Composition formulas of solid-solution alloys derived from chemical-short-range orders

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Solid solutions are the basis for most industrial alloys. However, the relationships between their characteristic short-range orders and chemical compositions have not been established. The present work combines Cowley parameter $\alpha$ with our cluster-plus-glue-atom model to accurately derive the chemical units of binary solid-solution alloys of face-centered cubic type. The chemical unit carries information on atomic structure and chemical composition, which explains prevailing industrial alloys. For example, chemical units in Cu₆₈.₉Zn₃₁.₁ alloy with $\alpha_1 = -0.137$ are formulated as [Zn-Cu₁₀Zn₂Cu₂]Zn₂Cu and [Zn-Cu₁₀Zn₂]Zn₃Cu₁ with 64.0–70.0 wt% Cu corresponding to the most widely used cartridge brass C26000 (68.5–71.5 Cu). This work answers the long-standing question on the composition origin of solid-solution-based industrial alloys, by tracing to the molecule-like chemical units implied in chemical short-range ordering in solid solutions.

In one of the early review on solid solutions in 1925, Bruni¹ raised a preliminary question: does the chemical molecule continue to exist in the crystalline state? This question looks quite naive at present but must be answered in his time as most of the metals are based on solid solutions and they all have specific chemical compositions, just like any molecular substance whose chemistry is contained in the molecular structure. The first results of X-ray analyses by Bragg² answered this question in the negative, by affirming that within the crystal edifice only atoms exist and the molecule vanishes into the lattice. However, the structural origin of chemical compositions of industrial alloys remains open. The key to understanding the composition mystery must lie in the structure of solid solutions, which has been a hot topic in the early twentieth century. Bragg and Williams were among the first to propose a statistical model that considers the order and disorder in solid solutions as a co-operative long-range phenomenon.³ This model was then extended to a more elaborated theory by Bethe⁴, assuming the short-range interaction in nearest neighborhood. The long- and short-range orders are well unified in Cowley’s³ short-range order parameters $\alpha_i$, expressing the interaction of a given atom A with the atoms of the $i$th shell of atoms surrounding it:

$$\alpha_i = 1 - \frac{n_i}{m_{Bc_i}}$$

where $n_i$ is the number of B atoms among the $c_i$ atoms of the $i$th shell, and $m_{B}$ is the mole fraction of B atoms in A–B binary alloy. Equations for the long-range order parameter of Bragg and Williams are obtained by considering the limiting case of $i$ very large. Since then it is well recognized that short-range ordering is the major structural feature of solid solutions.

In an effort to explore the composition origin implied in such ordered and disordered local structures, our team has been engaged in developing a so-called cluster-plus-glue-atom model⁶–⁸ which simplifies any short-range order into a local unit covering a nearest-neighbor cluster plus a few next-neighbor glue atoms, expressed in cluster formula form as [cluster](glue atoms). This structural unit, showing charge neutrality and mean density following Friedel oscillation⁹, resembles in many ways chemical molecules and henceforth is termed 'chemical unit'.⑦ The only difference from common concept of molecule lies in the way the chemical units are separated: instead of relatively weak inter-molecular forces between molecules, here the chemical units are linked by chemical bonding. We have shown by analyzing many industrial alloys that popular alloys are all based on

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simple cluster-plus-glue-atom formulas, such as [Zn-Cu12]Zn4 for Cu-30Zn, [Ni-Fe12]Cr2(Ni,Nb,Ti) for maraging stainless steel Custom465, etc.7.

However, despite of the proved capacity of the cluster-plus-glue-atom model in interpreting composition origins of alloys, there is an obvious gap between the idealized formulas (e.g., the nearest neighbors are always fully occupied by solvent atoms such as [Zn-Cu12]Zn4) and the real chemical short-range ordering (the nearest neighbors are always mixed-occupied) that can be measured, for example using parameter α. The α parameter describes the statistical deviation from the average alloy composition in each radial shell. The composition deviation appears most prominently in the first and second nearest neighbors, which agrees perfectly with the picture of the cluster-plus-glue-atom model that covers also the same radial range. The present work is our first attempt to fill in the gap, by showing how to relate the measurable parameters αi within the framework of the cluster-plus-glue-atom model, to the construction of composition formulas of typical binary solid solution alloys with face-centered cubic (FCC) structure.

