A Comparison between the Structures of Amorphous and Liquid Ag–Cu and Cu–Mg alloys*

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Amorphous films of AgCu and CuMg₂, approximately 3000 Å in thickness, were prepared by co-evaporation of Ag and Cu, and Cu and Mg, respectively, onto 25 μm thick Be sheets, held at liquid nitrogen temperature. Mo Kα X-rays were used as a radiation probe to determine the structure of the films, at room temperature, and of the liquid alloys of Cu with 50 at.% Ag and with 0 and 67 at.% Mg at 50°C above the liquidus temperature. With the transmission technique, the interference functions (or structure factors) \( I(K) \) were determined in the range of \( K = 4\pi \sin \theta/\lambda \) between 0.8 Å⁻¹ and 12.5 Å⁻¹, and then Fourier transformed to obtain the radial distribution functions (RDF). The \( I(K) \) and RDF of the amorphous AgCu and CuMg₂ films were compared with those of the liquid Ag–Cu and Cu–Mg alloys, respectively. It was found that the structures of the amorphous and liquid Ag–Cu alloys were similar with a more well-defined short-range order occurring in the solid alloys, whose \( I(K) \) exhibited the well-known shoulder on the second peak. The \( I(K) \) and RDF of the amorphous CuMg₂ and the liquid Cu–Mg alloys cannot be explained by a common structure, although \( I(K) \) showed a small premaximum below the first main peak in both the amorphous and liquid alloys, a feature observed in many liquid Mg alloys.

I. Introduction

Metals and alloys usually possess a crystalline structure in their solid form. However, amorphous films and foils have been prepared by vapor deposition on cold substrates, a process usually called vapor-quenching. In this method, the vapor phase is condensed in vacuum onto a very cold substrate in order to reduce the mobility of the arriving atoms. Mader (1965) prepared films of Ag–Cu, Au–Co, and Cu–Mg at liquid nitrogen temperature. From the appearance of the electron diffraction patterns, which showed only diffuse halos, it was concluded that these films were indeed amorphous.

Non-crystalline alloys have also been prepared by rapid quenching of the liquid phase (Duwez & Willens, 1963), and by electrodeposition (Bagley & Turnbull, 1968).

The diffraction patterns of many non-crystalline, metallic alloys produced by these techniques show remarkable similarities (Giessen & Wagner, 1972; Cargill, 1975) indicating that the short-range atomic configuration might be similar. However, there are differences in the diffraction patterns of non-crystalline solids and liquids, which might indicate that their structures are indeed dissimilar. This is most clearly seen in the interference function \( I(K) \) which can be deduced from the diffraction pattern, i.e.

\[
I(K) = \frac{I_d(K) - \langle f^2 \rangle - \langle f \rangle^2}{\langle f \rangle^2},
\]

where \( \langle f \rangle \) and \( \langle f^2 \rangle \) are the mean and mean square atomic scattering factors of the alloys, respectively, and \( I_d(K) \) is the elastically scattered intensity, corrected for absorption, polarization, inelastic and multiple scattering, and expressed in electron units.

The interference functions of many non-crystalline solids exhibit a shoulder on the second peak. No such shoulder has been seen in liquid alloys. In addition, the maxima and minima of the interference functions are more pronounced in amorphous solids, and the positions of the maxima do not yield the same ratios for liquids and amorphous alloys (Giessen & Wagner, 1972; Wagner, 1972).

If measurements were made on a non-crystalline, solid alloy and then on the liquid alloy of the same composition under similar conditions, it would be reasonable to attribute any differences to a structural dissimilarity between these specimens. But, obviously, one experimental condition must be changed drastically for the determination of the structure of the liquid, and that is the temperature. Thus, the temperature difference in the study of these non-crystalline solid alloys usually done at room temperature and the liquid alloys done at approximately 50°C above the melting point is quite substantial. It has been shown in studies of liquid metals (Wagner, 1972), that the temperature has a great effect on the diffraction pattern, an effect which if extrapolated through the melting point, could make all of the differences noted before either disappear or become much less noticeable.

The present investigation on Ag–Cu and Cu–Mg alloys was carried out to compare the structure of the
non-crystalline solid and liquid alloys of similar compositions. Previously, the structure of a vapor-quenched AgCu alloy had been compared to the liquid Ag–Cu alloy of similar composition (Wagner, Light, Halder & Lukens, 1968). The interference function \( I(K) \) of this solid film is shown in Fig. 1 and is compared with the liquid and a model consisting of microcrystals containing 125 atoms. It is obvious from Fig. 1 that this vapor-quenched film has a microcrystalline structure with particle sizes less than 20 Å. In this investigation, attempts were made to produce vapor-quenched Ag–Cu and Cu–Mg films which showed only a few diffuse halos. The structure of these films and of the corresponding liquid alloy were then deduced from their X-ray diffraction patterns.

