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TOPOLOGICAL AND CHEMICAL SHORT RANGE ORDER IN METAL-METAL GLASSES

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The atomic-scale structure of metallic glasses can be determined from their x-ray scattering patterns. For this short review, we will report on the topological and chemical short-range atomic order in metal-metal glasses, consisting of the elements Zr(Hf), Ti and Ni with different atomic radii i.e., 3.17, 2.89 and 2.49 Å, respectively, i.e. Ni-Zr-Hf [1] and Ni-Ti [2] prepared by melt-spinning. The x-ray intensities, scattered by the amorphous samples, were measured in transmission using AgK $\alpha$  radiation and a Si(Li) solid state detector in the conventional, scanning 2 $\theta$  mode [3]. In addition, the neutron scattering pattern of a Ni-Ti alloy has been obtained by Ruppertsberg [2].

The measured intensities were used to calculate  $I_a(k)$ , the scattered intensity per atom, from which the total interference functions were evaluated using the definitions [3]

$$I(k) = \{I_a(k) - [\langle f^2 \rangle - \langle f \rangle^2]\} / \langle f \rangle^2$$

or

$$S(k) = I_a(k) / \langle f^2 \rangle$$

where  $\langle f \rangle$  and  $\langle f^2 \rangle$  are the mean and mean square scattering factors, respectively.

In the context of the present paper, it is advantageous to express  $I(k)$  and  $S(k)$  in terms of the Bhatia-Thornton partial structure factors  $S_{NN}(k)$ ,  $S_{NC}(k)$  and  $S_{CC}(k)$  [4].

It has been shown [3] that

$$(1) \quad \langle f \rangle^2 [I(k) - 1] = \langle f^2 \rangle [S(k) - 1] = \langle f \rangle^2 [S_{NN}(k) - 1] + 2\Delta f \langle f \rangle S_{NC}(k) + [\langle f^2 \rangle - \langle f \rangle^2] \{ [S_{CC}(k) / (c_1 c_2)] - 1 \}$$

where  $\Delta f = f_2 - f_1$ . The Fourier transform of  $k[I(k) - 1] = \langle f^2 \rangle [S(k) - 1] / \langle f \rangle^2$  is given by  $G(r)$ , i.e.,  $G(r) = (2/\pi) \int k[I(k) - 1] \sin kr \, dk$ .

In terms of Bhatia-Thornton partial functions, we can write [3]:

$$(2) \quad \langle f \rangle^2 G(r) = \langle f \rangle^2 [G_{NN}(r)] + 2\Delta f \langle f \rangle G_{NC}(r) + [\langle f^2 \rangle - \langle f \rangle^2] G_{CC}(r).$$

Introducing the quantity  $\rho_i(r)$  which represents the number of atoms per unit volume about an i-type atom, we can write [3]

$$(4) \quad G_{NN}(r) = 4\pi r [c_1 \rho_1(r) + c_2 \rho_2(r) - \rho_0]$$

$$(5) \quad G_{NC}(r) = 4\pi r [\rho_1(r) - \rho_2(r)]$$

$$(6) \quad G_{CC}(r) = 4\pi r [c_2 \rho_1(r) + c_1 \rho_2(r) - \rho_{12}(r) / c_2]$$

Using the abbreviation  $\rho_w(r) = c_2 \rho_1(r) + c_1 \rho_2(r) \neq c_1 \rho_1(r) + c_2 \rho_2(r) = \rho_{NN}(r)$ , we can express  $G_{CC}(r)$  in terms of the Warren chemical short-range order (CSRO) parameter  $\alpha(r)$ , i.e.,

$$(7) \quad G_{CC}(r) = 4\pi r \rho_w(r) \alpha(r)$$

and

$$(8) \quad \alpha(r) = 1 - \rho_{12}(r) / [c_2 \rho_w(r)].$$

Amorphous Ni-Zr-Hf Alloys: Since Zr and Hf belong to the same column in the periodic table, and the atomic diameters of 3.17 and 3.15 Å, for Zr and Hf respectively, are very close, it is not surprising that they form an almost ideal solid solution.

These facts seem to indicate that the chemical behavior of Zr and Hf is almost identical, and that each can freely substitute for the other without affecting their local environment in liquid or amorphous alloys. Thus, the ternary alloy Ni-Zr-Hf may be considered to be a quasi-binary system of Ni and average Zr-Hf atoms. However, the Hf atom has many more electrons and consequently, a much larger scattering factor for x-rays. It seems, therefore, possible to change the weighting factors  $\langle f \rangle$ ,  $\Delta f$ , and  $\langle \Delta f^2 \rangle$  in equations (1) and (2) by increasing the Hf concentration in a series of Ni<sub>35</sub>(Zr-Hf)<sub>65</sub> alloys, i.e. by performing an isomorphous substitution of Zr by Hf [5].

