Originally, this experiment was conducted to detect any possible instantaneous infra-red radiation accompanied by crystallization. The observation in Fig. 1c, however, clearly shows that the luminescence occurred only at the places where the germanium film peeled off. In the figure, portions of the crystallized film remained attached to the substrate, as seen by the dark areas along the circular perimeter, indicating that no measurable infra-red radiation of this wavelength region was emitted by the heating of crystallization. The "explosive" crystallization of the film proceeds by the rapid crystallization of the non-crystalline film followed by rapid peeling as has been demonstrated by a high speed motion picture [3]. Thus, immediately after the crystallization, the film is still remaining on the substrate. Instead of the expected infra-red heating, however, the present result indicated that even after the crystallization reaction there is an apparent strong bonding between the germanium film and the substrate, which can be broken a moment later by the internally accumulated stress in the film through the crystallization.

Acknowledgement

This work was started under ARPA Contract No. DA-49-083-0SA-3140 and completed under NSF Grant GH-34547.

References

1. TAKESHI TAKAMORI, RUSSELL MESSIER and RUSTUM ROY, *Appl. Phys. Lett.* **20** (1972) 201.
2. *Ibid*, *J. Mater. Sci.* **8** (1973) 1809.
3. The film was shown by the authors at the Glass Division Meeting of the American Ceramic Society, Bedford, Pa., 13 October 1971.

Received and accepted
2 August, 1973

TAKESHI TAKAMORI*
RUSSELL MESSIER
RUSTUM ROY
Materials Research Laboratory,
Pennsylvania State University,
University Park, Pennsylvania, USA

*Present Address: IBM Corporation, Thomas J. Watson Research Center, Yorktown Heights, New York 10598.

On the excess volume of mixing of liquid alloys

In a recent article surveying density measurements in liquid metals and liquid binary alloy systems [1], the discussion of the alloy densities was based on plots of specific volume against *atomic* concentrations of the components. It is useful to remember, however, that, when specific and atomic volumes are plotted against composition, the former must be plotted against the composition in weight fraction and the latter against the composition in atomic fraction, otherwise deviations from a linear relationship will appear which are not meaningful and which can, in certain cases, be very misleading. This communication outlines analytically the reasons for this, illustrating the point with two examples, the Cd-Bi and Na-K systems. Thus, in the Cd-Bi system, the atomic volume plotted against atom fraction Bi will give a correct positive deviation while the specific volume plotted on the same atom fraction scale gives a meaningless negative deviation.

Let us first consider ideal mixing of a binary alloy system. The atomic volume $V_{\mathrm{id}}{}^{\mathrm{A}}\,(c_1)$ for a given composition is given by

$$V_{\mathrm{id}}{}^{\mathrm{A}}\,(c_1) = c_1\,V_1 + c_2\,V_2$$

where c_1, c_2 are the respective atom fractions and V_1, V_2 the respective atomic volumes of components 1 and 2; $V_{\mathrm{id}}{}^{\mathrm{A}}\,(c_1)$ is, therefore, linearly related to c_1 and c_2.

The specific volume for a given composition $V^{\mathrm{S}}\,(c_1)$ is given by

$$V^{\mathrm{S}}\,(c_1) = \frac{V^{\mathrm{A}}\,(c_1)}{A\,(c_1)} \tag{1}$$

where $A\,(c_1)$ is the atomic weight of the alloy which can be expressed by

$$A\,(c_1) = \frac{w_1 + w_2}{(w_1/A_1) + (w_2/A_2)}\,,$$

where w_1 and w_2 are the respective weights and A_1, A_2 are the respective atomic weights of the components 1 and 2.

The weight fraction of component 1,

$$W(c_1) = \frac{w_1}{w_1 + w_2}$$

Hence, since $c_1 = \dfrac{w_1}{A_1}\Big/\left(\dfrac{w_1}{A_1} + \dfrac{w_2}{A_2}\right)$,

$$W(c_1) = \frac{c_1\,A_1}{A(c_1)}\,. \tag{2}$$

© *1974 Chapman and Hall Ltd.*

It can be seen from Equations 1 and 2 that, since A_1 is independent of composition, a plot of specific volume $V^S(c_1)$ against weight fraction $W(c_1)$ is equivalent to a plot of atomic volume $V^A(c_1)$ against atom fraction c_1. On the other hand, a plot of $V^S(c_1)$ against c_1 will not be linear for an ideal system except for the hypothetical case where $A_1 = A_2$. For a non-ideal system, with finite excess volumes of mixing, the c_1 dependence of $V^S(c_1)$ will be different from that of $V^A(c_1)$; the greater the difference between the atomic weights of the components, the greater will be the difference between the atomic concentration dependence of $V^A(c_1)$ and $V^S(c_1)$.