II. Experimental procedure

A. Preparation of vapor-quenched alloy films

The alloy films were prepared in an evaporator consisting of a 12 in diameter pyrex belljar mounted on top of two aluminum vacuum collars and evacuated by an oil diffusion pump through a baffle and cold trap. A liquid-nitrogen cooled Meissner trap was placed over the high-vacuum opening for the diffusion pump in the base plate. The system was modified during the course of experimentation by using a 12 in diameter pyrex collar with an aluminum cover, instead of the belljar, as a vacuum enclosure. The system was capable of reaching a vacuum of about \( 10^{-7} \) torr measured with a hot cathode ion-gauge mounted on the lower aluminum vacuum collar. During evaporation the pressure remained below \( 10^{-5} \) torr.

All alloy films were prepared by simultaneous evaporation of the two components from separate sources. Both resistance and electron-beam heating were used as methods of evaporation. The deposition rate and thickness of each component were monitored by quartz oscillators. The film thicknesses were also obtained by use of an optical interferometer. The thickness values obtained by these two methods generally agreed to within 100 Å. The control of deposition was performed manually. Typical total deposition rates were about 5 Å/sec at a source to substrate distance of 25 cm.

The films were deposited onto substrates clamped onto a liquid-nitrogen filled reservoir. The temperature of the substrate was approximately 80 K before deposition was begun. Beryllium sheets 25 μm thick were used as substrates. Beryllium was chosen because of its low scattered intensity for X-rays. All substrates were cleaned ultrasonically and coated with a 500 Å layer of collodion to assure a uniform, non-crystalline surface so as to avoid epitaxic effects.

The compositions of the three Ag–Cu alloys prepared in this way were Ag–45 at.%, Cu, Ag–51 at.%, Cu and Ag–55 at.%, Cu, with thicknesses of 1800 Å, 4000 Å, and 1900 Å, respectively. A film of Cu–65 at.% Mg, with thickness of 2800 Å, was also prepared.

B. Preparation of liquid alloys

The alloys needed for the investigation of the liquid structure were prepared directly in the high temperature X-ray camera (North & Wagner, 1969a, b). The desired composition and thickness (chosen to be close to \( \mu t = 1 \), where \( \mu \) is the linear absorption coefficient, and \( t \) the thickness) were obtained by sandwiching together foils of the pure materials (Cu and Ag, and Cu and Mg respectively), and of the appropriate thicknesses. The composition was determined from the weights of the elemental foils used. These foils were placed in the sample holder assembly which consisted of two 0.13 mm pyrolytic graphite sheets sandwiched between two graphite frames, each approximately 3 mm thick with a vertical, machined window, 5 mm wide and 16 mm high.

After the X-ray camera was flooded with an inert gas (80% He–20% H for Ag–Cu alloys, 80% Ar–20% H for Cu–Mg) the temperature was raised to about 50°C above the liquidus of the alloys at a rate of 300°C per min.

C. X-ray technique

The scattering data of the liquid alloys, and of the Ag–45 at.% Cu and of the Cu–65 at.% Mg films were taken in the transmission mode of operation which has been described before by North & Wagner (1969a), and Lukens & Wagner (1973). X-rays from a line source (Mo target) impinged on a bent, asymmetric LiF monochromator for the alloy film studies, or on a flat

![Fig. 1. Interference function \( I(K) \) of a vapor-quenched alloy film and of a liquid alloy of Ag–52 at.% Cu. The film was produced by simultaneous vapor-quenching of Ag and Cu onto a vitreous silica substrate held at liquid nitrogen temperature. The X-ray intensity from the film was obtained at room temperature. The liquid alloy was measured in reflection at 1000°C. The model represents f.c.c. crystallites with 125 atoms, with correction for thermal vibration at room temperature.](image-url)
graphite monochromator for the liquid investigations. All measurements were made in the X-ray camera in an inert atmosphere (alloy films at room temperature; liquids at 50°C above the liquidus).

Because of the thinness of the vapor-quenched films, the scattering data of every sample had to be taken over a period of four days. Therefore, the scattered intensity (at least 4000 counts) at a given angular position 20 was determined for a period of time necessary to accumulate a given number of counts of yttrium fluorescence radiation, excited by the primary, monochromatic Mo beam. This permitted the elimination of any fluctuation of the primary X-ray intensity from the X-ray tube and generator.

The scattered intensities from the liquids were sufficiently high to permit all measurements in less than 6 h, still yielding at least 4000 counts at every angular position of the detector.

The reflection technique was employed to obtain the scattering data of the Ag–51 at % Cu and the Ag–55 at % Cu films. A Ni target X-ray tube, a Co filter in the diffracted beam, and a proportional counter (with 15% energy resolution) provided sufficiently monochromatic radiation to obtain the scattering data necessary for confirmation of the non-crystallinity of the structure. The primary beam was also monitored during these measurements.