The interference functions  $I(k)$  of seven Ni<sub>35</sub>Zr<sub>65-x</sub>Hf<sub>x</sub> with  $x = 0, 5, 10, 15, 20, 25$  and  $30$  at. % were obtained from the x-ray scattering patterns [1], and, as an example,  $I(k)$  is shown in Fig. 1 for the Ni<sub>35</sub>Zr<sub>65</sub> alloy. The Fourier transform of  $k[I(k) - 1]$ , i.e. the reduced radial distribution function  $G(r)$  exhibits a split first peak as shown in Fig. 2 for the same Ni<sub>35</sub>Zr<sub>65</sub> alloy. The first maximum, which decreases in height with increasing Hf content, lies at  $r_1' = 2.69$  Å, and the second is  $r_1'' = 3.19$  Å and becomes larger in height with increasing Hf concentration. This strongly suggests that the peak at  $r_1''$ , corresponds to the Zr-Zr interatomic distances.

The Bhatia-Thornton partial structure factors were calculated from three  $I(k)$  using equation (1) and are also shown in Fig. 1. It is readily seen that  $S_{NN}(k)$  strongly resembles  $I(k)$  because the factor  $(f_2 - f_1)/\langle f \rangle \leq 0.50$  and the functions  $S_{NC}(k)$  and  $[S_{CC}(k) - c_1c_2]$  are relatively small.

A similar conclusion can be reached when comparing  $G(r)$  of the Ni<sub>35</sub>Zr<sub>65</sub> alloy with  $G_{NN}(r)$ , the Fourier transform of  $k[S_{NN}(k) - 1]$  as shown in Fig.

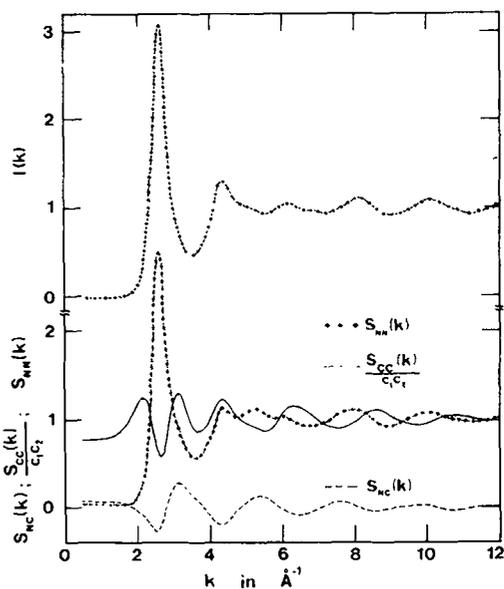


Fig. 1: Interference function  $I(k)$  of an amorphous Ni<sub>35</sub>Zr<sub>65</sub> alloy prepared by melt-spinning. Also shown are the Bhatia-Thornton structure factors  $S_{NN}(k)$ ,  $S_{NC}(k)$ , and  $S_{CC}(k)/(c_1c_2)$ .

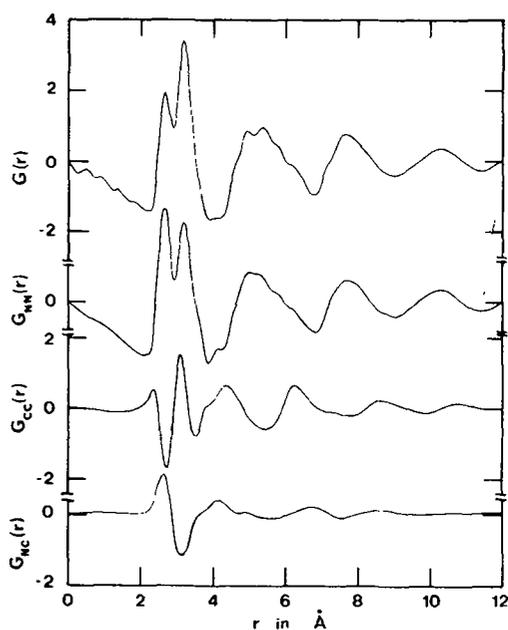


Fig. 2: Reduced atomic distribution function  $G(r)$  for the amorphous Ni<sub>35</sub>Zr<sub>65</sub> alloy. Also shown are the partial reduced atomic distribution functions of the Ni<sub>35</sub>Zr<sub>65</sub> alloy, i.e.,  $G_{NN}(r)$ ,  $G_{NC}(r)$ , and  $G_{CC}(r)$  which represent the Fourier transform of  $k[S_{NN}(k) - 1]$ ,  $k S_{NC}(k)$  and  $k[S_{CC}(k) - c_1c_2]/(c_1c_2)$ , respectively.