Theoretical methods

We first briefly review the fundamentals that lead to chemical units, as fully detailed in reference7. Short-range ordering is formed due to the charge shielding around any given atom that produces oscillating distribution of electron density, namely Friedel oscillations10,11. As shown in Fig. 1c, the total potential function \( \Phi(r) \propto -\sin(2k_F r)/r^5 \) felt by the electrons at radial distance r periodically decays with the third power of r, where \( k_F \) is Fermi wave vector. This oscillating behavior of electrons in turn causes the same oscillation of atomic density \( g(r) \) in the real space, which is prominent in short r range, especially at the nearest and next-nearest neighborhoods. A local chemical unit is defined using a charge-neutral cut-off distance of 1.76 \( \lambda_F \) being Friedel wavelength, that encloses the nearest-neighbor cluster and a few next-neighbor glue atoms. For FCC structure, its cluster-plus-glue-atom model is shown in Fig. 1b, the cluster is cuboctahedron with coordination number of 12 and the glue-atom shell in the next neighborhood is octahedron of coordination 6. A solid solution is then regarded as the random packing of such units as schematically illustrated in Fig. 1a. The chemical unit of a binary A–B system is expressed in cluster formula form as [A-M12]A3x with M12 = B12A3x, where x represents the number of glue atoms with 0 < x < y < 6.

Following13, the chemical unit volume is the sum of the each atomic volume \( (1 + x + y) \cdot R_A^3 + 12 \cdot R_M^3 + y \cdot R_B^3 \cdot (4\pi/3)/0.74 \), where R’s are atomic radii and 0.74 is the packing efficiency of FCC structure. This volume is also equal to the spherical volume enclosed by the charge-neutral cut-off distance 1.76 \( \lambda_{F} \). Since \( R_A + R_M = 1.25 \lambda_F \) is the nearest-neighbor distance, the x-y relationship is obtained:

\[
x \cdot R_A^3 + y \cdot R_B^3 \approx 2 \cdot (R_{AM} + 1)^3 - 12 \cdot R_{AM}^3
\]  

(2)



where \( R_{AM} \) and \( R_{BM} \) are respectively the ratios of \( R_A \) and \( R_B \) over \( R_M = (n_1 \cdot R_B + (12 - n_1) \cdot R_A)/12 \). Goldschmidt radii of atoms are generally adopted. When \( R_A = R_B, x + y = 3 \), which means a 16-atom cluster formula for an FCC solid solution composed of solute and solvent atoms of equal atomic radii, or \([A-B_{12}]A_B\).

As demonstrated in references7,14,15, compositions of commonly used industrial alloys such as Cu alloys, Al alloys, stainless steels, and Ni-based superalloys fall close to the model predictions, validating the presence of simple chemical units in metallic alloys and the generality of the cluster formulism. Our recent work16 shows that the model also applies in high-entropy alloys, after appropriate elemental classification. The solid solutions

Figure 1. (a) Schematic diagram of short-range order and long-range disorder distribution of solute atoms in binary solid solution alloys. (b) Cluster configuration of binary FCC structure. (c) Idealized pair distribution function \( g(r) \) and total potential energy \( \Phi(r) \) curve felt by electrons12.
of hexagonal closed-packed type can be treated similarly, as it shows the same coordination number of 12 (the nearest-neighbor cluster is twinned octahedron) and is also close-packed. The body-centered cubic structure, featuring a rhombohedral cluster with a coordination number of 14 and a non-close-packing, should be dealt with separately, which is an on-going work.

Now we show the two basic procedures towards constructing the chemical unit with formula \( [A-B]_{x}A_{1-y} \) \( A_{1}B_{y} \) using the short-range-order parameter \( \alpha \).

(1) Determination of nearest-neighbor atoms using \( \alpha \)

For a given alloy with a known B’s atomic fraction \( m_{B} \) and coordination number \( c_{t} \), the number of B atoms in the nearest-neighbor shell, \( n_{1} \), is directly obtained by using the measured \( \alpha \) value following Eq. (1):

\[
n_{1} = m_{B} \cdot c_{t} \cdot (1 - \alpha)
\]

The \( n_{1} \) value should be approximated into a nearby integer. When the short-range-order parameter \( \alpha \) is negative, the integer is the roundup of \( n_{1} \), for B atoms tend to be enriched in the nearest neighbor shell due to the attractive interaction mode between the central A and neighboring B atoms. Alternative, when \( \alpha \) is positive, the integer is the rundown of \( n_{1} \).

(2) Calculation of next-neighbor atoms glue via Eq. (2)

By introducing into Eq. (2) the atomic ratios \( R_{A/M} \) and \( R_{B/M} \), the relationship between \( x \) and \( y \) is established. This relationship should also agree with the alloy composition, i.e., \( (n_{1} + y)/(1 + c_{t} \cdot x + y) = m_{B} \). For FCC, the \( (x, y) \) solution is then limited to \( 0 < x + y < 6 \). A unique set of \((x, y)\) solution is then possible, from which two sets of close-integers are obtained, so that the measured alloy composition falls between the two chemical units.

These procedures will be detailed in analyzing typical examples of popular binary copper alloys in the next.

