The applicability of size-factor and electron concentration concepts to alloying behaviour of copper

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SYNOPSIS

The theory of alloy structures deals with many empirical correlations involving valencies, size-factors, etc. and these have been of much use to metallurgists. Difficulties are, however, experienced due partly to new experimental findings and partly to arbitrary nature of parameters governing these correlations. To overcome these difficulties alternative suggestions have been made to put the alloy theory on a satisfactory basis but not with much success. Besides, the application of Engel's electron concentration concept to the alloying behaviour of copper has given rise to much discussion. In this paper the rival views of the alloy theory and their application to the alloy phases of copper are discussed.

DURING the last forty years there has been much progress in the understanding of principles governing the formation of alloys. These have been put forward in the form of empirical generalisations and schemes involving factors like valencies, size-factors, etc. and as has happened with all other branches of science empirical formulations forming the basis for advances in theory, the enunciated empirical rules have formed the basis for advances in the theory of alloys. In the formulation of these empirical generalisations it is natural that alloys of simple metals should have played a major role, for with simple metals complicating influences governing alloy formation are minimised. Copper being a simple metal[1] has therefore found much favour for being chosen for understanding electronic structure of metals and it has also been used in the study of alloys for formulating empirical rules of alloy formation. These rules are due to the work of Hume-Rothery and his collaborators[2a] in 1930s and were advanced from a study of alloy systems of copper, silver and gold with other group B metals.

Some of these rules have been given theoretical support[3-6] on the basis of Fermi energy and Brillouin zone concepts and such explanations have formed part of metallurgical texts[2b] and are quoted in metallurgical literature though the calculation of Jones[6] contained a deduction, the significance of which was overlooked at the time it was put forward. These explanations though useful and accounted for the stability of alloy phases in a simple way, have run into serious difficulties in recent years due to new experimental findings about the Fermi surface of copper[7] (silver and gold) which has questioned some of the fundamental assumptions of alloy theory. Attempts have however been made[8-11] to reinforce the foundations of alloy theory which have begun to show serious cracks due to these findings and at present these cracks have not been satisfactorily cemented to make it the solid foundation it was to alloy theory. It is not clear as to whether one can build fresh structures on the present foundation or one has to reconstruct completely the existing foundation though it seems to the author one has to resort to reconstruction sooner than later. As this reconstruction is unlikely to be undertaken in the near future because of the incomplete understanding of electronic structure of metals, metallurgists using these rules may have to remain contended with the existing unsatisfactory state of alloy theory till a more satisfactory theory comes up. In making use of the existing theory it would therefore be better for metallurgists to be aware of the weaknesses existing in the structure and the suggestions made to rectify them to enable them to draw correct conclusions.

Alloy theory of copper

The theory of alloy structures may be stated to be the elucidation of the principles correlating crystal structures of phases with physical properties on the basis of electronic structure which governs both the factors. Though the theory is far from a clear elucidation of such a correlation, there have been some striking advances like the occurrence of certain crystal structures

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at definite electron concentrations, the size factor rule limiting solid solubility etc. Though no clear meaning can be seen in these correlations on the basis of electronic structure, these have been of much use to a practising metallurgist. However, to make these correlations more meaningful, attempts have been made to put them on a quantitative basis[6,12] but one finds that some of the assumptions, on which such derivations are made, are incorrect[7] and inadequate.[13,14] In the light of these changes, one has therefore to re-examine the validity of the principles of alloy theory to assess their utility and such a re-examination is made in this paper under the following groups :

(a) Size factor principle.
(b) Electron concentration rules.
(c) Engel correlation and its application to the alloying behaviour of copper.

