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W. M. KECK LABORATORY OF
ENGINEERING MATERIALS

CALIFORNIA INSTITUTE OF TECHNOLOGY

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Professor W. L. Johnson, principal investigator.

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NOTICE

ABSTRACT

The radial distribution function of four refractory alloys of composition $(W_{.5}Ru_{.5})_{.8}M_{.2}$ where M = some metalloid are presented, along with densities,atomic volumes of metalloids and coordination numbers. The results are discussed and some comparisons made with some model calculations of dense random packings of hard spheres.

INTRODUCTION

Recently several refractory transition metal-metalloid alloy systems were reported to have been produced in the amorphous state[1] by rapid quenching from the liquid melt. These systems include Mo-Ru, Mo-Re, and W-Ru base alloys with glass transition temperatures as high as ∿ 900°C. The authors have since made a study[2] of the electrical, mechanical, structural, and superconducting properties of some of these systems with various metalloids as functions of metalloid composition. This report presents the results of further structural studies on some of these refractory amorphous alloys. X-ray diffraction measurements were made on four amorphous refractory transition metal-metalloid alloys of the form $(W_{.5}Ru_{.5})_{80}M_{20}$ where M is a metalloid from the group B, P, $B_{.5}Si_{.5}$, $B_{.5}Al_{.5}$. Atomic distribution functions of these glasses were calculated and compared to model calculations of dense random packings of hard spheres.

EXPERIMENTAL

The samples used in this study were prepared by induction melting of the constituents on a silver boat under an argon atmosphere. Phosphorus alloys are prepared by initial sintering of powder compacts and subsequent melting as above. Rapid quenching from the melt is achieved using the piston and anvil technique[3] producing final samples in the form of foils typically 40-60 μ in thickness. To provide a specimen for x-ray diffraction studies several foils are stacked together with thinned Duco cement on a bakelite substrate. The specimen may therefore be taken to be infinitely thick for the purpose of x-ray absorption corrections.

Diffraction studies were performed on a GE scanning diffractometer with a doubly-curved LiF monochromator located in the diffracted beam. Data was recorded from $2\theta = 12°$ to $160°$ using filtered Mo Kα ($\lambda = 0.7107\text{Å}$) radiation with counting time and scanning rate adjusted to provide 10^4-10^5 counts per interval so that statistical errors are $\sim \pm 1\%$. Densities of the amorphous metal foils were measured by the hydrostatic weighing technique[4] using toluene as the working fluid.

RESULTS

The basic experimental and analytical techniques used in this study are described by Cargill.[5] The experimentally observed x-ray intensity is corrected for background (from Duco cement, fluorescent radiation, air scattering, etc.) and polarization (including polarization from scattering off (200) planes in the LiF crystal). The resolution of the LiF monochromator was experimentally determined to be about 0.03Å and a Lorentzian band pass function was used to determine the Compton profile.[6,7] The resulting coherent scattering intensity, normalized to $<|f|^2>$ by the high angle method[8], is shown in Fig. 1 for $(W_{.5}Ru_{.5})_{80}B_{20}$ where $<|f|^2> = \sum_\alpha w_\alpha |f_\alpha(K)|^2$ is the mean squared scattering form factor[9] for the alloy averaged over the alloy composition. From this normalized coherent scattering intensity one obtains the interference function I(K)[5]

$$I(K) = \frac{I_{\text{coherent}} - <|f|^2>}{<|f|^2>} + 1$$

The reduced radial distribution function $G(r) = 4\pi r\,(\rho(r)-\rho_0)$ is then