D. Data reduction and analysis

In order to determine the interference function I(K) from the raw data, the elastically scattered intensity must be recorded. The liquid samples and vapor-quenched films measured in transmission with Mo radiation were scanned from K = 0.8 to K = 12.5 Å⁻¹. The films studied with Ni radiation in reflection were scanned from K = 1.2 to K = 7.5 Å⁻¹.

In the case of the liquid samples and the vapor-quenched films, scattering from the sample holder assembly and substrate, respectively, had to be considered. This required two experiments for every sample studied. One experiment was run with the liquid in the sample holder assembly or the film on the substrate, and the other was run with the sample holder assembly or the substrate alone. The scattered intensities used in the analysis were then taken from the smooth curve drawn through the data points. Any distinct feature in the intensity function such as a shoulder on the second peak of I(K) (Cargill, 1975; Crewdson, 1966) or a prepeak before the first maximum (Lukens & Wagner, 1973) was clearly visible despite the scatter of the data points.

The substrate or sample holder scattering Ia(2θ) was corrected for absorption in the sample by the factor As, where

\[ A_s = \exp \left( -2\mu t / \sin \theta \right) \]  
for reflection

\[ A_t = \exp \left( -\mu t / \cos \theta \right) \]  
for transmission

where t is the thickness and \( \mu \) is the linear absorption coefficient of the sample. The sample scattering \( I_f(2\theta) \) corrected for sample holder scattering is then given by

\[ I_f(2\theta) = I_{\text{meas}}(2\theta) - I_a(2\theta)A_s. \]  
(4)

For the vapor-quenched alloys, the values of \( \mu \) of the elements were taken from Klug & Alexander (1954) and the values of \( t \) were taken to be thicknesses as determined from the quartz crystal oscillators and interferometer measurements.

The values of \( \mu \) of the liquid samples were readily obtained by the attenuation of the straight-through beam by the sample, after the intensity of the primary beam was lowered to manageable proportions with a 0.001 in Ta foil. The voltage was decreased so that \( \lambda / 2 \) radiation was not excited, as that would also be scattered by the monochromator.

To obtain the coherent intensity per atom \( I_a(K) \), the sample intensity \( I_f(2\theta) \) was divided by the polarization factor \( P \) and the absorption factor \( A_f \) for X-rays in the sample. The absorption factor \( A_f \) is given by

\[ A_f = \frac{1 - \exp \left( -2\mu t / \sin \theta \right)}{2(\mu) \sin \theta} \]  
for reflection

and

\[ A_f = \frac{(t / \cos \theta) \exp \left( -\mu t / \cos \theta \right)}{2(\mu) \cos \theta} \]  
for transmission

where \( \mu_t \) and \( t_s \) are the absorption coefficient and the thickness of the sample holder or substrate, respectively. The corrected intensity was then converted from 2\( \theta \) to \( K = 4\pi(\sin \theta) / \lambda \). This gave

\[ I_a(K) = \beta \frac{I_f(K)}{A_f} - I_a^n(K). \]  
(5)

\( I_a^n(K) \) is the inelastic scattering and \( \beta \) is the normalization constant (Wagner, 1972). There are two common normalization procedures; the high-angle method (Gringrich, 1943) and the radial distribution function method (Furukawa, 1962). In this investigation the average value of \( \beta \) obtained with the two methods was used. To evaluate \( \beta \) and to calculate \( I(K) \) from the normalized intensity \( I_a(K) \) using equation (1), the atomic scattering factors of Cromer & Waber (1965), which were corrected for anomalous dispersion, (Cromer, 1965) and the inelastic or Compton scattering factors of Cromer & Mann (1967) were employed.

The Fourier transform of the interference function, \( I(K) \), yields the reduced atomic distribution function, \( G(r) \), i.e.

\[ G(r) = 4\pi r \left[ \varrho(r) - \varrho_0 \right] = \frac{2}{\pi} \int_0^\infty F(K) \sin KrdK \]  
(6)

where \( F(K) = K[I(K) - 1] \), \( \varrho_0 \) is the average atomic density, and \( \varrho(r) \) can be expressed as (Kaplow, Strong & Averbach, 1966; Wagner, 1972)

\[ \varrho(r) = [c_1 f f_1 \varrho_{11}(r) + c_2 f^2 \varrho_{22}(r) + 2c_1 f f_2 \varrho_{12}(r)] / \langle f \rangle^2 \]  
(7)