The size-factor principle

From a study of the phase diagrams of copper, silver and gold with polyvalent group B metals, Hume-Rothery et al.[2] advanced some empirical rules governing solid solubility in these metals and one of them is the size-factor principle. This principle states if the atomic diameters of two metals differ by more than 14–15%, the solubility of these two metals in each other will be restricted. This rule is more of a negative principle and its success lay in predicting the insolubility of one metal in another rather than predicting the solubility. In a recent survey by Waber et al.[15] this principle has been used in conjunction with electro-negativity of Darken and Gurry[16] for predicting solid solubility in some 1455 binary alloy systems and they find that 90% of binary diagrams obey the size-factor principle of restricted solid solubility (less than 5 at.%). In spite of much success in predicting solid solubilities this principle has many defects though a few have been recognised by Hume-Rothery and Raynor.[2b] All these doubts and defects about the utility of size-factor principle can be traced to be arising from the question : is the atomic diameter, as defined for the purpose of this rule, a correct parameter to define the size of the atom ? If not what is the alternative parameter that can be used instead ?

The atomic diameter as used in the formulation of this principle is defined to be the closest distance of approach between atoms which is calculated by assuming the electron cloud round the nucleus of the atom to be spherical.[2b] This assumption that the electron cloud of metals can be considered to be spherical is incorrect as has been pointed out by Brewer[17], Balasundaram[18] and the idea of directed bonding[19] also suggests that the electron cloud around an atom in a metal lattice can no longer be considered spherical.

The computation of atomic diameter defined for the size-factor principle is subject to another limitation viz. provided the nature of bonding between atoms is metallic, the atomic diameter will be influenced by the number of nearest neighbours it has. Recognising this limitation Goldschmidt[20] suggested correction to atomic radius of metals for making comparisons. These corrections have been shown by Rudman[21] to be illustrating the principle of conservation of volume during structural changes besides emphasizing the point that atomic diameter as defined above will lead to erroneous conclusions if they are compared in structures with different co-ordination numbers.[13,14]

Recognising that the size of the atom may change in solid solutions of different crystal structures, Axon and Hume-Rothery[22] introduced the concept of apparent atomic diameter (A.A.D.) as a relative measure of atomic size and defined it as the atomic diameter obtained by extrapolating the closest distance of approach in a solid solution to 100 at.% solute. They analysed the reasons for the difference between atomic diameter and apparent atomic diameter and this analysis indicates as to how atomic diameter and A.A.D. are unsatisfactory to be a measure of atomic size.

As has been stated by Hume-Rothery and Raynor[2b] the atomic diameter as used in the size-factor principle besides being uncorrected for coordination number is also taken to be independent of electronic state of the metal. Thus for instance the larger atomic diameters of metals like indium, thallium and lead were considered to be due to incomplete state of ionisation in the metal and these on entering into solid solution get completely ionised. Though these ideas found favour in the earlier days, it appears the reasons advanced are arbitrary and cannot be accepted in toto.[13] Similarly the large atomic diameter of aluminium cannot be exclusively attributed to be due to Brillouin zone overlaps, as such a contribution is likely to be small because of smaller band gaps.[23] The reasons for the larger value of atomic diameter of these metals may lie in the arbitrary definition of atomic diameter for if the size-factor derived from atomic volume is used for these metals, the anomalous behaviour of these metals arising from the atomic diameter concept disappears.[13]

Further, in the case of certain metals as solute the sign of the size factor is at variance with the distortion produced in the solvent lattice of copper. Thus for instance gallium, silicon and germanium which have a negative size-factor with respect to copper instead of producing a contraction in the lattice parameter of copper when dissolved in copper show an increase.[13]

In all these considerations the atomic diameter has been computed from measurements of lattice parameter and such computations do not give the atomic radius of either of the components but may give a parameter which may bear little relationship to the actual size of the component atoms as shown by the work of Warren et al.[24]