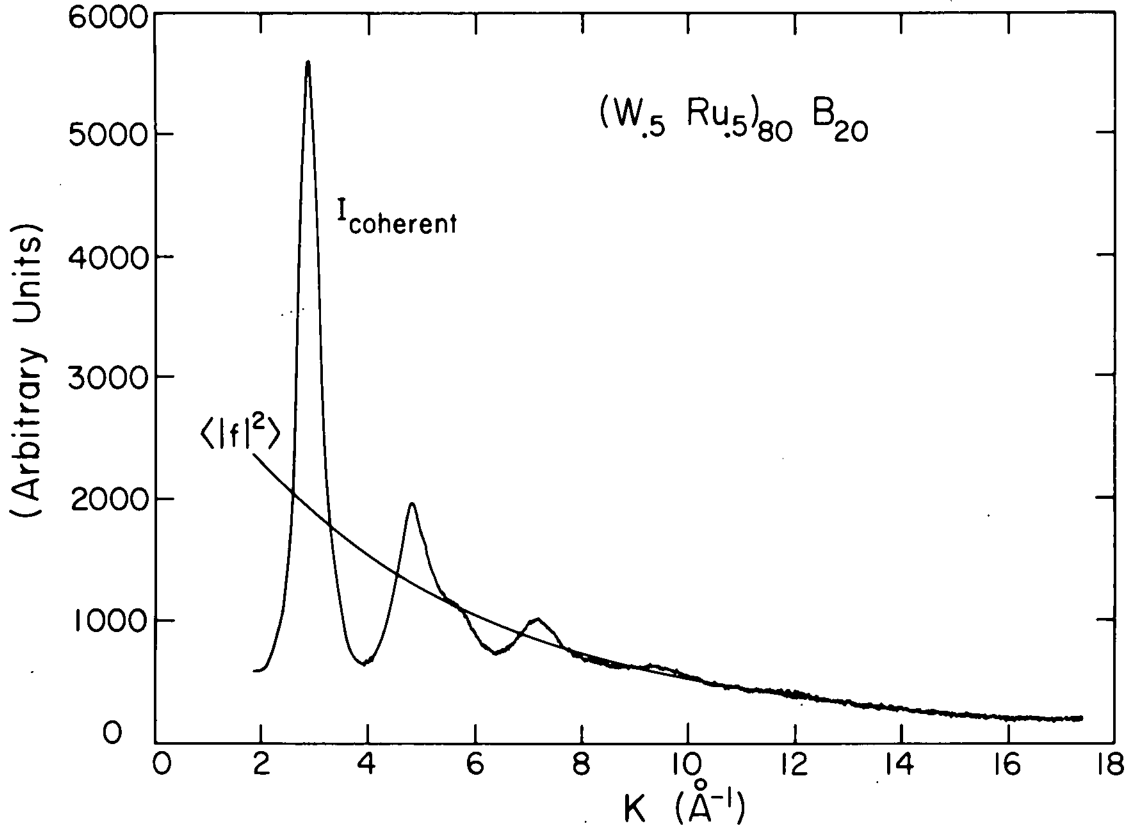

Fig. 1. Normalized coherent scattering intensity shown on the same scale with $<|f|^2>$, the compositional mean squared average atomic form factor.

obtained from the sin transform[5]

$$G(r) = \frac{2}{\pi}\int_0^{K_{max}} K(I(K) - 1)\, e^{-bK^2} \sin Kr\, dK$$

where K_{max} is the maximum obtainable wavevector ($\sim$ 17 Å^{-1} for Mo Kα). The decaying exponential is included to help reduce or eliminate the well known high frequency ripples[5] which occur in the integral transform due to its abrupt termination at K_{max}. The convergence factor, b, was typically taken between $0.001 \leq b \leq 0.005$ until the function G(r) appeared to be free of conspicuous high frequency ripple beyond the first peak.

DISCUSSION

Fig. 2 shows the G(r) obtained for four $(W_{.5}Ru_{.5})_{80}M_{20}$ alloys with various metalloids. The position of the primary maximum in the distribution function is essentially the average nearest neighbor distance (NND) of two transition metal atoms in the glass. Table I shows this NND to be typically somewhat higher than the average Goldschmidt diameter, (typical RDF studies depict values as much as 3% higher), which for W and Ru (Goldschmidt radii 1.39 Å and 1.34 Å respectively) is 2.73 Å. The notable exception to this case is for $(W_{.5}Ru_{.5})_{80}B_{10}Al_{10}$ with a NND of only 2.69 Å.

$\overline{V}_B$ in Table I is the average volume per metalloid atom as determined by the equation[10]