assuming that the \( K \) dependence of \( f_i f_j \langle f \rangle^2 \) is small. In equation (7), \( c_i \) is the concentration of element \( i \) and \( \varrho_i(r) \) represents the number of \( j \)-type atoms per unit volume at the distance \( r \) from an \( i \)-type atom averaged over all \( i \)-type atoms in the alloy.
Unfortunately, the values of $F(K)$ needed in equation (6) are known to the upper limit $K_{\text{max}}$ imposed by the experimental conditions, introducing the so-called termination-of-series error, which produces subsidiary peaks in the neighborhood of the main peak in $G(r)$. Since the separation $\Delta r = r_1 - r$ between the maximum of the main peak, $r_1$, and the subsidiary peak, $r$, depends on $K_{\text{max}}$, i.e. $\Delta r = \pm 7.8/K_{\text{max}}$ (Warren, 1969), the values of $K_{\text{max}}$ in equation (6) were varied between $K_{\text{max}} = 7.5$ and $12.5\, \text{Å}$. Thus it became possible to ascertain whether small ripples close to the main peak were due to this error. In addition, a damping factor, $\exp(-\alpha^2 K^2)$ was employed with $\alpha^2 K_{\text{max}}^2 = 1.5$. This reduces greatly the magnitude of the subsidiary peaks (Warren, 1969).

However, large modulations were usually visible in $G(r)$ at small values of $r$ due to slowly varying errors in $F(K)$. These modulations were removed with the Kaplow procedure (Kaplow, Strong & Averbach, 1965) yielding refined interference functions $I(K)$ and atomic distribution functions $G(r)$.

To calculate the radial distribution function (RDF), $4\pi r^2 g(r)$ from $G(r)$, the values of the average atomic density $\rho_0$ must be known. Since no experimental values were available for the liquid and the films, $\rho_0$ was taken as the reciprocal of the average atomic volume of the alloy, i.e.

$$\rho_0 = \left(\sum_i c_i/\rho_i^0\right)^{-1}$$

where $\rho_i^0$ is the atomic density of element $i$ which was calculated from the macroscopic densities $\rho_i$, i.e. $\rho_i^0 = N_0 \rho_i/\Lambda_i$, $N_0$ being Avogadro’s number and $\Lambda_i$ the atomic weight of element $i$.

IV. Experimental results

A. Ag–Cu alloy system

The interference functions $I(K)$ of the as-deposited non-crystalline solid films with 45, 51, and 55 at.\% Cu and the liquid alloy with 50 at.\% Cu, are shown in Figs. 2 and 3. The solid films were measured at room temperature and the liquid alloy was measured at...
850 °C. Also shown in Fig. 2 is the interference function \( I(K) \) of a liquid-quenched Pd–Si foil. It is interesting to note that the \( I(K) \) for the solid films are similar; in particular, both exhibit a shoulder on the high-angle side of the second peak. This indicates that the Ag–Cu films are non-crystalline in agreement with the results of Mader et al. (1967) who showed that Ag–Cu alloys in the range of 35 to 65 at.\% Cu exhibited only diffuse halos in the selected area electron diffraction patterns. When the film with 55 at.\% Cu is annealed for 1 h at 77 °C, the slow appearance of crystalline reflections can be detected (Fig. 3).

The reduced total distribution functions, \( G(r) \), obtained by Fourier transformation of \( F(K) = K[I(K) - 1] \) by application of equation (6), and refined by the Kaplow procedure are shown in Fig. 4 for the film with 45 at.\% Cu and the liquid with 50 at.\% Cu. The most striking feature of the \( G(r) \) of the solid films is the asymmetric broadening or shoulder on the high \( r \)-value side of the second peak. After 1 h at 77 °C, the \( G(r) \) curve in Fig. 5 already reveals peaks and shoulders which correspond to atomic positions in the crystalline solid solution of Ag–Cu; they are not caused by the termination-of-series error due to the low value of \( K_{\max} = 7.5 \) Å\(^{-1}\).

The position of the first peak in \( G(r) \) is a measure of the interatomic distance \( r_1 \). Values of \( r_1 \) are given in Table 1, together with values of \( r_2 \) of the position of the second maximum of \( G(r) \).

The total radial distribution functions RDF = \( 4\pi r^2 g(r) \), are shown in Fig. 6. There is a broadening, but not what could be termed a splitting of the second peak of the solid films.

The area under the first peak of the RDF represents the coordination number, \( \eta \), defined as

\[
\eta = \int_{r_0}^{r_0} 4\pi r^2 g(r) \, dr,
\]

Fig. 4. Reduced atomic distribution functions \( G(r) = 4\pi r^2 [g(r) - \rho_0] \) of liquid Ag–50 at.\% Cu, of vapor-quenched Ag–45 at.\% Cu, and of liquid quenched Pd–Si alloy. Solid curves represent \( G(r) \), refined by the Kaplow procedure (Kaplow et al., 1965). Dotted curves below the first peak in \( G(r) \) represent the original data, with \( z^2 = 0 \).

Fig. 5. Reduced atomic distribution functions \( G(r) = 4\pi r^2 [g(r) - \rho_0] \) of Ag–55 at.\% Cu, in the as-deposited condition, and annealed for 1 h at 60 and 77 °C. Also shown are the positions of the 1st, 2nd, 3rd, 4th, 5th, 7th and 9th coordination shells in Ag, Cu and metastable \( \gamma \)-AgCu solution. The number of atoms in each shell (coordination number) is given in the parentheses.
where $r_0$ is the value below which $4\pi^2 q(r)$ is zero, and $r_0$ is the position of the first minimum of the RDF. Values of $\eta$ are also given in Table 1.

