Composition formulas of Cu-Ni industrial alloy specifications

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It was recently known that the compositions of industrial alloy specifications generally satisfy simple composition formulas issued from short-range-order structural units in their basic solid solutions. In present work, Cu-Ni face-centered-cubic alloys were further addressed by introducing the cluster-plus-glue-atom model for the short-range-order structural descriptions. Composition formulas covering only the first twelve and the second six neighbor shells in the face-centered-cubic lattice are proposed, $[\text{Cu-Cu}_{12}](\text{Cu,Ni})_6$ for the Cu-rich alloys and $[\text{Ni-Ni}_{12}]\text{Cu}_6 \sim [\text{Ni-Ni}_{12}](\text{Cu}_5\text{Ni})$ for Monel alloy, the only Ni-rich alloy specification, where the square-bracketed part represents a cuboctahedral cluster. The alloy specification selection is also discussed in terms of valence electron numbers per unit formula. The present work confirms that well-established industrial alloys have simple composition rules that reflect the intrinsic short-range-order local structures in the solid solutions.

INTRODUCTION

Industrial alloys have specific composition as stated in standard specifications. It was recently pointed out by us that the compositions of the industrial alloys are actually the result of idealized short-range-order structural units as described by the cluster-plus-glue-atom model [1]. For instance, simple cluster formulas $[\text{Zn-Cu}_{12}]\text{Zn}_{1-6}$ explain most of Cu-Zn alloy specifications as listed in ASM (American Society for Metals) handbook, which exemplifies binary single-phase face-centered-cubic (FCC) solid solution alloys consisting of elements with a weakly negative enthalpy of mixing. In the present paper, industrial Cu-Ni alloys, composed of elements with a weakly positive enthalpy of mixing, $\Delta H_{\text{Cu-Ni}} = +2 \text{ kJ mol}^{-1}$, are further analyzed in detail using the same approach. Such a weakly positive enthalpy of mixing means that Cu and Ni are generally miscible but tend to segregate into Cu-Cu or Ni-Ni nearest neighbors.

Cu and Ni are completely miscible at high temperatures, forming a continuous FCC solid solution. However, in industrial specifications such as those listed in ASTM (American Society for Testing and Materials) standard, common alloy compositions are only a few. In the Cu-rich side, there

are for instance C70600 (10 wt.% Ni, corresponding to B10 in Chinese standard (GB)) and C71500 (~30 wt.% Ni, B30 in GB), both possessing superior comprehensive properties, such as corrosion resistance, thermal conductivity, and plasticity [2,3]. They are often used in ships and power station condensers. For the Ni-based alloys, the only specified alloy is Monel alloy containing about 70 wt.% Ni, well known for its excellent corrosion resistance in both oxidation and reduction environments [4,5].

The properties of single-phase Cu-Ni solid solution alloys show obvious dependence on composition, and it has been known for a long time that such dependence arises from different short-range-order structures [6,7]. Some property-composition relationships are summarized as follows (Fig. 1):

1) Mass density ρ [8] increases with increasing Ni content, and the maximum value is reached at about 70 wt.% Ni, the composition of Monel alloy.

2) Thermal potential S [9] increases with increasing Ni content, rapidly at the low Ni end. The rising tendency slows down above 10 wt.% Ni. Beyond 30 wt.% Ni, thermal potential is nearly stabilized.

3) Impact toughness a_K [9] behaves similarly as thermal potential, i.e., increasing rapidly till about 10 wt.% Ni and slowing down after 30 wt.% Ni.

4) Thermal conductivity coefficient λ [9] decreases rapidly with increasing Ni content at the low Ni end, and slows down at about 10 wt.% Ni, and it is stabilized after 30 wt.% Ni.

5) Cu is strongly passivated by Ni, and the corrosion rate increases with increasing Ni contents in $\text{HF}+\text{CuF}_2$ solutions [10], with the minimum corrosion rate showing up at 70 wt.% Ni.

In the above property-composition dependence at 10, 30, and 70 wt.% Ni compositions, the alloys show special comprehensive properties, and these compositions correspond respectively to the commonly-used C70600 (B10), C71500 (B30), and Monel400 industrial specifications.

