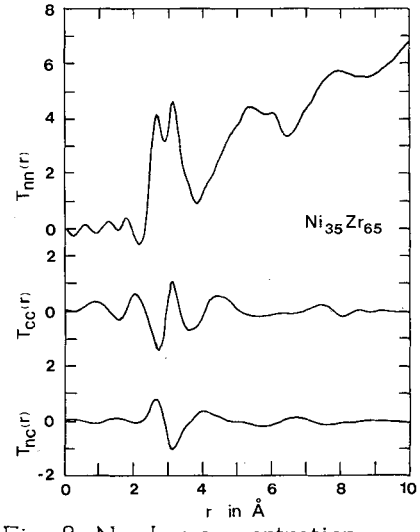

Fig. 8 Number-concentration functions $T_{ik}(r)$ of $Ni_{35}Zr_{65}$.

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