Solid Solutions in Metals: from Hume-Rothery's Rules to High Entropy Alloys

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Abstract. *An overview on the development of the concept of solid solutions in metal alloys is provided following a historical approach with mention of the latest findings in the field. Craftsmen, goldsmiths, and smelters of artistic objects have exploited metal blends for centuries, but the first scientific approach to metallic solid solutions is due to Matthiesen (London, 1864) with the study of the resistance of metal elements containing impurities. After the industrial revolution and the discovery of a wealth of alloys, the elaboration of the rules that determine the mutual solubility of the elements was due to William Hume-Rothery, founder of the school of materials at Oxford. Starting with the first paper in 1926, he identified empirically size, electronegativity, and electronic concentration factors providing also predictive tools for improving the mechanical properties of alloys. A semi-quantitative basis to the empirical rules was then posed by A. R. Miedema (Amsterdam, 1969) and D. Pettifor (Oxford, 1990) while the developments of quantum-mechanical techniques provided the ab-initio justification of rules (Mizutani, 2011). In recent years, the search for multi-component equimolar solutions of several elements, typically five, led to the identification of a new class of alloys called* high entropy alloys *introduced by Yeh (Taiwan, 2004) and Cantor (Oxford, 2004), which are currently being developed. They display interesting mechanical resistance and ductility properties both at high and cryogenic temperatures possibly because of the inherent disorder and size mismatch in the lattice.*

1. Introduction

The periodic table of elements lists almost 90 elements which can be termed metallic in their reduced state. They are mostly solid at room temperature (Mercury is the exception), conduct electricity and heat, absorb light and other electromagnetic radiations, and are chemically electropositive (noble

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elements are the exception). Some elements are known since early civiliza-
tion of mankind, e.g. the Bronze era derives its name from an alloy which
is the mixture of two main elements: Copper and Tin. Ancient blacksmiths
and craftsmen made metallic objects exploiting the experience accumulated
through the centuries. In the first book ever published on metallurgical topics,
Biringuccio stated: «lega altro [...] non vuol dire che mescolamento d'amica-
bile amicitia lun metallo con laltro»[1] (alloy does not mean anything else than
the mixing because of amicable friendship of a metal with another) referring
mostly to noble metals. In which state the metals were intimately mixed was
obviously unknown.

2. The scientific approach to solid solutions in metals

It is recognized that the first extensive scientific evidence of elements
mixing as atoms in a single phase, i.e. solid solution, was provided by the
work of Matthiessen who measured the electrical conductance in a series of
alloys as a function of temperature[2]. His results showed the contribution to
the conductance by impurities which added up to the intrinsic conductance
of the element. Matthiessen statement was: «the law which we have dedu-
ced from our experiments only holds good in cases where the alloy may
be considered a solution of one metal in the other». A milestone in scien-
ce in the nineteen century has been the work of J.W. Gibbs on equilibrium
thermodynamics[3] which paved the way to build the essential tool of phase
diagrams to represent the occurrence of phases and their coexistence. With
the industrial revolution of the second half of the century, the use of metals
expanded quickly and scientific knowledge on them built up. The most im-
portant metallurgical phase diagram, the Iron-Carbon phase diagram, was
known to a good extent at the turn of the century, as shown in Fig. 1, adap-
ted from a classical paper by Roberts-Austen, where a zone extending in a
range of C concentrations and temperatures was identified as «solid solution

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[1] Vannoccio Biringuccio, *De la Pirotechnia*, Siena 1540.

[2] A. Matthiessen and C. Vogt, *On the influence of temperature on the electric conducting-power of alloys*, Phil. Trans. R. Soc., London, 154 (1864), pp. 167-200.

