

## THE APPLICABILITY OF SIZE-FACTOR AND ELECTRON CONCENTRATION CONCEPTS TO ALLOYING BEHAVIOUR OF COPPER (\*)

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The theory of alloy structures deals with many empirical correlations involving valencies, size factors etc. and these were advanced by Hume-Rothery and his collaborators from a study of alloys of simple metals like copper, silver and gold. Though these correlations have been of much use to the practising metallurgist, no clear meaning can yet be seen in these correlations. Attempts have however been made to put them on a quantitative basis but not with much success. This is probably due to the fact that some of the assumptions on which quantitative derivations of the correlations have been made are incorrect besides some of them being inadequate. In addition some recent experimental findings have begun to question some of the basic assumptions on which alloy theory is based. In view of these developments it would be advantageous to reexamine the validity of the principles of alloy theory to assess their applicability to the alloying behaviour of metals. In this paper such an examination is carried out in relation to copper.

Size Factor Principle:

The principle of size factor advanced for the purpose of determining solid solubility of one metal in another may be stated as if the atomic diameters of two metals differ by more than 14-15%, their solubility in each other will be restricted ( $< 5\text{at}\%$ ). Though this rule as first put forward was of a negative principle it had much utility in understanding and predicting solid solubility of one metal in another. In spite of much success in its use this rule has quite a few defects, for the basis on which this rule is advanced involves arbitrary assumptions. Firstly the atomic diameter as defined in this principle assumes the electron cloud round the nucleus of the atom to be spherical whereas recent developments suggest that such an assumption can no longer be considered correct. Moreover the diameter of atom of the element in the solid state would be influenced by the nature of bonding as well as by the number of nearest neighbours which an atom has in the solid. Hence if the atomic diameter of an element in two different solids are to be compared, the crystal structures of the solids should be the same. If the crystal structures are different corrections

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of the atomic diameter for the same near neighbours should be done to avoid drawing erroneous conclusions about the size of the atom. Recognising this difficulty corrections to atomic diameters were introduced for the purpose of comparing them in structures with different coordination numbers and such a correction emphasises the principle of conservation of volume in structural transformations. Another concept that has been introduced in this connection is the apparent atomic diameter which has been defined as the atomic diameter obtained by extrapolating the closest distance of approach in a solid solution to 100 at% solute. An analysis of the factors influencing this concept shows this concept too is an unsatisfactory one.

Application of size factor principle to alloys of copper shows that in the case of certain copper alloys the lattice distortion produced in the lattice of copper by certain solutes is at variance with their sign of size factor. Thus for instance gallium, silicon and germanium which have a negative size factor with respect to copper instead of producing a contraction of the lattice parameter of copper increases it. Moreover atomic diameter as used in this concept is computed from lattice parameter measurements and such a computation does not yield correct results as lattice parameters commonly measured in alloys is a measure of mean lattice distortion and do not yield the actual sizes of component atoms.

Further atomic diameters, as defined above, of some metals like aluminium, indium, thallium and lead are large which on entering into solid solution change their size which have been attributed to be due to electronic factors. Such anomalous behaviour of these metals however disappears if the concept of atomic volume is used instead of atomic diameter suggesting that atomic diameter as defined above is an unsatisfactory measure of the size of the atom.

In view of the defects pointed out above in the concept of atomic diameter, an alternate concept called atomic volume for atom has been advanced and it has been defined as the volume of the unit cell divided by the number of atoms in the unit cell. This concept as defined above though it measures the average volume per atom and does not take into consideration local distortion it has the following advantages: (a) it is independent of the crystal structure of the lattice of the metal or alloy provided of course the bonding does not change on alloying and (b) it is easy to calculate. As the changes in volume produced depends upon the changes in lattice dimensions the changes in atomic volume will be in direct line with changes in lattice parameters. From this parameter of volume per atom, a linear parameter called Seitz Radius similar to atomic diameter is calculated.

From these parameters giving size of the atom, volume size factors and linear size factors have been calculated and they are used to determine solubility of one metal in another. An examination of the solubilities of metals in noble metal solvents on the basis of above size factors show that the limiting size factor is 30% for volume size factor and 10% for linear size factor.