In view of the above analysis that atomic diameter as defined by the closest distance of approach is an unsatisfactory measure of the size of the atom either in the pure metal or in an alloy, an alternate parameter called volume per atom and represented by the symbol Ω has been advanced as a measure of the size of the atom.[13,14,21] It is defined as the volume of a unit cell divided by the number of atoms per unit cell. Though it measures

the average volume per atom and does not take into consideration the local distortion, this concept has two advantages : (a) it is independent of the crystal structure of the lattice of either 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 depend upon the changes in lattice dimensions, the change in atomic volume will be in direct line with changes in lattice parameters.[13] Further in the absence of electronic effects like Brillouin zone overlaps the changes in volume of intermediate phases like β' in Cu-Zn system are in the same line as the primary solid solution. In addition to the advantages stated above, this is considered to be basic parameter of the state of the metal or alloy.[25]

From the parameter of volume per atom a linear parameter similar to atomic diameter is calculated from the formula.

$$\Omega = \tfrac{3}{4}\pi \ r_{\Omega}^{3}$$

where Ω is the volume per atom and r_{Ω} is called the

Seitz Radius.

Similar to apparent atomic diameter, Massalski and King[13] introduce a concept of effective atomic volume obtained by extrapolating mean volume per atom to 100 at.% solute and when such data of solutes like aluminium, indium, thallium and lead in copper are examined it is found their atomic volume shows a decrease on going into solid solution. Such a decrease in volume of these metals is in accord with other solutes of β subgroup whereas our earlier discussion of these metals on the concept of atomic diameter showed these metals to be exceptional.

This concept of volume per atom with its stated advantages has been used as a measure of size-factor for predicting solid solubilities. It has been termed volume size-factor[13,14] similar to atomic size-factor and is defined as

$$\Omega_{sf} = \frac{\Omega_{B'} - \Omega_A}{\Omega_A}$$

where

  Ω_A volume per atom of solvent A,
  Ω_{B}' effective volume per atom of solute B.

If a linear size-factor is required it is given by the relation

$$\text{l.s.f.} = \left\{ \left(\frac{\Omega_{B}'}{\Omega_A} \right)^{\tfrac{1}{3}} - 1 \right\} \simeq \tfrac{1}{3}\Omega_{sf}\text{[14]}$$

An examination of the solubilities of metals in noble metal solvents on the basis of above size-factor shows[14] that the limiting size-factor is 30% for Ωs.f or 10% for l.s.f and this value is much less than the value of 14–15% for atomic size-factor. In spite of the advantages advanced for the volume size-factor, Hume-Rothery[26] is unable to accept the contention that volume size-factor is a better parameter in an atomic size-factor for predicting solubilities of, metals in each other.
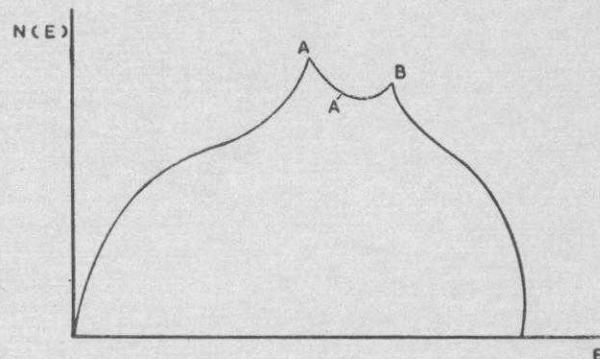
Electron concentration rules

In addition to the size-factor rule discussed above, another rule that is of much significance in the theory of alloy formation is the electron concentration rule. If one examines the form of primary solid solubility curves of copper, silver and gold with polyvalent solutes of group B metals, one notices a striking resemblance and this is all the more so if the plot is done in terms of electron concentration.[2b] In such a plot it would be noticed that the primary solid solubility curves almost coincide with minor differences suggesting that electronic structure is playing an important role in the determination of alloy structures. As the limit of primary solid solubility indicates the stability limit of primary solid solution, this factor of electron concentration can therefore be taken to indicate stability limits and the this occurs at an electron concentration of $\sim 1{\cdot}40$ for α phase. Similar electron concentration values of $1{\cdot}50$, $21/13, 7/4$ have been given for β and other intermediate phases like γ and ϵ phases respectively. In calculating the electron concentration values the question arises as to the valency scheme to be adopted for these metals. There has been much discussion as to the valencies to be adopted for these metals,[27–32] the relevance of some of which will be discussed subsequently. For the present purpose the scheme that will be adopted will be the picture adopted by Hume-Rothery[10] which is essentially that of Mott and Jones[3] and in this scheme these metals are considered to be univalent. Though these ideas of the occurrence of alloy phases at definite electron concentrations were advanced empirically, Jones[4–6] in a series of papers advanced theoretical justification for the occurrence of these compounds as is given below.