[3] J. Willard Gibbs, *On the Equilibrium of Heterogeneous Substances*, Trans. Connecticut Acad. of Sciences, III, 1874-1878, pp. 108-248, 343-520.
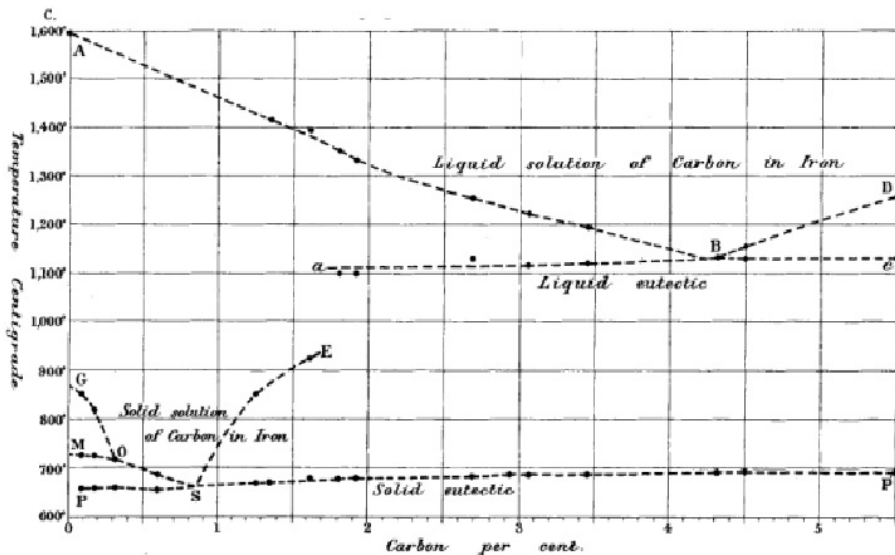
Fig. 1. Aspects of the Fe-C phase diagram which was building up in Roberts-Austen work. The dots refer to arrest points in thermal analysis curves obtained on cooling of alloys with various C content. The eutectic point (B) is well identified as the lowest temperature at which the liquid solution of Carbon in Iron occurs. Similarly, the eutectoid point (S, here called solid eutectic) where the solid solution of Carbon in Iron transforms is correctly located. The phases of Fe were not known yet, therefore, the MO line was drawn to mark the ferro- to para- magnetic transition of Fe and alloys. It was shown later that it is not needed since there is no phase transformation at the Curie point (adapted from Ref. 4).

of Carbon in Iron»[4]. Where the atoms of the elements sit was not known until the discovery of X-ray Diffraction by crystals which prompted the determination of lattice constants of elements and alloys[5]. Examples for fully miscible binary couples are reported in Fig. 2 adapted from a later collection of data: in a few cases a rule of mixture (Vegard's law) represents well the experimental findings, while in most cases a deviation occurs indicating volume reduction or expansion on mixing. According to the size of the alloying element two types of metallic solid solutions occur: substitutional when the solute substitutes for the

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[4] W.Ch. Roberts-Austen, *Fourth Report to the Alloys Research Committee*, in «Proc. Inst. Mech. Eng.», 1897, pp. 31-100.

[5] Ch.S. Barrett, *Structure of Metals. Chystallographic Methods, Principles, and Data*, McGraw-Hill, London 1953.
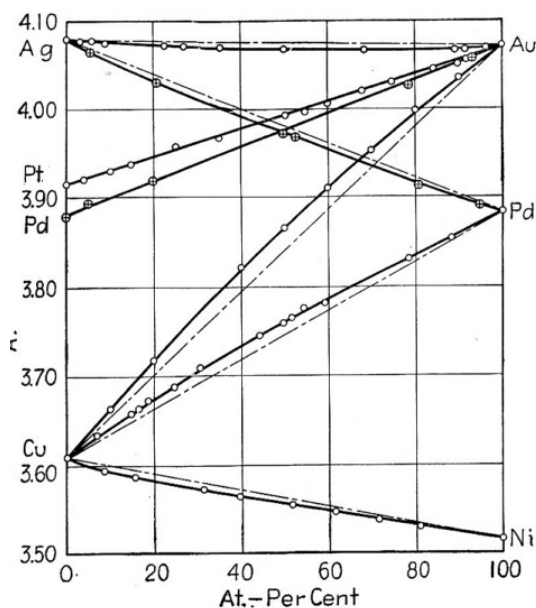
Fig. 2. The lattice constant of alloys of the noble metals which are fully miscible in the face centered cubic (fcc) structure over the entire composition range. The Au-Pd and Au-Pd systems follow strictly Vegard's law. The other systems display either positive of negative slight deviation (adapted from Ref. 5).
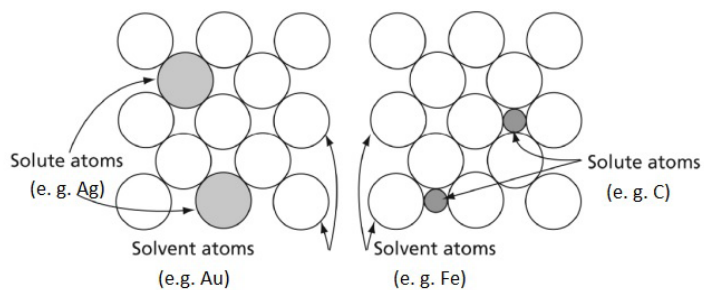