#### Electron Concentration Rule:

Another rule that is of much significance in the theory of alloys is the electron concentration rule. An examination of the shape of primary solid solubility curves with GrIB metals as solvent shows a striking similarity which becomes very evident if the plot is done in terms of electron concentration instead of at% of the alloying element. In such a plot it would be noticed  $\alpha$  phase is stable upto an electron concentration of 1.40 and  $\beta$ ,  $\gamma$  and  $\epsilon$  phases occur at 1.5,  $21/13$  and  $7/4$  respy. if one assumes a valency one for GrIB metals. Such occurrence of these intermediate phases at definite electron concentration were justified theoretically by Jones as follows. Assuming an electron distribution in which the  $3d^{10}$  electron of copper form the ionic core and  $4s^1$  electron in the conduction band, Jones takes the Fermi surface of conduction electron of copper to be spherical. Adding an element like zinc which contributes two electron per atoms to the conduction band of copper the Fermi surface of copper expands and touches the octrahedral faces of first Brillouin zone and thus would produce a peak in  $N(E)$  curve. Addition of more zinc increases the electron concentration in the conduction band of copper and as these cannot be accommodated without an increase in energy, the  $N(E)$  curve shows a fall. It on the other hand there is a structure whose  $N(E)$  curve shows a rise even after the peak of the original structure electrons would prefer it for they can be accommodated with a lesser energy as compared to its earlier structure. With this kind of approach Jones showed the peaks in  $N(E)$  curves of f.c.c. and b.c.c. of these alloys occur at electron concentrations of 1.36 and 1.48 respy. which fitted very well with what has been observed in these alloys. However a point made by Jones in his original calculation showed that the Fermi surface touches the first Brillouin zone of copper at an electron concentration of  $\sim 1.0$  and this point though overlooked at the time it was first put forward was found to be correct experimentally twenty years later. As this finding questions the basis of  $\alpha/\beta$  phase equilibrium in alloys of noble metals, it was suggested that Fermi surface of Gr IB metals shows a contraction with smaller additions of solute but with increasing additions shows an expansion making contacts with the Brillouin zone at electron concentration values suggested by Jones Theory. This explanation though has tried to support Jones Theory suffers from a few flaws and it does not appear to hold good for all Gr.IB metals. An alternative explanation has been attempted in which the second peak of  $N(E)$  curve is associated with  $\alpha$  phase boundary but this idea fails when extended to b.c.c.  $\beta$  phase. Thus though Jones

Theory has been unable to give complete theoretical justification of electron concentration concept, Engel has attempted an explanation of the same as follows:

Engel Correlation and its application to the alloying behaviour of Copper:

Adopting Pauling's ideas of metallic bond and examining the properties of metals in relation to their position in the periodic table, Engel has put forward a scheme that metallic structures, b.c.c. c.p.h. and f.c.c. correspond to one, two and three bonding electrons per atom and these electrons are in s or s and p states. He further suggests these structures can exist over a range of electron concentrations as follows b.c.c.  $\surd$  1 - 1.75, c.p.h. 1.8 - 2.2 and f.c.c. 2.25 - 3.

According to Engel correlation copper being f.c.c. should have a valency of 2.25 - 3 and to have such a valency Engel proposes an electron distribution for metallic copper as 75%  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^1$  and 25%  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$  which gives 2.5 outer bonding electrons and 1.5 d bonding electrons. Though this electron distribution has been severely criticised, Engel uses this scheme to explain the alloying behaviour of copper. He states that on alloying copper with an element like zinc with a full d shell leads to a breakdown of d bonds of copper as copper is unable to form d bonds with zinc. Such a breakdown of d bonds will be catastrophic at a composition at which copper will have less than one unpaired d electron for the formation of bonds and this corresponds to an electron concentration of 1.4 which is the limit of occurrence of  $\surd$  phase. On a similar basis the occurrence of  $\beta$ ,  $\gamma$  and other intermediate phases have been explained.

Engel's explanation of the alloying behaviour of copper with zinc, gallium, aluminium etc. shows that these solute elements decrease d bonds in  $\surd$  phase hence melting points, Yongs Moduli of these phases should also show a decrease which have been found to be the case. On the other hand adding nickel to copper increases d bond formation hence elastic modulus, melting point should increase which have been found to be the case. Based on these views Engel also explains the shape of primary solid solubility curves of these alloys.

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