It is of interest to consider in greater detail the relative behaviour of $V^A(c_1)$ and $V^S(c_1)$ for the general case of a non-ideal system.

Let $\Delta V^A(c_1)$ be the excess atomic volume of mixing at a concentration c_1. This may be positive or negative. Therefore,

$$V^A(c_1) = c_1 V_1 + c_2 V_2 + \Delta V^A(c_1)$$

and

$$V^S(c_1) = \frac{c_1 V_1 + c_2 V_2 + \Delta V^A(c_1)}{c_1 A_1 + c_2 A_2} .$$

The linear interpolation between specific volumes of the pure components is given by

$$\left(c_1 \frac{V_1}{A_1} + c_2 \frac{V_2}{A_2}\right)$$

therefore, the "excess specific volume of mixing" $\Delta V^S(c_1)$

$$= \left[\frac{c_1 V_1 + c_2 V_2 + \Delta V^A(c_1)}{c_1 A_1 + c_2 A_2}\right] - \left(c_1 \frac{V_1}{A_1} + c_2 \frac{V_2}{A_2}\right)$$

$$= \frac{c_1 c_2 (V_1 + V_2) - c_1 c_2 \left(\frac{A_1}{A_2} V_2 + \frac{A_2}{A_1} V_1\right) + \Delta V^A(c_1)}{c_1 A_1 + c_2 A_2} . \quad (3)$$

In the hypothetical case where $A_1 = A_2$ then

$$\Delta V^S(c_1) = \frac{\Delta V^A(c_1)}{A_1}$$

and $\Delta V^S(c_1)$ will always have the same sign and c_1 dependence as $\Delta V^A(c_1)$.

Now consider cases where $A_1 \neq A_2$. We are interested in the sign of the numerator of Equation 3, i.e. whether

$$\left[V_1 + V_2 - \left(\frac{A_1}{A_2} V_2 + \frac{A_2}{A_1} V_1\right) + \frac{\Delta V^A(c_1)}{c_1 c_2}\right]$$

is positive or negative.

Dividing through by V_1 and rearranging terms, this expression becomes

$$\left(\frac{V_2}{V_1} - \frac{A_2}{A_1}\right)\left(1 - \frac{A_1}{A_2}\right) + \frac{\Delta V^A(c_1)}{c_1 c_2 V_1}$$

or

$$f(V, A) + \frac{\Delta V^A(c_1)}{c_1 c_2 V_1}$$

where

$$f(V, A) = \left(\frac{V_2}{V_1} - \frac{A_2}{A_1}\right)\left(1 - \frac{A_1}{A_2}\right).$$

We adopt the convention that $A_2 > A_1$

(a) if $\frac{V_1}{V_2} > \frac{A_1}{A_2}$ then $f(V, A) > 0$.

Hence, if $\Delta V^A(c_1) > 0$, then $\Delta V^S(c_1) > 0$.

But, if $\Delta V^A(c_1) < 0$ and $|f(V, A)| > \left|\frac{\Delta V^A(c_1)}{c_1 c_2 V_1}\right|$

then, $\Delta V^S(c_1) > 0$.

An example of this type, the liquid binary Na-K system at 100°C [2, 3], is given in Fig. 1 ($V_2/V_1 = 1.93$ and $A_2/A_1 = 1.70$).

(b) If $\frac{V_2}{V_1} < \frac{A_2}{A_1}$, then $f(V, A) < 0$.

Hence, if $\Delta V^A(c_1) < 0$, then $\Delta V^S(c_1) < 0$.

But, if $\Delta V^A(c_1) > 0$ and $|f(V, A)| > \left|\frac{V^A(c_1)}{c_1 c_2 V_1}\right|$

then, $\Delta V^S(c_1) < 0$.

An example of this type, the liquid system Cd-Bi at 350°C [2, 4] is given in Fig. 2 ($V_2/V_1 = 1.49$ and $A_2/A_1 = 1.86$).