Table 1. Values of positions $r_n$ of the first and second peaks of $G(r)$ for the liquid and solid Cu–Ag and Cu–Mg alloys, also the coordination number $\eta$ determined from the radial distribution function

The data for liquid Ag–45 at.\% Cu are interpolated values taken from the plots of $r_n$ and $\eta$ versus at.\% (Lukens & Wagner, 1975). $K_{\text{max}}$ is the upper limit of the Fourier integral [equation (6)].

<table>
<thead>
<tr>
<th>$r_1$ (Å)</th>
<th>$r_2$ (Å)</th>
<th>$r_2/r_1$</th>
<th>$\eta$</th>
<th>$K_{\text{max}}$ (Å$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag–45 at.% Cu</td>
<td>2.83</td>
<td>4.90</td>
<td>1.73</td>
<td>13</td>
</tr>
<tr>
<td>Ag–51 at.% Cu</td>
<td>2.78</td>
<td>4.75</td>
<td>1.71</td>
<td>13</td>
</tr>
<tr>
<td>Ag–55 at.% Cu</td>
<td>2.75</td>
<td>4.74</td>
<td>1.72</td>
<td>13</td>
</tr>
<tr>
<td>Ag–50 at.% Cu</td>
<td>2.71</td>
<td>5.05</td>
<td>1.86</td>
<td>13</td>
</tr>
<tr>
<td>Cu–O at.% Mg</td>
<td>2.51</td>
<td>4.75</td>
<td>1.89</td>
<td>12.5</td>
</tr>
<tr>
<td>Cu–67 at.% Mg</td>
<td>2.69</td>
<td>5.05</td>
<td>1.93</td>
<td>9.5</td>
</tr>
<tr>
<td>Cu–65 at.% Mg</td>
<td>2.60</td>
<td>4.30</td>
<td>1.65</td>
<td>14</td>
</tr>
</tbody>
</table>

V. Discussion

A. Comparison of liquid and non-crystalline solid alloys of the system Ag–Cu

By comparing the interference functions of the vapor-quenched Ag–Cu alloys and the $I(K)$ of the liquid Ag–Cu alloy, one can see that the vapor-quenched films exhibit a small shoulder on the second peak whereas no shoulder is apparent for the liquid alloy. The apparent greater order of the non-crystalline solid alloy films is also reflected in the more intense first peak of the solid as compared to the liquid alloy. Table 2 gives the values for the first peak heights of the $I(K)$ of the solid films and the liquid.

Table 2. Values of the positions $K_n$ of the first and second peak maxima of the interference function $I(K)$ for liquid and solid Cu–Ag and Cu–Mg alloys, also the heights $I(K_1)$ of the first peak

<table>
<thead>
<tr>
<th>$K_1$ (Å$^{-1}$)</th>
<th>$K_2$ (Å$^{-1}$)</th>
<th>$K_2/K_1$</th>
<th>$I(K_1)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag–45 at.% Cu</td>
<td>2.83</td>
<td>4.88</td>
<td>1.73</td>
</tr>
<tr>
<td>Ag–51 at.% Cu</td>
<td>2.87</td>
<td>4.97</td>
<td>1.73</td>
</tr>
<tr>
<td>Ag–55 at.% Cu</td>
<td>2.90</td>
<td>4.98</td>
<td>1.72</td>
</tr>
<tr>
<td>Ag–50 at.% Cu</td>
<td>2.78</td>
<td>5.12</td>
<td>1.84</td>
</tr>
<tr>
<td>Cu–O at.% Mg</td>
<td>3.00</td>
<td>5.50</td>
<td>1.83</td>
</tr>
<tr>
<td>Cu–67 at.% Mg</td>
<td>2.70</td>
<td>5.05</td>
<td>1.87</td>
</tr>
<tr>
<td>Cu–65 at.% Mg</td>
<td>2.97</td>
<td>5.08</td>
<td>1.70</td>
</tr>
</tbody>
</table>

Various studies of the temperature dependence of the structure of liquid metals (Wagner, 1972; Fessler, Kaplow & Averbach, 1966), have shown that the intensities of the first peak in $I(K)$ decrease as the temperature increases. This might explain why the non-crystalline solid films of Ag–Cu measured at room temperature exhibit more intense first peaks in $I(K)$ than that of the liquid alloy measured at 850°C.
It has also been observed that the positions of the maxima of $I(K)$ change with temperature. An exact evaluation of the position $K_1$ of the first peak maximum has shown that $K_1$ moves to smaller values of $K$ with increasing temperature, $T$. Table 2 shows the peak maxima positions for the first and second peaks in $I(K)$ for the liquid and solid films. It can be seen that the value of $K_1$ for the solid is larger than that for the liquid, which was measured at a temperature about 800°C higher than those of the solids. A change in $K_1$ with temperature has been observed in liquid Cd (North & Wagner, 1969b), i.e. $\Delta K = 0.03 \text{ Å}^{-1}$ for $\Delta T = 300°C$. The change in $K_1$ observed in the Ag–Cu alloys is of the same order of magnitude.