Fig. 3. A sketch of the (100) lattice plane of fcc solutions showing the substitution of a solvent atom at lattice points (left, substitutional solid solution) and the insertion of solute atoms in interstices of the host lattice (right, interstitial solid solution).
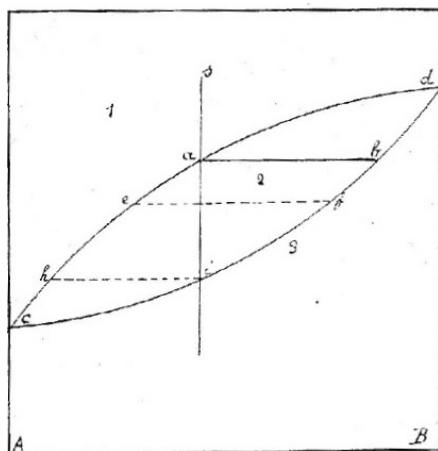
Fig. 4. A binary phase diagram showing full miscibility of two elements in the liquid and solid state. The horizontal lines show how the fraction of each phase is computed using the lever rule (adapted from Ref. 6).

main element in lattice sites and interstitial when the solute is small enough to enter empty spaces in the host lattice (Fig. 3). There is clearly an effect of atomic size in mixing but how much does it count? and are there other reasons for solid solubility, especially in cases where the solubility is limited to a given extent? Many examples of phase diagrams (Fig. 4) were provided in the first book ever written on chemical combinations of metals which described «mixed crystals» and many intermetallic compounds[6]. In the same period, the use of C for Fe cementation[7], implying its miscibility in the Fe lattice at high temperature before quenching to obtain martensite, was becoming an established industrial process. Refs. 6 and 7 show the attention of prominent Italian scientists of the time to the current international literature and the contribution to industrial innovation.

3. The Hume-Rothery rules

The issues outlined by the questions above represented the basis of the lifelong activity of William Hume-Rothery and his group at Oxford starting

[6] M. Giua and Cl. Giua-Lollini, *Chemical Combinations among Metals*, J&A Churchill, London, 1918 (the Italian book appeared in 1917).

[7] F. Giolitti, *The Cementation of Iron and Steel*, McGrow-Hill, New York 1915 (the Italian book appeared in 1912).
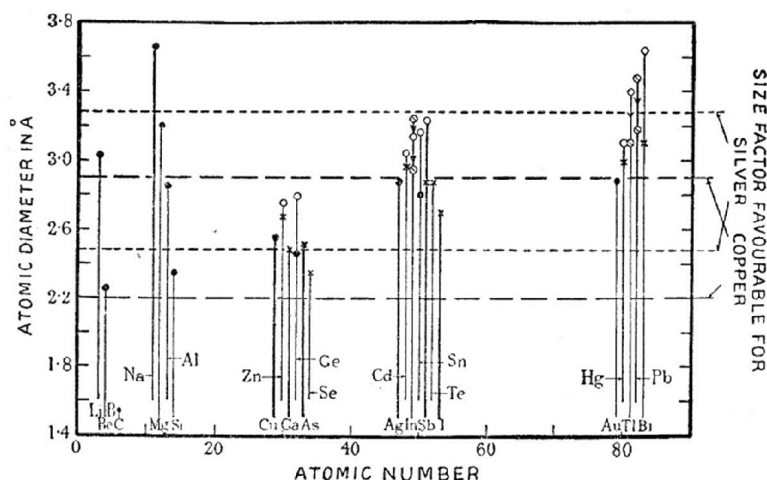
Fig. 5. Illustration of Hume-Rothery's "size factor" rule. The atomic diameter of elements is plotted as points of various type as a function of atomic number. The long-dashed and short-dashed horizontal lines show the extension of the range from +7% to -7% for *sp* solutes in Cu and Ag, respectively. Some elements are similarly soluble in both Cu and Ag (e.g. Zn, Ge), some are more soluble in one of the elements (e.g. Si in Cu, In in Ag) (adapted from Ref. 9).

with the publication of the first paper in 1926[8]. The essential concepts were exposed in a concise book on «The Structure of Metals and Alloys» published in 1936[9] which had several new editions in the following decades. The conditions, now called Hume-Rothery rules (HRRs), for elements to be soluble into others are summarized below using some of the original statements.

The size factor effect

Since the formation of a solid solution is accompanied by a distortion of the lattice, it is only natural to expect a connection between the atomic diameters of any two metals and their tendency to form solid solutions. […]. where the atomic diameters of solvent and solute differ by more than about 14-15 per cent of that of the solvent, the *size factor*

[8] W. Hume-Rothery, *Research on the Nature, Properties and Conditions of Formation of Intermetallic Compounds*, with Special Reference to Certain Compounds of Tin , in «J. Inst. Met.», 35, 1926, 1926, pp. 295-299, cit. p. 300.