Examples of binary Cu alloys

Cu-30Zn alloy. Though industrial Cu–Zn binary alloys cover a Zn range up to ~40 wt%, Cu-30Zn, or cartridge brass, is the most widely used grade. The \( \alpha \) parameters reaching a few tens of shells are accurately measured in a single crystal \( Cu_{80.5}Zn_{19.5}\) by elastic neutron diffraction using \(^{65}Cu\) isotope over a wide reciprocal range\(^{18}\). All through the paper the subscript number after the element indicates atomic fraction or percentage and the number before the element is weight percentage. The measured alloy composition \( Cu_{68.9}Zn_{31.1} \) just falls between the two chemical unit compositions. The corresponding mass percentage 64.04–69.99 wt% Cu agrees exactly with the most widely used cartridge brass C26000 (nominal 70Cu–30Zn, with composition ranges being 6.0–8.5 Al, 0.05 Fe, 0.05 Pb max, 0.20 Zn max, 0.10 Si max, 0.50 max other (total), bal Cu), which is commonly used as condensers, condenser plates and electrical springs\(^{20}\).

The corresponding chemical units are then \([Zn-Cu_{12}]_{Zn}Cu_{1}Zn_{2} = Cu_{12}Zn_{5} = Cu_{70.59}Zn_{29.41} = Cu-30.01Zn (wt.%)\) and \([Cu-Cu_{10Ni2}]_{Cu}Ni_{2} = Cu_{12Ni} = Cu_{75.00Ni_{25.00}} = Cu-17.57Ni\), where M is the averaged nearest-neighbor atom.

First, the number of Cu atoms \( n_{1} \) in the nearest-neighbor shell is calculated by \( \alpha \), following Eq. (3): \( n_{1} = 0.68 \)

9.12–(1 + 0.137) = 9.40, which is further approached into round integer 10 according to the negative interaction mode between Zn and Cu. Then the chemical unit becomes \([Zn-Cu_{10}Zn_{2}]_{Zn}Cu_{1}Zn_{2} = Cu_{12}Zn_{5} = Cu_{70.59}Zn_{29.41} = Cu-30.01Zn \) and the corresponding chemical unit becomes \([Zn-Cu_{10}Zn_{2}]_{Zn}Cu_{1}Zn_{2} = Cu_{12}Zn_{5} = Cu_{70.59}Zn_{29.41} = Cu-30.01Zn \).

Second, the relationship between \( x \) and \( y \) is calculated by introducing \( R_{Zn/M} \) and \( R_{Cu/Zn} \) into Eq. (2):

\[
R_{Zn/M} = 1.28/1.30 = 0.98. In combination with the alloy composition, \( m_{B} = 0.68 \), \( c_{t} = 12 \) and to chemical unit \([Zn-Cu_{12}]_{Zn}Cu_{1}Zn_{2} = Cu_{12}Zn_{5} = Cu_{70.59}Zn_{29.41} = Cu-30.01Zn \) and \([Cu-Cu_{10}Ni2]_{Cu}Ni_{2} = Cu_{12Ni} = Cu_{75.00Ni_{25.00}} = Cu-17.57Ni\). The alloy composition \( Cu_{68.9}Zn_{31.1} \) just falls between the two chemical unit compositions. The corresponding mass percentage 64.04–69.99 wt% Cu agrees exactly with the most widely used cartridge brass C26000 (nominal 70Cu–30Zn, with composition ranges specified being 68.5–71.5 Cu, 0.05 Fe max, 0.07 Pb max, 0.15 max other (total), bal Cu)\(^{20}\).

Cu-8Al aluminum bronze. In \( Cu_{61}Al_{12} \), \( \alpha \) is −0.17 is measured by X-ray diffuse scattering over an angular range from 8° to 60°, which leads to \( n_{1} = 11.93 \approx 12 \) and to chemical unit \([Al-Cu_{12}]_{Al}Cu_{1}Ar_{1} = Cu_{12}Al_{1} = Cu_{75.00}Al_{25.00} = Cu-7.83Al\) and \([Al-Cu_{12}]_{Al}Cu_{1}Ar_{1} = Cu_{12}Al_{1} = Cu_{75.00}Al_{25.00} = Cu-7.83Al\).

Cu-20Ni alloy. In \( Cu_{80}Ni_{20} \), the \( \alpha \) value, as measured by neutron diffuse scattering using \(^{65}Cu\) isotope, is +0.058\(^{20}\), which indicates the tendency of same element neighboring. The number of Cu atoms in the nearest-neighbor shell as calculated using \( \alpha \) is 10 and the corresponding chemical unit is \([Cu-Cu_{80}Ni_{20}]_{Cu}Ni_{20} \) using \( m_{B} = 0.25 \), \( c_{t} = 12 \) and to chemical unit \([Cu-Cu_{80}Ni_{20}]_{Cu}Ni_{20} = Cu_{12}Ni_{20} = Cu_{75.00}Ni_{25.00} = Cu-23.54Ni\). The range from 17.57 to 23.54 of Ni atoms explains the alloy C71000 (80Cu-20Ni, specified ranges being 19–23 Ni, 0.05 Pb max, 1.00 Fe, 1.00 Zn max, 1.00 Mn, 0.5 max other (total), bal Cu), which is commonly used as condensers, condenser plates and electrical springs\(^{20}\).
Table 1. Chemical units of typical binary solid-solution-based alloys with FCC structure, derived by combining the measured Cowley's parameter $\alpha_1$ from Refs. 17, 21–26 and the cluster-plus-glue-atom model. The calculated weight percent compositions are comparable to certain alloy specifications. The grades in the table are all ASTM standard UNS numbers, except NCr10 and NCu40-2-1 which are GB/T 5235 standard of China.