It has also been shown that the positions of the higher maxima move slowly toward higher $K$ values with increasing $T$. Again, this appears to be consistent with the results of the present investigation as seen in Table 2.

In addition to changing the peak heights, changes in temperature also affect the depths of the minima of $I(K)$. As temperature increases, the minima become shallower. This is apparent in Fig. 2 which shows the $I(K)$ of the liquid and solid Ag–Cu alloys. Thus, the temperature has the effect of smoothing out details in the $I(K)$. The small shoulder on the second peak of $I(K)$ of the solid Ag–Cu films could very easily be washed out in the $I(K)$ of the liquid Ag–Cu foil because of the effect of temperature alone. In addition, the shift in peak positions of $I(K)$ of liquid metals, where the first maximum goes to lower $K$ and the higher maxima go to higher $K$ with increasing temperature, is shown to be true when the solid films are compared to the liquid Ag–Cu alloy. Taking these effects into account, we can say that the $I(K)$ of the vapor-quenched solid and liquid Ag–Cu alloys are quite similar, and that the major differences can be explained by the fact that the temperatures of measurement were different, and not necessarily by structural differences.

Let us now consider the $G(r)$ of the vapor-quenched and liquid alloys. The positions $r_n$ of the maxima of $G(r)$ are shown in Fig. 8 and 9.

![Fig. 8. Reduced atomic distribution functions $G(r) = 4\pi r^2 \rho(r)$ of liquid Cu (1100°C), liquid CuMg$_2$ (600°C) and vapor-quenched CuMg$_2$ (room temperature). Solid curves represent $G(r)$ refined by the Kaplow procedure. Dotted curves below the first peak in $G(r)$ represent the original data, with $\sigma^2 = 0$.](image)

![Fig. 9. Radial distribution function $4\pi r^2 \rho(r)$ of liquid Cu, liquid CuMg$_2$, and vapor-quenched CuMg$_2$ film.](image)
G(r) are taken as a measure of the interatomic distances in the alloy. It has been shown that as the temperature increases, the peak heights in G(r) decrease and the minima increase. This tends to wash out details and may be the reason why a splitting of the second peak usually observed in liquid-quenched foils, e.g. Pd-Si (Fig. 4), cannot be noticed in the liquid. The value of \( r_1 \) has also been shown to decrease whereas the positions of the higher maxima increase with increase in temperature in liquid metals. This is true for the Ag–Cu vapor-quenched solid films as compared to the Ag–Cu liquid as seen in Table 1. It should be pointed out that the position \( r \) is affected by the value of the upper limit \( K_{\text{max}} \) in equation (6). Therefore, a direct comparison is only possible between the film with 45 at.\% Cu and the liquid with 50 at.\% Cu. Taking into account that the position \( r_1 \) changes by \( \Delta r = +0.02 \) Å (Lukens & Wagner, 1975) when the composition decreases from 50 at.\% Cu to 45 at.\% Cu in the liquid alloy, it is found that the interatomic distance \( r_1 \), is much larger in the amorphous film \( (r_1 = 2.83 \) Å), than in the liquid alloy \( (r_1 = 2.73 \) Å).

The cut-off of the experimental data \( F(K) \) at \( K_{\text{max}} = 12.5 \) Å \(^{-1}\) will be equivalent to a broadening function in \( r \) space, with a full width at half maximum height of \( \Delta r = 0.30 \) Å, which will convolute with the true function \( G(r) \). The application of the convergence factor \( \exp(-r^2K_{\text{max}}^2) \) with \( z^2K_{\text{max}}^2 = 1.5 \) Å \(^{-1}\) in equation (6) will introduce an additional broadening which will increase \( \Delta r \) to a value of 0.36 Å as shown by Warren (1969). However, this increase in width is much less than that produced by lowering \( K_{\text{max}} \) to a value of 7.5 Å \(^{-1}\), yielding \( \Delta r = 0.5 \) Å even with \( (zK_{\text{max}})^2 = 0 \). Thus, the relatively large width of the first peak of \( G(r) \) in Fig. 5 is solely due to the termination of the \( K \)-space data at \( K_{\text{max}} = 7.5 \) Å \(^{-1}\), and is of no structural significance.