2. Again,  $G_{NN}(r)$  shows the splitting of the first peak with maxima at  $r = 2.68$  and  $3.20$  Å. Also shown in Fig. 2 are the functions  $G_{NC}(r)$  and  $G_{CC}(r)$ . It is readily seen that  $G_{CC}(r)$  has a strong minimum at  $r = 2.68$  Å which results in a negative value of  $\alpha(r)$  indicating preference for unlike neighbors. Thus, the maximum in  $G_{NN}(r)$  at  $r = 2.68$  Å corresponds to Ni-(Zr-Hf) neighbors. The positive peak in  $G_{CC}(r)$  at  $r = 3.1$  corresponds to like neighbors and confirms our suggestion that the second peak in  $G_{NN}(r)$  or  $G(r)$  must correspond to Zr-Zr neighbor pairs. The integral of the  $r G_{NC}(r)$  over the range of  $r$  corresponding to the first coordination shell in the radial distribution function  $r G_{NN}(r) + 4\pi r^2 \rho_0$  is quite small. This permits us to use the coordination number  $\eta = c_1 n_1 + c_2 n_2 = 12.6$  to calculate the Warren CSRO parameter [equation (8)], i.e.,

$$\alpha_1 = (1/\eta) \int r [G_{CC}(r)] dr$$

where the integral is taken again over the values of  $r$  of the first coordination shell, which yielded the value of  $-0.50$ . Thus, the Warren CSRO parameter  $\alpha$ , was calculated as  $-0.04$ , indicating a slight preference for unlike neighbors in the first coordination shell.

**Amorphous Ni-Ti Alloys:** X-ray diffraction measurements were made on the amorphous binary alloys of  $Ni_{35}Ti_{65}$  and  $Ni_{40}Ti_{60}$ , and a neutron experiment was carried out on  $Ni_{40}Ti_{60}$  by Ruppertsberg [3]. The corresponding interference functions  $I^x(k)$  for x-rays and  $S^n(k)$  for neutrons are shown in Fig. 3, together with the Bhatia-Thornton partial structure factors  $S_{NN}(k)$ ,  $S_{NC}(k)$  and  $S_{CC}(k)/(c_1 c_2)$  which were obtained from the two x-ray and the neutron diffraction curves, assuming that the 35% and 40% Ni alloys possess the same local structure.

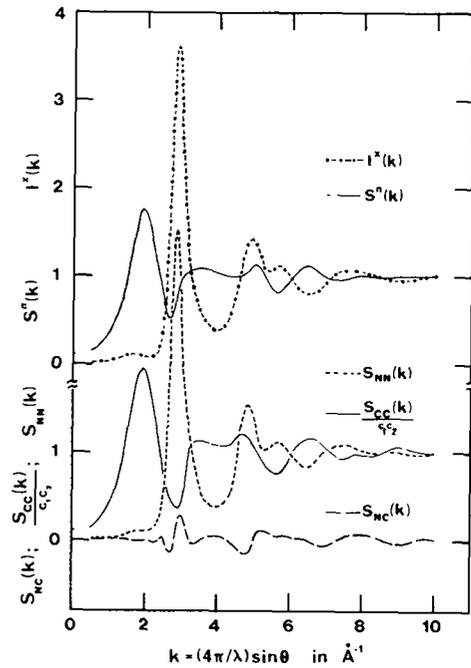


Fig. 3: Interference function  $I(k)$  evaluated from the x-ray scattering  $I_a(k)$  of an amorphous  $Ni_{40}Ti_{60}$  alloy, prepared by melt-spinning, and the corresponding structure factor  $S(k)$  determined from the neutron scattering  $I_a(k)$ . Also shown are the partial functions  $S_{NN}(k)$ ,  $S_{NC}(k)$ , and  $S_{CC}(k)/(c_1 c_2)$  for the  $Ni_{40}Ti_{60}$  alloy.

