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Compressibilities of copper alloys

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Abstract. We study the compressibility of Cu alloys with Au, Sn, Zn and Ni, according to the recently proposed model by Varotsos and Alexopoulos. It is shown that this model applies to the above alloys as well.

Therefore the compressibility of an alloy can be determined for any concentration provided that the compressibility is experimentally known for a single concentration.

1. Introduction

Some years ago Varotsos (1980), Varotsos and Alexopoulos (1980a, b, 1986) presented a model that can be used for the estimation of the compressibility κ of an alloy as a function of its density and the properties of the end materials. A short description of their model is as follows.

Assume a (pure) crystal with N atoms with a mean atomic volume Ω_0 ; therefore its volume V_0 is equal to $N\Omega_0$.

When we add to this crystal a foreign atom the volume will be different from Ω_0 . Generally we can assume that this addition of the foreign atom will increase the initial volume by $\Omega_0 + v^d$. Therefore the volume V_{N+n} of the alloy containing $N + n$ atoms, i.e. N atoms of the host crystal and n foreign atoms, can be written as

$$V_{N+n} = N\Omega_0 + n(\Omega_0 + v^d)$$

which can be alternatively written as

$$V_{N+n} = V_0 + (n/N)(V_0 + Nv^d). \quad (1)$$

For reasons of brevity in the following equations we delete the subscript $N + n$ and hence when we write V we mean the quantity V_{N+n} . We clarify that, as already mentioned by Varotsos and Alexopoulos (1986, p 326) the volume v^d is not necessarily equal to the difference of the mean atomic volumes of the constituents because it is determined from the density of the alloy as explained below.

By differentiating equation (1) with respect to pressure, we get

$$\kappa V = \kappa^0 V_0 + (n/N)(\kappa^d Nv^d + \kappa^0 V_0) \quad (2)$$

where κ^0 is the adiabatic compressibility of the pure crystal, κ is the adiabatic compressibility of the alloys and κ^d is defined by

$$\kappa^d = -(1/v^d)(dv^d/dp).$$

From density measurements, one obtains V from the relation

$$V = [M_1 + (n/N)M_2]/\rho$$

where M_1 and M_2 are the atomic weights of the host crystal and the added component respectively, ρ is the density of the alloy, and $n/N = x/(1-x)$ (x is the atomic concentration of the added component).

If the plot $V = V(n/N)$ is a straight line then, taking into account equation (1), we conclude that v^d is constant, i.e. independent of composition.

According to the basic physical assumption of Varotsos and Alexopoulos the volume v^d is considered as the volume of the defect; then the compressibility κ^d can be considered as independent of composition. If this assumption is correct (i.e. whenever v^d and κ^d are independent of composition), then the plot of V versus n/N is a straight line (equation (2)). We emphasise that according to this model the linearity of κV versus n/N should hold even in cases when κ does not vary linearly with composition. It is the scope of the present paper to investigate a number of copper alloys that exhibit such behaviour, i.e. although the κ versus n/N plots are not linear, however, we confirm that the κV -values do vary linearly with n/N . The latter result is significant for the following practical reason: in the case when V varies linearly with n/N and the compressibility of an alloy is known for a single concentration, then κ^d can be determined from equation (2); once the κ^d -value is known, then equation (2) can give the compressibility values for the whole composition range.

2. Copper-gold alloys

O'Hara and Marshall (1971) measured the bulk moduli of single crystals of Cu containing 0.23–10.9% Au (i.e. in the low-concentration range) at several temperatures, using the well known pulse echo technique.

Figure 1 shows the volume V as a function of the concentration n/N in Cu–Au alloys. The values of V were calculated from the density data at room temperature given in table 1 of O'Hara and Marshall (1971). We can see that the above plot is linear with a correlation factor (CF) of 0.999. From the slope we calculate:

$$Nv^d = 3.177 \times 10^{-6} \text{ m}^3.$$

It is the subject of the present paper to examine the validity of the Varotsos–Alexopoulos model for a case of a noble metal such as Cu alloyed either with another noble metal (e.g. Au) or with a transition metal. Such a complete study of a metal alloyed with different rows of the periodic table has not been attempted to date.

From figure 2 we can also see that the plot of κV versus n/N is a straight line with CF = 0.991:

$$\begin{aligned} \kappa^d &= -1.66 \text{ TPa}^{-1} & \kappa^0 &= 7.26 \text{ TPa}^{-1} \\ \kappa^d/\kappa_0 &= -0.229 & & (1 \text{ TPa} = 10^{12} \text{ N m}^{-2}). \end{aligned}$$

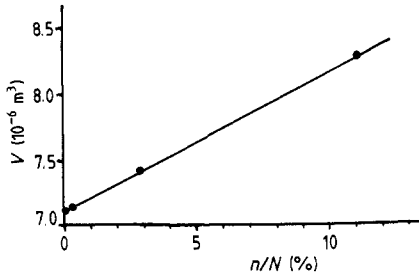


Figure 1. The plot of V versus n/N for Cu-Au alloys (data from O'Hara and Marshall (1971)).