$$\overline{V}_B = \left[\frac{\overline{V} - (1-x)V_A^0}{x}\right]$$

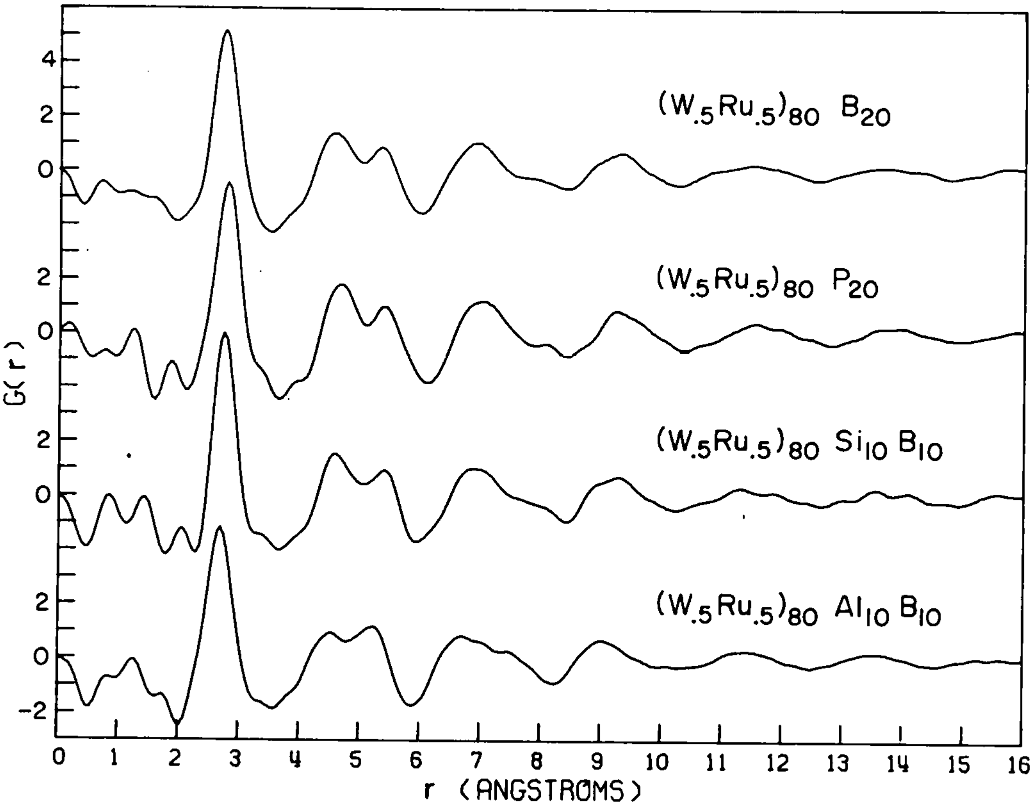

Fig. 2. Reduced radial distribution functions for four $(W_{.5}Ru_{.5})_{80}M_{20}$ amorphous alloys. The convergence factor used was .005

TABLE I. First, second, and third maxima in the RDFs, coordination numbers, average atomic volumes, average atomic volumes of metalloids and atomic densities for four $(W_{.5}Ru_{.5})_{80}M_{20}$ alloys and for the Bernal-Finney DRPHS model.

metalloid	1st max $R_1(\mathring{A})$	2nd max R_2/R_1	3rd max R_3/R_1	CN	$\overline{V}(\mathring{A}^3)$	$\overline{V}_B(\mathring{A}^3)$	$\rho\left(\frac{\text{atoms}}{\mathring{A}^3}\right)$
B_{20}	2.75	1.66	1.94	11.5	13.2	7.11	.0759
P_{20}	2.78	1.66	1.95	14.4	13.9	11.0	.0717
$B_{10}Si_{10}$	2.76	1.68	1.93	13.5	14.4	13.3	.0694
$B_{10}Al_{10}$	2.69	1.69	1.95	13.3	13.8	10.0	.0727
DRPHS	2.73	1.73	1.99	12	16.7	0	.0599

where x is the metalloid content in an alloy of the general form $TM_{1-x}M_x$ and $\overline{V}$ is the mean atomic volume as determined from density measurements for the amorphous alloy. V_A^o is the mean atomic volume for a hexagonal close packed solid solution of W and Ru using lattice parameters interpolated from ref. 11. For the composition $W_{.5}Ru_{.5}$, V_A^o was determined to be 14.7 $\mathring{A}^3$. If the average volume of B atoms in the $Al_{10}B_{10}$ and $Si_{10}B_{10}$ alloys is taken to be 7.11 $\mathring{A}^3$ then the average Si and Al atomic volumes are found to be 19.5 $\mathring{A}^3$ and 12.9 $\mathring{A}^3$ respectively. Except for the aluminum alloy, $\overline{V}_B$ and the metal-metal NND tend to increase with increasing size (i.e. Goldschmidt radii) of the metalloid atoms. The behavior of aluminum in this system is puzzling, for with the largest Goldschmidt radii (1.43 Å) of all the metalloids investigated, $(W_{.5}Ru_{.5})_{80}B_{10}Al_{10}$ maintains the smallest NND and a surprisingly large density. A suggested explanation for this is that some mechanism for charge transfer is available in the amorphous alloy which allows for the ionization of a substantial number of aluminum atoms. The presence of very small Al^{+3} ions (ionic radius 0.50 Å) might explain the small $\overline{V}$ and NND for this alloy.

Included in Table I are the results of the Bernal-Finney Model[12] for a dense random packing of hard spheres (DRPHS) with the hard sphere diameter set equal to 2.73 Å. Fig. 3 shows the results of this model compared to those obtained for amorphous $(W_{.5}Ru_{.5})_{80}B_{20}$. The agreement is quite impressive and is taken as strong evidence for the amorphous nature of these refractory metal-metalloid alloys.