In the metal copper, with the following picture for its electronic structure $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4d^1$, the distribution of electrons is such that, the electrons in $3d^{10}$ subshell form part of the ionic core whilst the $4s^1$ electron is in the conduction bond. This picture of electron distribution is the one adopted by Mott and Jones[3] and is shown in Fig. 1. In this model as the 3d electrons form the ionic core, only the $4s^1$ electron in the conduction band is to be taken for consideration for combination in metallic structures. The Fermi surface of this conduction electron was considered to be nearly spherical and this lies well within the first Brillouin zone of copper as shown in Fig. 2. Addition of higher valency element like zinc contributes two electrons per atom of added zinc and these electrons go into the conduction band of copper thereby increasing its electron concentration. This increases the density of states in the conduction band of copper and produces an expansion of the original Fermi surface of copper. This expansion of the Fermi surface continues till the face of the Brillouin zone is touched
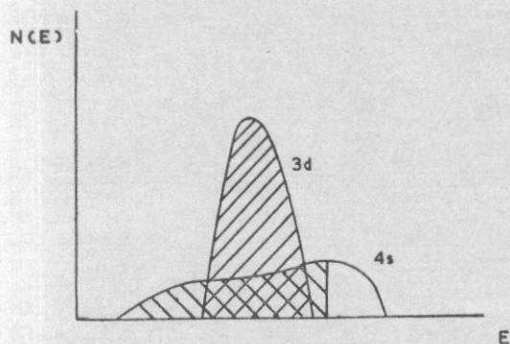
1 *Density of states in copper (schematic)*

3 *Density of states curve for f.c.c. structure (schematic)*

and this happens at the octahedral faces of the zone. This corresponds to the position A in the density of states, N (E) curve of Fig. 3. 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 density of states curve shows a fall as shown by AA′ (Fig. 3). With further increase in electron concentration the square faces of the zone will also be touched and this corresponds to the second peak B after which the density of states curve shows a fall. If on the other hand at the stage A in N(E) curve there is another structure that can accommodate the added electrons with lesser energy than the f.c.c. structure then electrons will prefer that structure. With this kind of approach Jones[3-6] showed that the peaks in N(E) curves for f.c.c. and b.c.c. structures for these alloys occur at 1·36 and 1·48 electron concentrations respectively. These values fitted well with the limit of primary solid solubility of α-phase in these alloys at electron concentrations of 1·40 and that of b.c.c. β phase at 1·50. This theoretical justification of the empirical electron concentration rule was so striking that a point stated by Jones[6] in his original derivations was overlooked and this contained the seed for the fall of this theory. This point was that in copper, Fermi surface touches the octahedral face of the first Brillouin zone at an electron concentration of ~1·0. Though this point was overlooked at the