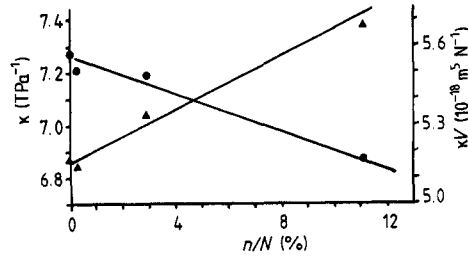


Figure 2. The plots of κ versus n/N (●) and κV versus n/N (▲) for Cu-Au alloys (data from O'Hara and Marshall (1971)).

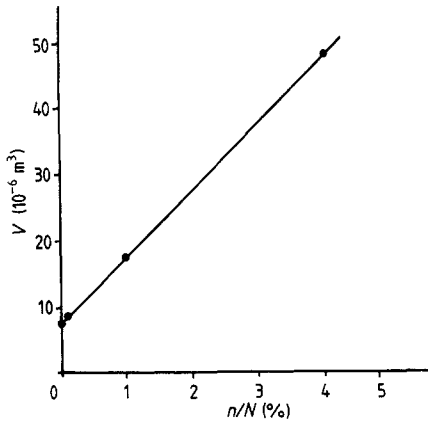


Figure 3. The plot of V versus n/N for Cu-Au alloys (data from Chiarodo *et al* (1972)).

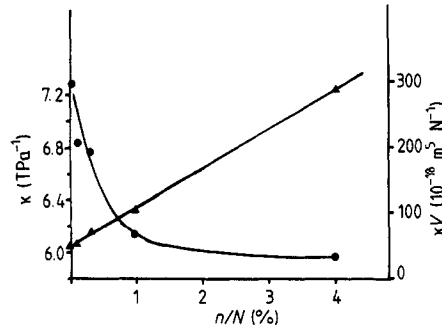


Figure 4. The plots of κ versus n/N (●) and κV versus n/N (▲) for Cu-Au alloys (data from Chiarodo *et al* (1972)).

The adiabatic bulk moduli of crystals of Cu containing a high Au concentration (10–80%) have been measured by Chiarodo *et al* (1972) using the McSkimin pulse superposition method.

In figure 3 we plot V versus n/N which is well described by a straight line with $CF = 0.999$. We find that

$$Nv^d = 3.165 \times 10^{-6} \text{ m}^3$$

in good agreement with the value $3.177 \times 10^{-6} \text{ m}^3$ found above.

In figure 4 we plot the experimental values of the compressibility κ obtained from Chiarodo *et al* (1972) versus n/N . We see that this plot is not linear in contrast with the plot κV versus n/N which is a linear one (with $CF = 0.999$) in agreement with the model by Varotsos and Alexopoulos.

The slope of this line leads to

$$\kappa^d = 2.77 \text{ TPa}^{-1} \quad \kappa^d/\kappa^0 = 0.392.$$

The latter value of κ^d ($=2.77 \text{ TPa}^{-1}$) is considered as more reliable than the value

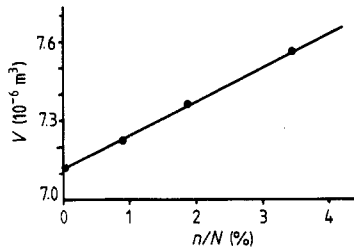


Figure 5. The plot of V versus n/N for Cu-Sn alloys (data from Moment (1972)).

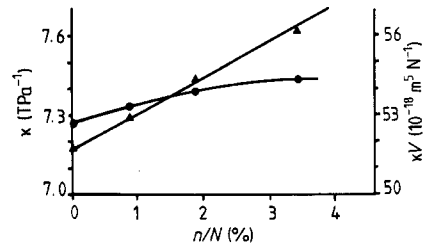


Figure 6. The plots of κ versus n/N (●) and κV versus n/N (▲) for Cu-Sn alloys (data from Moment (1972)).

$\kappa^d = -1.66 \text{ TPa}^{-1}$ found above (from the low-concentration range) because it results from an extensive composition range.

There is also an alternative explanation for the difference of these two κ^d -values; it might be that, as κ^d is a property at a defect, it depends slightly on the properties of the surrounding material that change with the alloy concentration. If this is true, the value $\kappa^d = -1.66$ reflects the compressibility of the defect when the surrounding material is Cu whereas the value $\kappa^d = 2.77$ corresponds to an average value.