It has previously been noted that the \( r_2/r_1 \) ratio in liquids is approximately 1.80–2.00 (Ruppersberg, 1967), while that observed in the non-crystalline solid films is approximately 1.7 (Giessen & Wagner, 1972). This difference has been interpreted as an indication of a real difference in the structure of the non-crystalline solid and liquid alloys. However, as pointed out here, the decrease in \( r_1 \) value and the increase in \( r_2 \) value as the temperature of measurement is increased may be solely responsible for the liquid structures exhibiting an \( r_2/r_1 \) ratio of between 1.8 and 2.0 while the solid vapor-quenched structures exhibit an \( r_2/r_1 \) ratio of approximately 1.7. To lend more credence to this argument, a vapor-quenched alloy stable to a higher temperature is needed to verify that the peak shifts in the solid vapor-quenched alloy are in the same direction as those observed in the liquid alloys as a function of temperature.

That only a broadening or slight splitting of the second peak in the RDF of the vapor-quenched Ag–Cu alloys is observed is a consequence of the difference in sizes of the Ag and Cu atoms (Polk, 1973). Its absence in the liquid may again be explained by the damping effect of temperature: i.e. an indication of a less well-defined short-range order, rather than a structural change in the liquid.

Thin Ag–Cu films (\( \sim 500 \) Å in thickness) have been investigated by Mader (1965) using selected area electron diffraction. An analysis of the diffraction patterns of these films has recently been carried out by Breitling, Mader & Richter (1973). The positions of the first and second peaks of the intensity patterns agree reasonably well with our data in Table 2. Their Fourier transforms, represented as \( rG(r) = 4\pi r^2[\delta(r) - \delta_0] \) show many subsidiary peaks which have been interpreted as structural features of the amorphous films, arising partly from amorphous regions of Cu, Ag, and Ag–Cu. However, it has been our experience that such ripples in the \( G(r) \) or \( rG(r) \) curve are largely a consequence of inaccurate normalization of the raw data. Minute errors in the interference function \( I(K) \) may yield an appreciable modulation of the \( G(r) \) function as shown in the case of liquid Hg by Halder & Wagner (1968). Therefore, any assignment of the subsidiary peaks to interatomic distances in the amorphous films by Breitling et al. (1973) should be considered with caution.

B. Comparison of liquid and non-crystalline solid alloys of the system Cu–Mg

By comparing the interference function \( I(K) \) of the vapor-quenched Cu–65 at.\% Mg alloy with that of the liquid Cu–Mg alloy it can be seen that the positions of the first peak of the film and liquid are quite different, whereas the higher peaks agree fairly well. In addition, the \( I(K) \) of the vapor-quenched alloy exhibits a shoulder on the second and third peaks whereas no shoulder is apparent for the liquid alloy. It is interesting to note that the first peak of liquid Cu agrees with that of the film. However, the maximum before the first peak is present in the liquid alloy and in the vapor-quenched alloy. It could be caused by an atomic arrangement similar to that observed in CuMg\(_2\) which gives rise to Bragg reflections at \( K = 1.36, 1.42 \) and \( 1.71 \) Å \(^{-1}\). These three peaks will merge to a single peak at \( K = 1.5 \) Å \(^{-1}\), when the particle size is \( < 15 \) Å.

In a system like Cu–Mg the values of the peak maximum positions are very sensitive to concentration (Lukens & Wagner, 1973). To formulate conclusions based on the relative peak positions of the liquid as compared to the vapor-quenched alloy, accurate knowledge of concentration is required. The concentration of the liquid alloy is known to a higher degree of accuracy than that of the vapor-quenched alloy. The concentration of the liquid was determined from the weight of the elements used to prepare the alloy. In addition, there was very little evaporation since the intensity of the first peak was the same when measured before and after the actual X-ray intensity measurements. In addition, there was no indication of peak shifts which shows that very little, if any, change in concentration was experienced by preferential evaporation or oxidation. The first peak position could be
measured to an accuracy of \( \pm 0.02^\circ \) in 2\( \theta \) which converts to \( \pm 0.01 \) \( \text{Å}^{-1} \) in \( K \). An uncertainty of \( \pm 0.02^\circ \) or \( \pm 0.01 \) \( \text{Å}^{-1} \) in \( K \) would result in an uncertainty in concentration of \( \pm 2 \) at.\%.

It is apparent, then, that during the experiment the concentration did not change any more than \( \pm 2 \) at.\%. From the accuracy of measuring the weights of the alloy components it was ascertained that the initial concentration was accurate to within \( \pm 0.05 \) at.\%.

The knowledge of concentration of the vapor-quenched alloy was not as great because it was determined from thickness measurements of Cu and Mg with quartz crystal oscillators. This method of evaluating the concentration was relatively accurate when elements were evaporated from a liquid pool (\( \pm 5 \) at.\%) as was the case of Ag and Cu. However, at the temperature and pressure used for evaporating Mg, sublimation occurs. As evidenced visually, some portions of the Mg charge evaporated more quickly than other portions so that the rate of evaporation was not always uniform. Another complication was that the high vapor pressure of Mg as compared to Cu made secondary evaporation of Mg from the shielding a possibility, some of which could have been deposited on the Cu measuring crystal.