[9] W. Hume-Rothery, *The Structure of Metals and Alloys*, The Institute of Metals, London 1936.
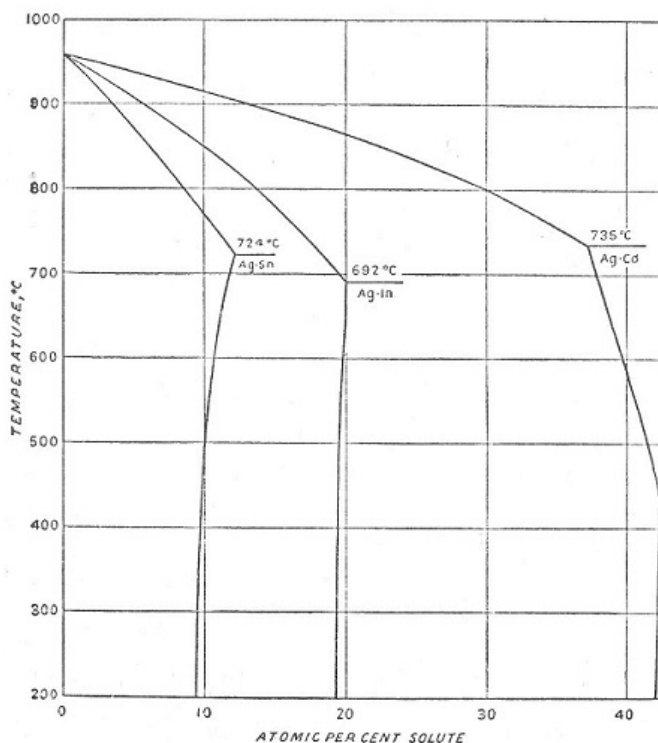
Fig. 6. Portions of the Ag-Sn, Ag-In, Ag-Cd phase diagrams reporting solidus and solvus curves as a function of atomic percent solute. The terminal solubility of the three element ranks as Cd > In > Sn. The number of outer electrons of the solutes are, 2, 3, and 4, respectively showing an inverse trend with respect to solubility (adapted from Ref. 9).

is unfavourable and the solid solution is very restricted whilst when the atomic diameters are within this limit the size factor is favourable.

This is illustrated in Fig. 5 where the atomic diameters of *sp* elements plus Cu, Ag, and Au are plotted versus atomic number. Two ranges are marked extending ± 7 % around the value of the atomic diameter of Cu and Ag. The elements whose diameters fall into these ranges are soluble in Cu and Ag, respectively. The elements whose diameter falls outside one of the ranges (e.g. Mg for Cu) display limited solubility in the element while may be soluble into the other one. Both large and small elements with respect to the ranges are not soluble in Cu and Ag.
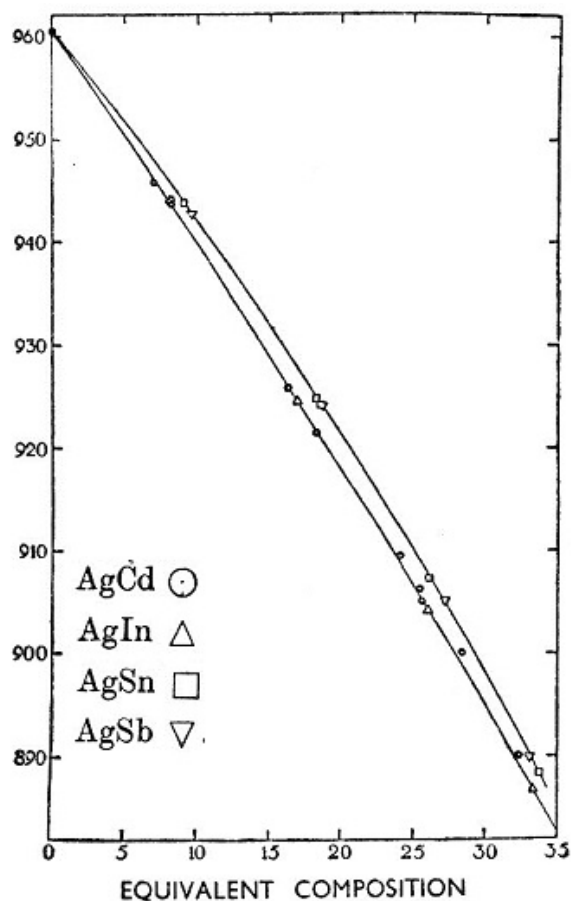
Fig. 7. The liquidus curves of Fig. 6 plotted versus equivalent composition. The different curves in each series are superimposed showing the occurrence of an electron concentration effect. Hume-Rothery explained further the slight shift between the two curves in terms of lattice distortion: the larger the lattice distortion, the steeper the curve.