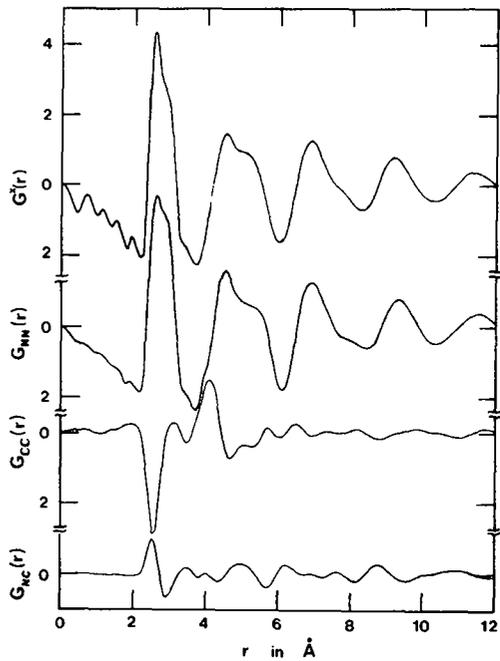


Fig. 4: Reduced atomic distribution function  $G^x(r)$  determined from  $I(k)$  for the amorphous  $Ni_{40}Ti_{60}$  alloy. Also shown are  $G_{NN}(r)$ ,  $G_{NC}(r)$  and  $G_{CC}(r)$ .

It is readily apparent that the total x-ray interference functions exhibit a prepeak at  $k \sim 1.8 \text{ \AA}^{-1}$  which becomes the main peak in the neutron data. This can be readily understood when one realizes that  $f_{\text{Ni}}$  and  $f_{\text{Ti}}$  are positive and equal to  $Z_{\text{Ni}} = 28$  and  $Z_{\text{Ti}} = 22$  at  $k = 0$ , whereas the neutron scattering cross-section  $b$  of Ni and Ti are opposite in sign, i.e.  $b_{\text{Ni}} = 1.03$  and  $b_{\text{Ti}} = -0.34$ . Thus the value  $\alpha = \langle f^2 \rangle / \langle f^2 \rangle = 0.986$  for x-rays is quite different from the value  $\alpha = \langle b^2 \rangle / \langle b^2 \rangle = 0.088$  for neutrons, and as a consequence, the x-ray interference functions are dominated by  $S_{\text{NN}}(k)$ , whereas  $S_{\text{CC}}(k)$  is the major component in the neutron interference function, because the factor  $\gamma = [\langle f^2 \rangle - \langle f \rangle^2] / \langle f^2 \rangle = 1 - \alpha$  is 0.014 and 0.912 for x-rays and neutrons, respectively. The strong modulation of the neutron structure factor  $S^{\text{n}}(k) \sim S_{\text{CC}}(k) / (c_1 c_2)$  is already an indication for the existence of chemical short-range order in the alloy. It is readily apparent from Fig. 3, that  $S^{\text{n}}(k)$  and  $S_{\text{CC}}(k) / (c_1 c_2)$  resemble each other quite closely.

The Fourier transforms  $G(r)$  of total interference functions and the Bhatia-Thornton partial structure factors are shown in Fig. 4. The partial function  $G_{\text{NN}}(r)$  is similar to the x-ray total  $G^{\text{x}}(r)$  as should be expected from the values of  $\langle f \rangle^2 / \langle f^2 \rangle$  in equation (1).  $G_{\text{NN}}(r)$  shows a broad first peak resulting from the superposition of  $G_{\text{NiTi}}(r)$  with a maximum at  $r_{\text{NiTi}} = 2.58 \text{ \AA}$  corresponding to the sharp minimum in  $G_{\text{CC}}(r)$ , and  $G_{\text{TiTi}}(r)$  with  $r_{\text{TiTi}} = 2.92 \text{ \AA}$ . The Ni-Ti interatomic distance is much smaller than the mean value of the Ni atomic diameter ( $r = 2.5 \text{ \AA}$ ) and Ti-Ti distances.

The Warren CSRO parameter  $\alpha$ , has been evaluated using equation (8). The integration of  $rG_{\text{CC}}(r)$  was carried out with the integration limits  $r = 0$  and 3.7 which again corresponds to the mini-

mum of  $G_{\text{NN}}(r)$ , and yielded a value of -2.80. The values of  $\eta_{\text{Ni}}$  and  $\eta_{\text{Ti}}$  are quite close as indicated by the small oscillations in  $G_{\text{NC}}(r)$ , and can be taken from the radial distribution function, i.e.,  $\eta = 13$ . Thus the Warren CSRO value  $\alpha_1$  was found to be -0.21, which is smaller than the value of -0.67 for a completely ordered alloy. Again the negative sign corresponds to preference for unlike nearest neighbors. The value of  $\alpha_1 = -0.21$  corresponds to a Ni atom having 9.5 Ti neighbors instead of 7.8 for a random distribution.

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