time it was put forward, this was found to be correct by Pippard[7] from measurements of anomalous skin effect and the shape of Fermi surface of copper is shown in Fig. 4. This finding of Pippard has posed the problem, if the Fermi surface touches the octahedral faces of the first Brillouin zone in pure copper itself, then the basis of Jones theory for α/β phase equilibrium in copper alloys is incorrect. This has made some theorists to re-examine this theory to advance alternate explanation to the phenomenon, for it was felt that this simple theory of Jones was so successful that the main idea must be correct. Cohen and Heine[8] have attempted to do this by re-examining the fundamental assumptions of Jones theory. They suggest that for monovalent noble metals copper, silver and gold, one can retain the rigid band model for pure metals and account for the distortion of the Fermi surface as follows. The energy states in the centre of Brillouin zone faces are either s-like or p-like in character or vice versa but the two do not mix. They proceed to calculate the distortion of Fermi surface from a sphere with a parameter called distortion parameter and their calculation shows, the distortion parameter for copper suggests a large distortion of Fermi surface with p-states being inside and s-states outside the face of Brillouin zone. This is in qualitative agreement with the assumption of Jones of 4·1 ev for the energy gap in pure copper. Adding to copper solutes like zinc,
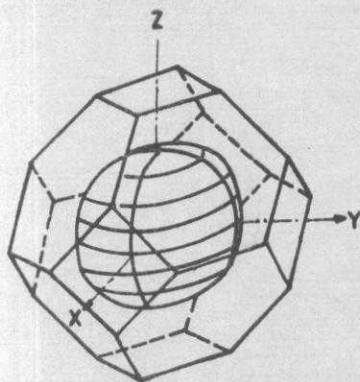
2 *The first Brillouin zone of f.c.c. structure*
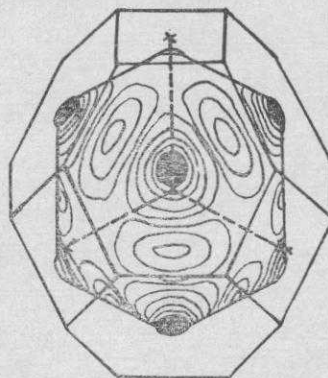
4 *Fermi surface of copper (Pippard)*

gallium, germanium, etc. which have a larger s-p excitation energy than copper, will increase the energy of p-state as compared to s-state thereby reducing the band gap and the distortion parameter. Thus in the case of copper alloying with solutes like Zn, Ga, etc. will make the distorted Fermi surface to get spherical. Such a change of shape of Fermi surface will make it to loose contact with the face of Brillouin zone i.e. in other words the Fermi surface shrinks. Increasing additions of solute make the Fermi surface to expand and again make contacts with the faces of Brillouin zone corresponding to electron concentrations of 1·36 and 1·48 respectively as suggested by Jones theory. This explanation of Cohen and Heine though has tried to support the theory of Jones suffers from a few flaws. One of them is that the distortion parameter for silver suggests a nearly spherical surface which has not been borne out.[33] For gold though the magnitude of distortion parameter suggests distortion of Fermi surface, the sign of the parameter suggests that the electron levels are just the reverse as found for copper. Hence solution of elements like Zn, Ga, etc. in gold would produce an expansion and not a contraction of Fermi surface i.e. more distortion of Fermi surface. In spite of these flaws the ideas of Cohen and Heine have a few suggestions which offer promise. One is that the band gaps in noble metals show a change on alloying, meaning thereby that band picture of electron distribution is not rigid but soft. This is in agreement with the suggestion of Engel[30a] that the electronic structure of copper changes on alloying though Engel's explanation involves a change of d, s and p-electrons whereas Cohen and Heine are concerned with s and p-electrons only.

An alternate explanation of Jones theory has been attempted by Hume-Rothery and Roaf.[9] Accepting that the Fermi surface of pure copper to be distorted at an electron concentration of ~1·0 as suggested by Jones calculation, they associate this distortion with the first peak A of the N(E) curve (Fig. 3). In the original calculation of Jones this peak was associated with an electron concentration of 1·36 and they argue if we assume this peak to be shifted backward to an electron concentration of one, we can also expect the second peak B, associated by Jones with electron concentration of 1·88, to be shifted by nearly the same extent to an electron concentration of ~1·40 and this peak could then be associated with ∝-phase limit, for it is accompanied by a fall. Thus interest has now shifted from the first to the second peak of N(E) curve. Though this explanation does not resort to sphericity of Fermi surface on alloying and retains the original suggestion of Jones in associating the limit of solid solubility with the peak in N(E) curve, it is to be seen whether this idea is valid. Further, this idea fails when extended to b.c.c. β-phase for the b.c.c. phase does not have a second peak in N(E) curve.