The valency effects

In addition to the size factor, it was recognized the larger is the difference in electronegativity between solvent and solute, the greater is the tendency for the formation of stable intermetallic compounds which limits the reciprocal solubility of the alloy components. This was called *electrochemical factor* and the tendency of the solid solution to be restricted because of the occurrence of compounds was called the *electronegative valency effect*.

After a survey of data for Cu and Ag alloys, it was evidenced that the tendency to form solid solutions is not reciprocal. In fact, «other things being equal, a metal of lower valency is more likely to dissolve one of higher valency then vice versa». This was called the *relative valency effect*.

There are exceptions to these effects which Hume-Rothery was able to justify by accounting for the different crystal structures of the elements or the dependence of solubility with temperature.

The electron concentration

The most novel, and intriguing, rule makes use of the quantity now called *electron concentration*, i.e. the average number of valence electron which the components contribute to the alloy. The liquidus and solidus curves in binary phase diagrams of Cu and Ag with elements which follow them in the periodic table and, therefore, have favourable size effect, were examined. Although the general shape of the curves is similar, the conjugated lines are shifted to lower solute content on increasing the number of valence electrons of the solute (Fig. 6). Hume-Rothery defined «equivalent composition» the «atomic percentage of the solute multiplied by its valency». The conclusion was drawn that «if the liquidus curves were plotted in equivalent compositions the different curves in each series were superimposed» as shown in Fig. 7 for Ag based systems. Also, it was noted that the depression of the solidus curve increases with increasing difference in size factor and valency between solvent and solute. Examining then the form of the solvus curves which give the primary solid solubility, it came to no surprise that «favourable conditions for the formation of wide solid solutions» imply the atom have close size and valency. For alloys of Cu and Ag with the elements which follow in the periodic table where the size effect is small, it appeared clear that the limitation of solid solubility derives from the «electron concentration». This quantity is the «ratio of valency electrons to atoms». As an example, consider the solubility in Cu at room temperature of Zn, Al, Ge which is 38 at %, 20 at %, and 11 at %, respectively. The electron concentration turns out to be 1.38, 1.40, and 1.33 (about 21/15 on average), respectively, showing an approximately identical extent of primary solid solubility. The solutions, therefore, owe their stability to an electronic effect. In the following chapter of his book Hume-Rothery went on unveiling that the compounds occurring in Cu and Ag based systems (e.g. β- and γ-brasses in Cu alloys) are themselves stabilized by the electron concentration being 1.5 (21/12) and 1.61 (21/13), respectively.

This is a simplified telling of the Hume-Rothery story. His conception was more refined in that he looked for tiny differences in the phase diagrams and
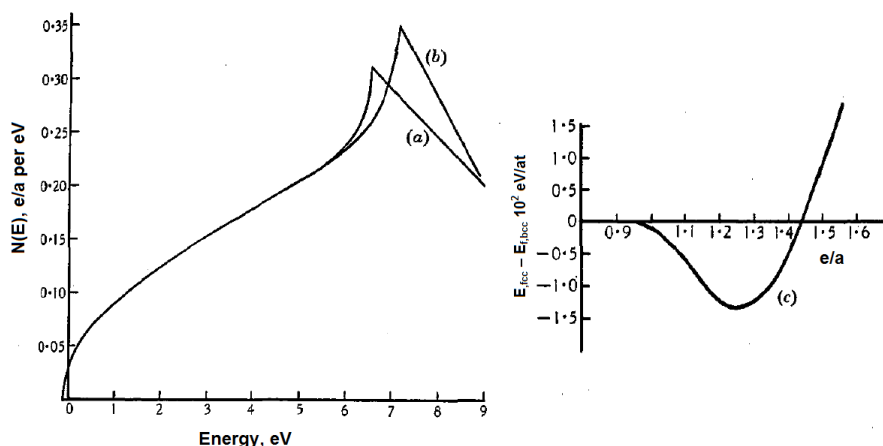
Fig. 8. (Left) The density of states as a function of energy for the fcc structure of Cu (a) and the bcc structure of Cu (b). The (a) curve has more states at lower energy than the (b) curve whereas at high energy the opposite occurs. When filling the states with the available electrons, the Fermi level is reached at lower energy for the fcc structure up to the number of electrons per atom of 1.43 and vice versa at higher number of electrons per atom. This is shown by the difference in Fermi energy between fcc and bcc structures in the right part of the figure (adapted from Ref. 12).

was able to explain some of them using the notion of volume contraction and lattice distortion when a solute enters the host lattice.