The two systems discussed above, in which $\Delta V^A(c_1)$ and $\Delta V^S(c_1)$ are opposite in sign, illustrate how volume data can be open to

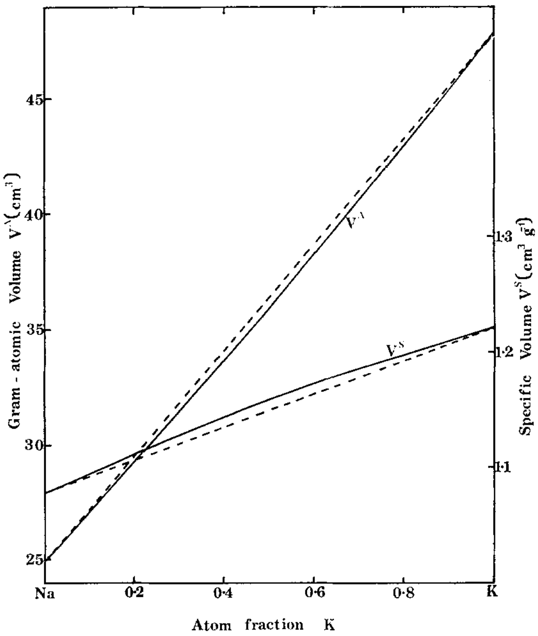

Figure 1 Plots of gram-atomic volume V^{A} and specific volume V^{S} against atom fraction for the liquid alloy system Na-K at 100°C. The dashed lines represent the linear interpolations between the values for the pure components.

misinterpretation when plotted as specific volume against atomic concentration and serve to emphasize that this method of plotting should be avoided.

References

1. S. D. VEAZEY and W. C. ROE, *J. Mater. Sci.* 7 (1972) 445.
2. "Liquid Metals Handbook" (U.S. Office of Naval Research, Washington D.C., 1952).

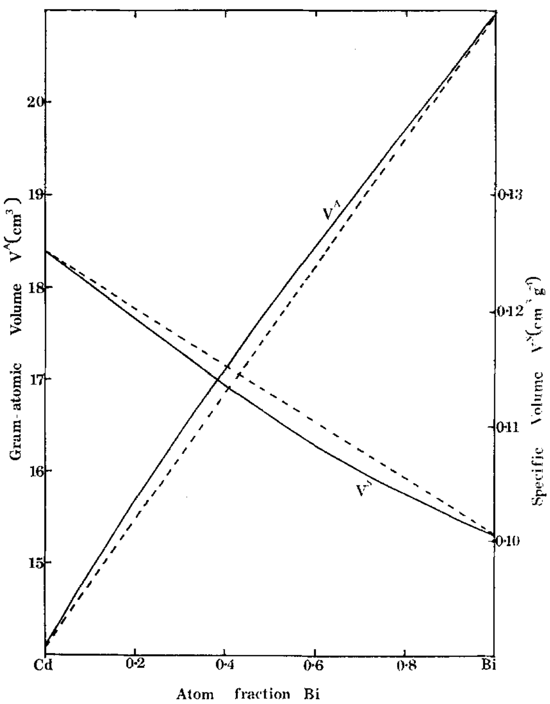

Figure 2 Plots of gram-atomic volume V^{A} and specific volume V^{S} against atom fraction for the liquid alloy system Cd-Bi at 350°C. The dashed lines have the same significance as those in Fig. 1.

3. O. J. KLEPPA, *J. Phys. Chem.* 64 (1960) 1542.
4. O. KUBASCHEWSKI and J. A. CATTERALL, "Thermochemical Data of Alloys" (Pergamon Press, London, 1956).

Received 3 July
and accepted 30 July 1973

H. A. DAVIES
Department of Metallurgy,
University of Sheffield,
Sheffield, UK

The effect of cooling rate on the mechanical properties of PAN-based carbon fibres

It has been postulated that the decrease in fracture strength exhibited by polyacrylonitrile (PAN) precursor carbon fibres on heat-treatment above 1500°C is related to the formation of cracks, particularly in the less well-ordered core regions of the fibres, during cooling from the final heat-treatment temperature [1-3]. More recently, transmission electron microscopy was used to indicate that a high proportion of voids associated with the core regions of the fibre might represent the primary factor in relation to fibre strength [4]. The origin of such voids is obscure, but it seems unlikely that their formation is associated with cooling [5].

The present experiment was designed to examine whether the cooling cycle has any significance in relation to fibre strength. If flaws occur during cooling owing to the anisotropic

© *1974 Chapman and Hall Ltd.*