The distinct double maxima in the second peak of G(r) is a common feature of many transition metal-metalloid glasses[5], as is the shoulder on the second peak of the intensity function (Fig. 1). Table I shows

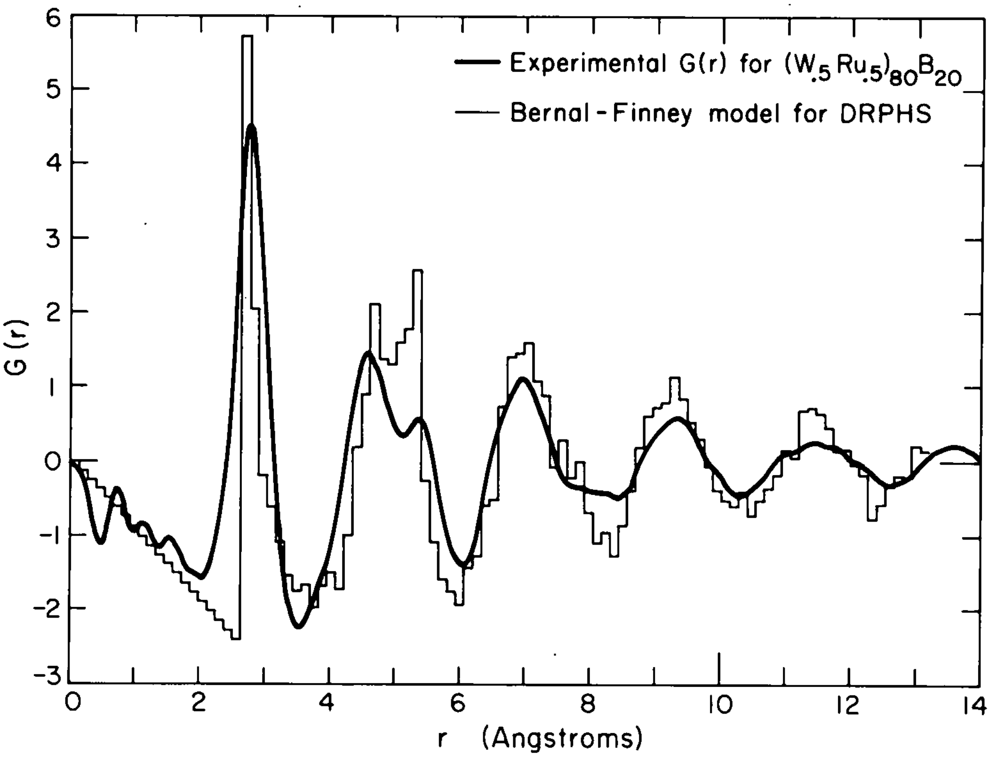

Fig. 3. A comparison of the reduced radial distribution functions of $(W_{.5}Ru_{.5})_{80}B_{20}$ and of the Bernal Finney DRPHS model.

that the second subpeak occurs in all cases at approximately twice the NND, corresponding to the collineation of three transition metal atoms. For the case of the first subpeak, however, the position obtained by DRPHS models is considerably larger than the experimental values. The configurations thought to produce these peaks are discussed by Finney[13] and Bennett.[14] The majority of DRPHS models favor only a peak near $r_2/r_1 = \sqrt{3}$ corresponding to the separation of opposite apices of two coplanar tetrahedron bases. W-Ru base alloys studied here exhibit a peak much closer to $\frac{2}{3}\sqrt{6} = 1.63$ which corresponds to the separation of opposite apices of two tetrahedra sharing a common base. Fig. 2 shows that in all but $(W_{.5}Ru_{.5})_{80}B_{10}Al_{10}$ this configuration is favored even over 3-fold collineations as is apparent from the relative sizes of the two subpeaks in the second maxima of the G(r). This type of structural short range order has been reproduced in the DRPHS model calculations of Sadoc et al[15] and is attributed to the prescence of five-fold symmetry rings characteristic of a pseudo-icosahedral structure.

Finally, the coordination numbers shown in Table I are arrived at by taking the area under the radial distribution function from r = o to $r = r_{min}$, the minimum following the primary maxima, i.e.

$$CN = \int_0^{r_{min}} 4\pi r^2 \rho(r)\, dr$$

where

$$G(r) = 4\pi r\,(\rho(r) - \rho_0).$$

The large values obtained for M = P, $B_{.5}Si_{.5}$, and $B_{.5}Al_{.5}$ are probably the result of the inclusion of some transition metal-metalloid pair contributions to the G(r). In the case of $(W_{.5}Ru_{.5})_{80}P_{20}$ for example, the W-P and P-W pairs have a weight of almost 20% that for the W-W pairs. The subsequent inclusion of some of the phosphorus atoms which are in the transition metal first coordination shell results in the somewhat exaggerated nearest neighbor coordination number.

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