Thus the above discussion shows that for copper alloys though we have empirical rules governing alloy formation, the explanation of the above rules are unsatisfactory. However, in recent years Engel[30] has advanced explanations for the alloying behaviour of copper with the views[34-36] developed by him. As these appear to offer some promise we shall consider them.

Engel correlation and its application to the alloying behaviour of copper

Adopting Pauling's[29] ideas of metallic bond and examining the properties of metals in relation to their position in the periodic table, Engel put forward a scheme that the metallic structures b.c.c., c.p.h. and f.c.c. structures correspond to one, two and three bonding electrons per atom and these electrons are in s or in s and p states. Extending this correlation he suggested these structures can exist over a range of electron concentrations as follows : b.c.c.1 < to 1·75, c. p. h. 1·8–2·2, f. c. c. 2·25–3. In the computation of these lattice controlling electrons in metals and alloys of transition group, he suggests that d-electrons though they take part in bonding are not lattice controlling electrons. If they enter into calculations of lattice controlling electrons they do so in an indirect manner. With these ideas and with the contention that copper, silver and gold belong to transition group metals, he accounts for the alloying behaviour of copper. These ideas of Engel have come in for much criticism though Brewer[17] from an examination of spectroscopic data of these metals finds Engel's correlation of electronic structure with crystal structure is generally valid barring a few exceptions. The controversy about Engel correlation and its usefulness in metallurgy is discussed in a recent paper.[37]

Copper being a metal with f. c. c. structure, should have a valency of 2·25–3 according to Engel correlation instead of the conventionally occepted valency of one. To have such a valency Engel[30,35] proposes the following electron configuration for metallic copper 75% $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^1 4p^2$ and 25% $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$—thus giving 2·5 outer bonding electrons and 1·5 d-bonding electrons per atom. This scheme of Engel has been severely criticised[31] in that it is at variance with Fermi surface and that it will give rise to paramagnetism and abnormal electrical resistance both of which are not shown by copper. Engel[30] and Brewer[32], on the other hand, point out other properties like melting point, density, cohesion, etc., suggest that on passing from copper to zinc the number of bonding electrons should decrease which is explained by the present scheme of Engel whereas earlier ideas do not explain this satisfactorily.

The electron distribution of free atom of copper is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ which on condensing to a solid takes up a configuration suggested above. Such a condensation though it promotes 1·5 d electrons/ atom to 4p level, this energy of promotion is more than compensated by the formation of 1·5 d bonds and this is responsible for the increasing cohesion of copper as compared to zinc which has a distribution $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1 p^1$ in the solid state (with no d bonds) as zinc has c. p. h. structure. Addition of such an element with a full d-shell to copper means copper will not be able to form d-bonds with the solute zinc atom. Lack of utilization of d-bonds will take

away the promotion energy required to promote d-electrons to p-levels and the electronic structure of solid copper will therefore approach that of the free atom of copper. This break-down of d-bonds in copper will happen at a composition at which copper will have less than one unpaired d-electron for the formation of bonds and will correspond to a d-electron concentration of nine per atom and at this stage in the equilibrium diagram, the alloy composition will be very sensitive to changes in electron concentration. Thus this effect of breaking d-bonds of copper is proportional to electron concentration and α-phase boundary is reached when this concentration of atoms with filled $3d^{10}$ shell reaches 56% in the alloy.

After this breakdown of d-bonds, the copper atom is able to supply one bonding electron per atom and this makes the b.c.c. phase to appear corresponding to an electron concentration of 1·5. Increase of zinc content would increase the outer electron concentration to two, thereby accounting for γ and ϵ brass structures.