Obviously, the choice of industrial specifications deter-

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Figure 1 Properties vs. Ni contents in Cu-Ni alloys. Curve (1) density [8]; (2) thermal potential [9]; (3) notch impact toughness [9]; (4) thermal conductivity coefficient [9]; (5) corrosion rate as measured by the breaking up time in 0.42 M CuF_2 + 0.5 M HF; (6) corrosion rate in 0.63 M CuF_2 + 0.38 M HF [10].

mines the properties, and the correlation between composition and short-range-order of the solid solutions is the key to understanding industrial alloy selection. However, the short-range-order description generally using Cowley short-range-order parameter α [11,12] is problematic, because it only tells the composition deviations on each neighboring shells from the average ones, but provides no information on the possible local structural units that may guide the selection of alloy compositions.

This problem has been addressed in the case of FCC solid solutions as exemplified by Cu-Zn alloys [1], using the cluster-plus-glue-atom model for stable solid solutions. Composition formulas out of this model, $[\text{Zn-Cu}_{12}] \text{Zn}_{1-6}$ and $[\text{Zn-Cu}_{12}](\text{Cu,Zn})_6$, indeed give satisfactory explanations of all known industrial alloy compositions of α brasses. The industrial Cu-Ni alloys were also dealt with very briefly to confirm that even in a binary system with a weakly positive enthalpy of mixing, the cluster based model applies equally well. In the following, this cluster-based short-range-order approach will first be summarized, and in connection with that the cluster-plus-glue-atom model for stable Cu-Ni solid solutions will be proposed in detail, considering the atomic interactions between Cu and Ni. Then the stability issue of the solid solutions in terms of the valence electron concentration will be discussed. Finally the industrial alloy compositions in ASTM standard will be explained using the cluster formulas.

CLUSTER-BASED SHORT-RANGE-ORDER STRUCTURAL MODEL OF FCC SOLID SOLUTION ALLOYS

At atomic level, the solute and solvent atoms in solid solutions tend to form short-range orders due to atomic interactions. The solute atoms tend to neighbor with solvent atoms when their mixing enthalpy is negative, such as the case of Cu-Zn; whereas, the solute atoms favor their own segregations separated from the solvent matrix when the mixing enthalpy is positive, which is the case for Cu and Ni. Short-range-order local structures should exhibit high stabilities, existing even in liquidus state, and their presence has been verified by many experiments, such as X ray and neutron diffuse scattering [13,14]. The long-range interaction is generally weak, in comparison with the strong short-range interactions occurring among the nearest and the next nearest neighbors [15].

However, the quantitative description of a short-range-order structure is always difficult, considering the involvement of disordering. The most common method used to deal with short-range-order structures was developed by Cowley [16], who termed short-range-order parameter α as $\alpha_i = 1 - P_A/X_A$, where P_A is the probability of finding A atoms at the i^{th} shell around a B atom in the real solid solution, and X_A is the mole fraction of A atoms. At $\alpha = 0$, A and B atoms are distributed in a completely disordered state; at

$\alpha < 0$, A-B type nearest neighbor is favored, corresponding to a negative enthalpy of mixing between A and B; at $\alpha > 0$, A-A and B-B bonds are favored, corresponding to a positive enthalpy of mixing between A and B.

Cu and Ni are both FCC metals and they have a weakly positive enthalpy of mixing, $\Delta H_{\text{Cu-Ni}} = +2 \text{ kJ mol}^{-1}$ [17]. It is revealed by diffraction experiment that there are always clusters of thirteen atoms in Cu-Ni binary alloy melts, which do not vary with alloy compositions [18]. In alloys $\text{Cu}_{90}\text{Ni}_{10}$, $\text{Cu}_{70}\text{Ni}_{30}$, $\text{Cu}_{50}\text{Ni}_{50}$, $\text{Ni}_{70}\text{Cu}_{30}$, and $\text{Ni}_{90}\text{Cu}_{10}$, the first-neighbor short-range-order parameters α_{110} are all positive [18], meaning that Cu-Cu and Ni-Ni nearest neighbors are abundant and the interaction between Cu and Ni is weaker than those between Cu-Cu and Ni-Ni. For instance, as measured by diffuse neutron scattering [19], the 1st and 2nd nearest-neighbor Cowley short-range-order parameters in the $\text{Cu}_{80}\text{Ni}_{20}$ alloy are respectively $\alpha_{110} = +0.058$ and $\alpha_{200} = -0.058$. They are relatively weak as compared with those in Cu-Zn alloys, indicating that more disordering is present here.