4. Explanations of Hume-Rothery rules

The clear empirical evidence that metallic phases can be stabilized by electronic effects showed the need for a proper description of the electron states in the metallic solid. Quantum mechanics was in its infancy when Hume-Rothery published his first paper on solid solubility. The first calculation of electronic states in metals, the free electron model, by Sommerfeld appeared in 1928[10].

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[10] A. Sommerfeld, *Zur Elektronentheorie der Metalle auf Grund der Fermischen Statistik*, in «Zeit. für Physik», 47 (1-2), 1928, pp. 1-32.

It was followed by the nearly free electron model shortly after with the identification of Brillouin zones in the space of wave vectors at whose limits energy gaps between zones appear[11].

The shape of the zones depends on crystal structure. Computing the density of available states as a function of energy in a unit volume of metal provided Jones with the famous sketch of the filling of states in face centred cubic (fcc) and body centred cubic (bcc) Cu[12]: the density of states derived for the fcc structure being denser than that derived for the bcc structure at lower energy and vice versa (Fig. 8). The Jones' calculation suggested that the turning point of electronic stabilization (equal number of occupied states as a function of energy) falls at the electron concentration of 1.4, in amazing agreement with the empirical findings that the fcc solid solution occurs up to this value in systems such as Cu-Zn and gives place to a bcc phase whose range of existence is centred at electron concentration of 1.5. This concept and Fig. 8 have been used since then in textbooks and lectures to illustrate the electron concentration rule[13]. Modern rigorous first principle calculations have shown that the Jones' basic idea was correct, i.e. the structural stability of similarly packed phases is largely determined by the density of states[14]. However, Jones was lucky in his calculations since he had to make approximations to resort to an analytical form of the problem by disregarding the role of *d* electrons. In fact, if *d* electrons were accounted for, the Cu would result bcc.

The author of this criticism, D. Pettifor, who headed in recent times the Department of Materials at Oxford, continued also the empirical classification of intermetallic compounds on the basis of their crystal structure and came up with assigning to each chemical element a "Mendeleev number"[15]. Some elements were displaced from their position in the periodic table and re-assigned a new position in order to group together the binary compounds having the

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[11] L. Brillouin, *Free electrons in metals and the role of Bragg reflections*, in «J. Phys. Radium», 1 1930, p. 367.

[12] H. Jones, *The phase boundaries in binary alloys, part 2: the theory of the α, β phase boundaries*, in «Proc. Phys. Soc.», 49, 1937, pp. 250-257.

[13] N.F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys*, Oxford University Press, London 1936.

[14] A.T. Paxton, M. Methfessel and D.G. Pettifor, *A bandstructure view of the Hume-Rothery electron phases*, in «Proc. Roy. Soc.: Mathematical, Physical and Engineering Sciences», 453, 1997, pp. 1493-1514.

[15] D.G. Pettifor, *Structure Maps in Alloy Design*, in «J. Chem. Soc. Faraday Trans.», 86 (8), 1990, pp. 1209-1213.
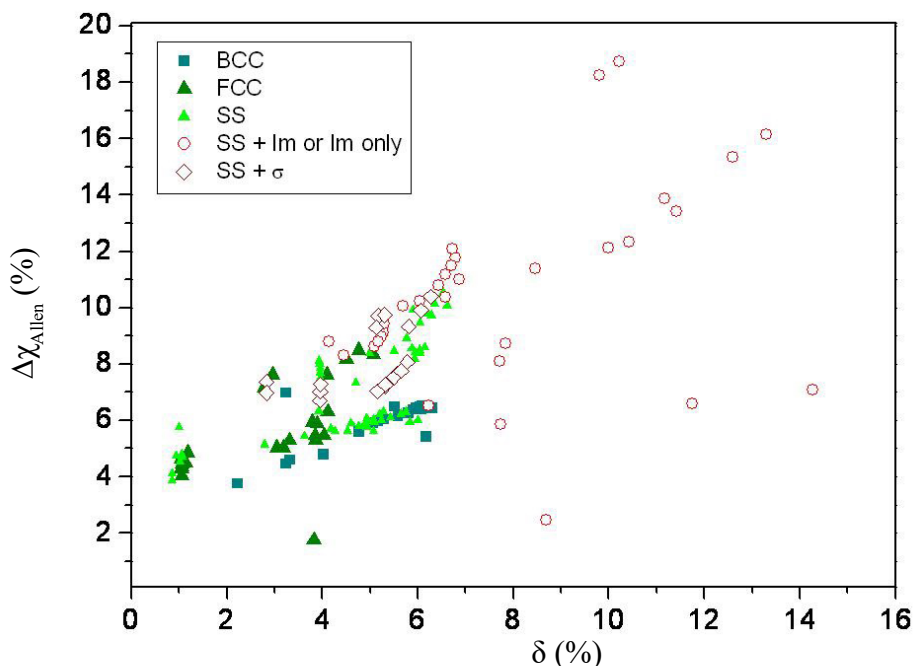
Fig. 9. The electronegativity mismatch ($\Delta\chi$)/size mismatch (δ) map for high entropy alloys. The points refer to at least quinary compositions reported in the literature. Full symbols indicate the occurrence of a high entropy single phase in the alloy. Open symbols indicate that multiple phases were formed: solid solution + intermetallic compounds of which the σ phase is rather frequent. The region were high entropy alloys are likely to form extends up to $\Delta\chi \approx 5$ and $\delta = 6$. Some full points are found in the "wrong" region where no single solution phase should occur. In some case it has been demonstrated that the alloys obtained by arc melting were not fully equilibrated and developed multiple phases on annealing.