This explanation of alloying behaviour of copper shows that they are accompanied by a decrease in the number of d-electron and outer electron bonds in the α-phase of these systems and hence melting points, Young's modulus would show a decrease. That such a decrease takes place is shown by Engel[30a] and Hume-Rothery.[10] On the other hand if an element like nickel is added to copper which can form d-bonds it will increase the elastic modulus and this is in agreement with the finding of Greer and Bucknall.[38] For the same reason of breaking of d-bonds, the activation energy of self-diffusion of copper shows a decrease in the α-phase and the activation energy in β is much less than either of the pure components (Cu or Zn).[36]

With the electron concentration concept of Engel, one is able to understand the shape of primary solubility curves of copper alloys. These curves show a shift to lower solute concentration with a rise of temperature which is contrary to those normally met with viz. decrease in solid solubility with fall of temperature. Though this is said to have been explained in the paper of Jones[6], Zener[39] questions such an explanation as it is thought to contain a mathematical inaccuracy. Engel's ideas of alloying behaviour of copper seem to explain this, though in a qualitative manner, as shown below. Rise of temperature will change the electronic structure of solid copper to that of free atom of copper which involves breaking of d-bonds. This effect is similar to the effect produced by alloying copper with elements with which it cannot form d-bonds ; hence sp-electrons revert to d-levels resulting in a decrease in the concentration of lattice controlling electrons and this shifts the boundary to lower solute concentration with elements like zinc as solute.

Conclusion

The above discussion of some of the rules of alloy formation shows that for copper alloys though these rules are generally applicable, the explanation of the above rules on the basis of theoretical concepts are unsatisfactory. However, Engel's explanation of alloying

behaviour of copper appears to hold promise though it has given rise to much controversy.

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Discussions

Dr J. K. Mukherjee (NML) : The concept of atomic diameter put forward by the author is not very clear as he has assumed it to be the diameter of the electron clouds around the atoms. According to Late Prof. Hume-Rothery's postulation, radial factor is more important in calculating atomic diameters as due to directed valency and/or covalent bondings ; the shape of the electron clouds are often complicated and are far from spherical or even ellipsoidal. In bonded structures where atoms are arranged in some crystalline form the free electrons combine together and form a common cloud and as such there should not be any electron clouds attached only with single atom. The concept of atomic diameter as given by Hume-Rothery (based on which the size-factor principle is worked out) is applicable to the atoms arranged in such crystalline form and the distance of their closest approach is taken to be the atomic diameter. That is why different atomic diameters are assumed for different allotropic modifications of elements. For example, Fe and Mn atoms have been assigned different atomic diameters in their different allotropic forms such as α, γ and β etc. I would also request the author to comment on this aspect on the basis of the information obtained from NMR (Nuclear Magnetic Resonance) studies of different elements.

Mr L. J. Balasundaram (Author) : The concept of atomic diameter discussed in the paper relates to atoms in crystalline lattices and not to single (or free) atoms. As stated in the paper this parameter is discussed in relation to size-factor principle and for this purpose it is estimated as the closest distance of approach between atoms. This concept, in spite of its utilitarian value, is unsatisfactory for many reasons discussed in the paper, one of which being the aspherical shape of the electron cloud around atoms which Dr Mukherjee mentions. This concept therefore needs revision and as pointed out in the paper a concept called volume per atom has been suggested to be used in its place. This alternate concept though not free from all the defects of the parameter of atomic diameter, is a better parameter and emphasises the point of conservation of volume in structural transformations obviating the necessity for corrections to sizes of atoms when comparing them in different crystal structures.

As for the information obtained from NMR on the subject of atomic diameters of elements, it may be pointed out that NMR is based on electronic transitions in metals and alloys and is of much use in the study of electronic structures of metals and alloys. It does not at present appear to be of much use in the evaluation of atomic diameters of metals and alloys.