Because of the resultant uncertainty in concentration of up to \( \pm 10 \) at.\% in the vapor-quenched Cu–Mg alloy and the significant effect this would have on the peak positions, \( K_1 \) and \( K_2 \), conclusions based on the relative positions of the maxima in \( I(K) \) of the liquid compared to vapor-quenched solid alloys are not valid. However, the ratio of \( K_2/K_1 \) in a particular sample could still be a meaningful measurement for comparing the structures of the liquid and vapor-quenched solid film. As shown in Table 2, the ratios \( K_2/K_1 \) of pure Cu and the liquid alloy are significantly greater than that of the non-crystalline solid.

The interference function \( I(K) \) of the CuMg\textsubscript{2} film shows features which have been observed in X-ray patterns of carbon black (Warren, 1956). From this observation it might be concluded that the structure of the alloy film consists of a random packing of close-packed layers of finite dimensions. Similar conclusions have been reached by Dixmier, Doi & Guinier (1965) for the structure of amorphous Ni–P. If this model is correct, we can deduce the dimensions \( L_a \) of the coherently diffracting domains within the close-packed layers from the width of the second peak maximum which corresponds to a two-dimensional reflection \( hk \).

The size of the thickness of the coherently diffracting domains normal to the layers can be evaluated from the width of the first peak assuming it to be a 001 reflection.

The Warren equation (Warren, 1941) relates the width \( \Delta K \) at half maximum height of the two-dimensional reflection to the dimension \( L_a \), i.e.

\[
L_a = \frac{(2\pi) 1.84}{\Delta K}
\]

which yields a value of \( L_a = 14 \) Å for the CuMg\textsubscript{2} film.

The Scherrer equation

\[
L_c = \frac{(2\pi) 0.89}{\Delta K}
\]

permits us to convert the half-width \( \Delta K \) of the first peak into a size \( L_c = 13 \) Å. These values are consistent with the assumption that the coherently diffracting domains must be smaller than 15 Å in order that the first three peaks of crystalline CuMg\textsubscript{2} merge to a single peak at \( K = 1.5 \) \( \text{Å}^{-1} \).

The regions over which there exists some short-range structural order can also be deduced from the functions \( G(r) \) [equation (6)]. The value of \( r \), beyond which \( G(r) \) modulates between \( 0 \pm 0.05 \), is usually called \( r_s \), and is of the order of 15 Å for the CuMg\textsubscript{2} film. This value, \( r_s \), is of the same order as those of \( L_c \) and \( L_a \).

The interatomic distances \( r_a \) deduced from the positions of the peak maxima of \( G(r) \) for both liquid and solid CuMg\textsubscript{2} also indicate that their structures are different. The ratio \( r_2/r_1 \) in liquid Cu and CuMg\textsubscript{2} is about 1.9, whereas that of the CuMg\textsubscript{2} film is 1.65. This small ratio is a consequence of the splitting of the second peak in \( G(r) \) of the alloy film. Such splitting cannot be explained by a dense packing of hard spheres of two different sizes (Polk, 1973), and must be produced by the particular structure of the Cu–Mg film.

V. Conclusions

The functions \( I(K) \), \( G(r) \) and \( 4\pi r^2 g(r) \) are similar for the liquid and non-crystalline solid alloy films of Ag and Cu. Where differences occur, they can be attributed to the effect of the temperature at which the measurement was made and not necessarily to a structural dissimilarity. The one major effect of increasing the temperature is to damp the oscillations in \( I(K) \) and \( G(r) \). This results in the liquid \( I(K) \) and \( G(r) \) exhibiting lower maxima and higher minima. It also has the effect of washing out details such as the shoulder on the second peak in \( I(K) \). The changes in the position of the peaks in the \( I(K) \) of the film and liquid measured at different temperatures are consistent with peak shifts observed in liquid metals as a function of temperature. This is also true for the observed peak shifts in \( G(r) \) with temperature of measurement. These data indicate that the structure of the vapor-quenched Ag–Cu alloy films could be similar to the liquid alloy. There is, however, the possibility that certain features of the \( I(K) \), such as the shoulder on the second peak in the films, could be structural. To clarify this point, a non-crystalline solid alloy with a high degree of stability would have to be studied so that data could be obtained on the solid structure at higher temperatures which could ascertain the effect of temperature on the diffraction pattern of the non-crystalline solid films.

In contrast to the Ag–Cu alloys, the structure of a thin CuMg\textsubscript{2} film exhibits features, some of which are common with those observed in the liquid alloy such as the premaximum below the first peak, while others such as the interatomic distances are quite different.
From this it is concluded that the interference function $I(K)$ and the reduced atomic distribution function $G(r)$ cannot be explained by a common structure in the CuMg$_2$ film and the liquid alloy.

References