3. Copper-tin alloys

Moment (1972) using the technique developed by McSkimin measured the elastic constants of single crystals of Cu with Sn additions up to 3.30%, i.e. for very low concentrations. In contrast with the low-concentration behaviour of Cu-Au alloys (see figure 2) the addition of Sn to Cu leads to a non-linear increase in compressibility as can be seen in figure 6.

Figure 5 shows the plot of V versus n/N , which is a straight line, with $CF = 0.999$.

From its slope we can calculate that

$$Nv^d = 5.603 \times 10^{-6} \text{ m}^3.$$

In figure 6 we can observe that κV versus n/N is also a straight line, with $CF = 0.999$.

From its slope we can calculate that

$$\kappa^d = 13.85 \text{ TPa}^{-1} \quad \kappa^d/\kappa^0 = 1.90.$$

4. Copper-nickel alloys

Density measurements for the calculation of volume V have been taken from Epstein and Carlson (1965) while bulk moduli values have been measured by Schmunk and Smith (1960). From figures 7 and 8 we can see that both V versus n/N as well as κV versus n/N functions are linear with $CF = 0.999$ for both.

From the slope of the V versus n/N plot we can find that $Nv^d = -0.607 \times 10^{-6} \text{ m}^3$ and from the κV versus n/N plot, we can find

$$\kappa^d = 21.19 \text{ TPa}^{-1} \quad \kappa^d/\kappa^0 = 2.90.$$

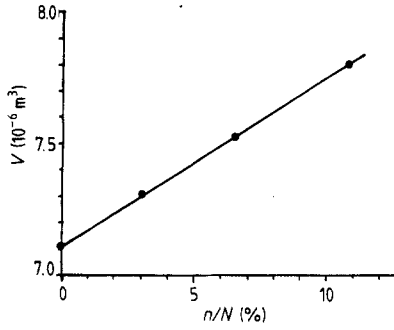


Figure 7. The plot of V versus n/N for Cu-Ni alloys (data from Epstein and Carlson (1965)).

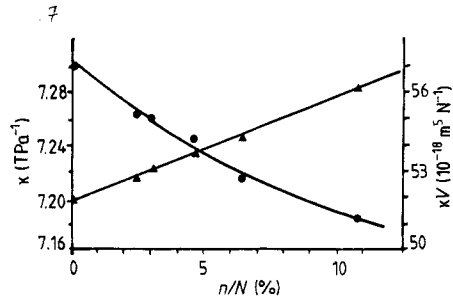


Figure 8. The plots of κ versus n/N (●) and κV versus n/N (▲) for Cu-Ni alloys (data from Schmunk and Smith (1960)).

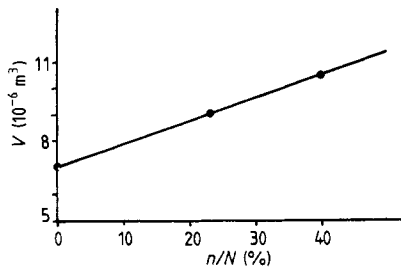


Figure 9. The plot of V versus n/N for Cu-Zn alloys (data from Chiarodo *et al* (1974)).

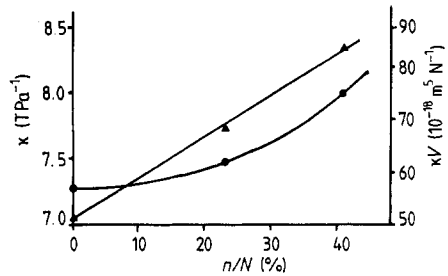


Figure 10. The plots of κ versus n/N (●) and κV versus n/N (▲) for Cu-Zn alloys (data from Chiarodo *et al* (1974)).

We see again here that κ does not vary linearly with composition (in contrast with κV versus n/N which is actually a linear plot).

5. Copper-zinc alloys

Various workers as Rayne (1958), Hopkin (1970) and McManus (1963) have studied Cu-Zn alloys. We used the measurements of Chiarodo *et al* (1974) which are more recent. In figure 9 we can see the variation in volume V versus n/N . The plot is linear, with $CF = 0.999$. From its slope we can calculate

$$Nv^d = 8.467 \times 10^{-6} \text{ m}^3.$$

In figure 10 we observe that κV versus n/N is a straight line, with $CF = 0.998$. We remark again that in these alloys the compressibility κ does not vary linearly with n/N . From the slope of figure 10 we calculate

$$\kappa^d = 20.64 \text{ TPa}^{-1} \quad \kappa^d/\kappa^0 = 2.89.$$

6. Conclusion

By summarising the result of the present investigation we can say that in a number of copper alloys (i.e. Cu–Sn, Cu–Ni, Cu–Zn, and the high-concentration case of Cu–Au) the compressibility κ does not vary linearly with composition; however, the quantity κV does depend linearly on n/N in agreement with the basic spirit of Varotsos–Alexopoulos model.

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