same crystal structure. The Pettifor "chemical scale" is now widely used in the dedicated literature[16].

   In this resumè of empirical methods for alloy classification it is worth mentioning the work by A.R. Miedema who used two electronic parameters, the difference in electron density of the two metals at the border of a Wigner-Seitz cell and the work function difference between alloy components in binary systems, to build simple equations for the enthalpy of formation of binary

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[16] W. Steurer and J. Dshemuchadse, *Intermetallics: Structures, Properties, and Statistics*, Oxford Science Publications, Oxford 2016.
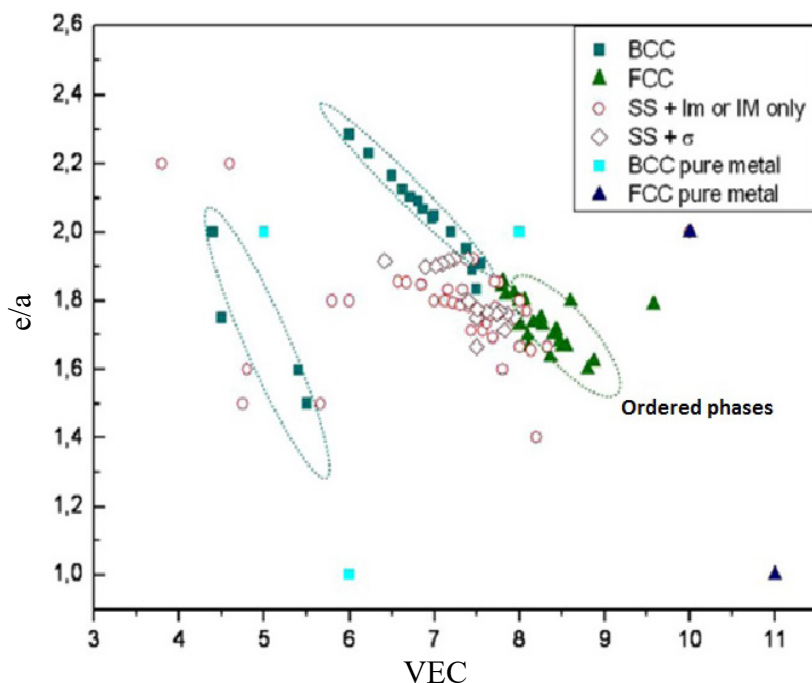
Fig. 10. The itinerant electrons (e/a) /valence electron concentration (VEC) for high-entropy alloys. Symbols have the same meaning as in Fig. 9. In addition, the position of pure metals is indicated. The zones in which single bcc of fcc phases are obtained are evidenced with a contour line. The regions for the occurrence of the bcc and fcc structures are well separated. Ordered fcc-based structures (points not reported here) occur at e/a ≈ 1.5 limiting the size of the fcc contour.

compounds, the interfacial energy and the work of adhesion between metallic couples[17]. Miedema's approach is in use to estimate thermodynamic quantities when no experimental data are available, e.g. for phase diagram calculation.

It is finally remembered that a comprehensive quantum mechanical treatment of HRRs in relation to the electron bands in complex alloys, using the leit-motiv of the Cu-Zn system, has appeared in a book[18] which has quickly become a reference in the field.

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[17] F.R. de Boer, R. Boom, W.C.M. Mattens, A.R. Miedema and A.K. Niessen, *Cohesion in Metals. Transition Metals Alloys*, North Holland, Amsterdam 1989.

[18] U. Mizutani, *Hume-Rothery Rules for Structurally Complex Alloy Phases*, CRC Press, Boca Raton, FL 2010.