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**Cu-2Be beryllium bronze.** In Cu$_{90}$Be$_{10.9}$ alloy, $\alpha_1 = 0.077$, as measured by X-ray diffusion scattering, which is indicative of same-element neighboring. Within the framework of [Cu$_{11/12}$Be$_{1/12}$]$_n$, the number of Cu atoms $n_1$ is 10.79 as calculated from $\alpha_1$ and is approximated into integer 11. Using $M = Cu_{11/12}Be_{1/12}$ and $R_0 = 1.13 \, \text{Å}$, the close-integer $(x, y)$ solution are $(2, 1)$ and $(3, 0)$, leading to chemical units [Cu$_{Cu_{11/12}Be_{1/12}}$]$_n$ = Cu$_{11/12}Be_{1/12}$ = Cu$_{11/12}Be_{1/12}$ = Cu$_{11/12}Be_{1/12}$ = Cu$_{11/12}Be_{1/12}$. This range explains alloy C17200 (1.8 to 2.0 Be, 0.20 Ni + Co min, 0.6 Ni + Co + Fe max, 0.10 Pb max, 0.5 max other (total), bal Cu), which is the most popular Cu-Be alloy for showing high strength and elasticity.

It should be stressed that all the above alloy examples refer to the industrial grades the most popularly used in each alloy system. More examples are shown in Table 1, where most of the chemical units explain common industrial specifications. Exceptions are the formulas from alloys Ni$_{80}$Cu$_{20}$  and Ni$_{60}$Cu$_{40}$, which indicates that not all formulas correspond to good alloys but the reverse is true: popularly used industrial alloys always satisfy specific cluster formulas as this is required to reach solute homogenization states.

It should be reminded that short-range order parameters such as Cowley’s $\alpha$ parameter are sensitive to processing parameters, especially temperature. In principle, the short-range-order parameters should be measured in alloys annealed near the critical temperature where long-range order disappears completely and the atomic distribution tends to be stochastically stable. However, the critical temperature is usually unknown in a given alloy. Therefore, the measured $\alpha$ parameters should be more appropriately taken as the tendency along which atomic partition between the nearest-neighbor sites and the next-neighbor glue sites within the molecule-like chemical unit. This is why, for example, Cu-30Zn brass can also be linked to the cluster formula [Zn-Cu$_{11/12}$Zn$_{1/12}$]$_n$ as we previously proposed, which can be regarded as the extreme case when the negative interaction model between Zn and Cu is fully complied, though this formula is equivalent to [Zn-Cu$_{11/12}$Zn$_{1/12}$]$_n$Cu as calculated from the measured $\alpha_1$.

Finally it should be emphasized that the present work is a combination of our theoretical model with measurable parameters such as the well-established Cowley’s $\alpha$. This endeavor strengthens the capability of our model in interpreting alloy compositions. However, the approach developed in the present work cannot be readily extended to multi-component systems (here we confine ourselves to binary systems only), where both the theoretical description and the experimental measurement on short-range ordering are highly difficult. It is noted that during the last decade, research on short-range ordering is reviving, especially in high-entropy alloys.

The information provided by sophisticated measuring techniques and by computer simulation will surely enrich our knowledge on chemical short-range ordering. It should be our future goal to use the up-to-date data to deal with composition-complex alloys.

**Conclusions**

To summarize, after combining the measured short-range-order parameters with our cluster-plus-glue-atom model, we are able to construct molecule-like chemical units which interpret existing industrial alloy composition as specified by standard grades. This work answers the long-standing question on the composition origin of solid-solution-based industrial alloys, by tracing to the molecule-like chemical units implied in chemical short-range ordering in solid solutions.
Data availability

The authors declare that the main data supporting the findings of this study are contained within the paper. All other relevant data are available from the corresponding author upon reasonable request.

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Author contributions

Z.L. conducted the major calculations and analyzed the alloy data. D.D. and C.D. proposed the theory. S.Z., Q.W., and L.Z. checked the alloy interpretations. All authors participated in writing the paper.

Competing interests

The authors declare no competing interests.

Additional information

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