5. High entropy alloys

In recent years the HRRs for solid solutions have been revisited because the idea, emerged and was experimentally verified by Yeh[19] and Cantor[20], independently, to explore multicomponent systems made of elements in equimolar amount with the aim of finding single phases in this zone of the phase space. Such an alloy is not based on any of its components since no one is more concentrated than the others, contrary to almost all the metallic materials used up to now which are based on a majority element, e.g. Fe in steels and Ni-based superalloys. A single solid solution phase containing several elements, typically at least five, would have a high configurational entropy, favouring its stability in case the chemical interaction between components does not prevail, i.e. the enthalpy of mixing is small. Also, the size of the constituents should differ, at least to some extent, with the consequence of inducing extensive local distortion in the lattice. The new type of alloys is now called *high entropy alloys* and is sparking interest at various levels both scientific and industrial. In order to explain the occurrence of these single phases, mostly fcc or bcc, it has been fascinating to resort to HR rules defining the relevant parameters appropriately for multicomponent systems[21]. The size factor is expressed as the sum of the difference of the atomic radii of elements with respect to the average radius in the alloy multiplied by the respective mole fraction over the average radius, and termed lattice mismatch. Similarly, the electronegativity mismatch was defined by making use of the most recent electronegativity scale due to Allen[22]. The outer electrons in the alloy were counted to express the valence electron concentration (VEC) and the free electrons, accounting both for *sp* states and *d* states, were counted to provide the itinerant electron concentration, e/a. Additionally, the Miedema model was employed to evaluate the thermodynamic stability of solid solutions. Maps based on the above parameters were built to single out regions in the parameter space corresponding to

[19] J.-W. Yeh, S.-K. Chen, S.-J. Lin, J.-Y. Gan, T.-S. Chin, T.-T. Shun, C.-H. Tsau, and S-Y. Chang, *Nanostructured High Entropy Alloys with Multi Principal Elements: Novel Alloy Design, Concepts and Outcome*, in « Adv. Eng. Mater.», 6, 2004, pp. 299-303.

[20] B. Cantor, I.T.H. Chang, P. Knight and A.J.B. Vincent, *Microstructural development in equiatomic multicomponent alloys*, in «Mater. Sci. Eng. A», 375-377, 2004, pp. 213-218.

[21] M.G. Poletti and L. Battezzati, *Electronic and thermodynamic criteria for the occurrence of high entropy alloys in metallic systems*, in «Acta Mater.», 75, 2014, pp. 297-306.

[22] J.B. Mann, T.L. Meek and L.C. Allen, *Configuration Energies of the Main Group Elements*, in «J. Am. Chem. Soc.», 122, 2000, p. 780.

alloys which were known experimentally to be single phased. Examples of maps are given in Fig. 9 for the electronegativity mismatch vs. lattice mismatch where the requirement for the formation of a high entropy alloy is that the two parameters have values below 6 and 5, respectively, and for the VEC vs the e/a in Fig. 10. The latter map highlights clearly the regions where bcc and fcc solid solutions are found. It is noted also that at e/a = 1.5 the phase occurring in the alloy is expected to be ordered as in the case of Cu-Zn alloys. The maps proved useful in rationalizing the findings on alloy systems known at the time of the publication of the paper and have become a tool for predicting the phases occurring in new systems.

There are obvious exceptions in the maps which suggests further analyses both experimental in order to find the proper equilibrium state of alloys which are usually produced by arc melting, a technique implying rather fast solidification which may lead to non equilibrium solubility, and theoretically for accurate band structure calculation with *ab-initio* methods.

The most studied high-entropy alloy, single-phase CoCrFeMnNi, displays tensile strength levels of about 1 GPa, excellent ductility (60–70%) and fracture toughness (K_{Ic} > 200 MPa$\sqrt{m}$)[23]. The reader experienced in mechanical behaviour of alloys will find that these properties altogether are exceptional. They stem from a synergy of multiple deformation mechanisms, rarely occurring together, providing high strength, work hardening and ductility. They involve the interaction of partial dislocations with stacking-faults, the blocking of undissociated dislocations by slip bands, and the delay in crack propagation by twins near-tip crack faces. The damage tolerance of the alloy also at cryogenic temperatures justifies the present high interest in this material for structural application.

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[23] Z.J. Zhang, M.M. Mao, J. Wang, B. Gludovatz, Z. Zhang, S.X. Mao, E.P. George, Q. Yu and R.O. Ritchie, *Nanoscale origins of the damage tolerance of the high-entropy alloy CrMnFeCoNi*, in «Nature Comm.», 6, 2015, p. 10143.