In FCC lattice, the first nearest neighbors construct a coordination polyhedral cluster of the cuboctahedron type with coordination number of twelve, and the second nearest neighbors form an octahedron shell with coordination number of six (Fig. 2). In accordance with the above short-range-order tendency, the idealized short-range-order structure in Cu-rich Cu-Ni alloys should be like this:

1) The cuboctahedron should be centered by Cu and formed with twelve Cu atoms, $[\text{Cu-Cu}_{12}]$, for the positive enthalpy of mixing between Cu and Ni that favors the segregation of Cu atoms separated from Ni. These 1st nearest neighbors are located at the $\{a/2, a/2, 0\}$ positions with re-

Figure 2 First and second neighbors centering a Cu atom in an FCC Cu-rich Cu-Ni solid solution. The first nearest neighbors located at the $\{a/2, a/2, 0\}$ position form a $[\text{Cu-Cu}_{12}]$ cuboctahedral cluster where a is the lattice constant. The second neighbor positions enclose an octahedron mix-occupied by Cu and Ni, located at $\{a/2, 0, 0\}$.

spect to the central atom Cu.

2) The second nearest neighbors at the six octahedral vertices at the $\{a/2, 0, 0\}$ positions are mix-occupied by Cu and Ni for the weaker atomic interaction than that between the first nearest neighbors, thus favoring mixed-occupancy by both Cu and Ni.

This short-range-order picture shows that the structure unit formed by the first and second neighboring atoms is representative of the overall structure of the solid solution alloy, primarily in chemical composition but more importantly in terms of average chemical short-range-order. By building a model describing this short-range-order unit, the description of the whole alloy can be realized.

This short-range-order unit is then formulated as $[\text{Cu-Cu}_{12}](\text{Cu,Ni})_6$, which means that the Cu-rich Cu-Ni stable solid solutions, ideally satisfying local atomic interactions, only adapt a few compositions formulated as $[\text{Cu-Cu}_{12}]\text{Cu}_{6-N}\text{Ni}_N = \text{Cu}_{19-N}\text{Ni}_N$, where N is an integer ranging from 1 to 6. This model is quite the same as in the Zn-lean Cu-Zn alloys formulated as $[\text{Zn-Cu}_{12}](\text{Cu,Zn})_6$, whose mixing enthalpies are quite weak in comparison with that of the equi-mole alloy, with the only difference lying in the $[\text{Zn-Cu}_{12}]$ dissimilar atomic cluster.

The cluster-plus-glue-atom model is originally developed for interpreting composition rules of quasicrystals and amorphous alloys [20,21]. In a general sense, any structure can be divided into two parts, the first-neighbor cluster and the outer glue atoms located outside of the clusters, and can be described with a cluster formula $[\text{cluster}](\text{glue atom})_x$. For ideal metallic glasses with large glass forming abilities, the cluster formulas obey a simple rule: $[\text{isolated clusters}](\text{glue atom})_{1 \text{ or } 3}$, with a constant total valence electron number per unit formula being close to 24, independent of the alloy compositions. The cluster formula can be regarded as the molecular formula of the amorphous alloys [20].

In the present case, a short-range-order unit formulated as $[\text{isolated cubic octahedral clusters}](\text{glue atoms located at next nearest neighbors})_6$ can also be regarded as the molecular formula for an idealized Cu-rich Cu-Ni solid solution. The clusters are not allowed to share between the first and the second nearest neighbors to avoid the generation of a longer-range-order that eventually breaks the disorder solid solution structure.

In a similar manner, in the Ni-rich side, there should exist a short-range-order local structure described as $[\text{Ni-Ni}_{12}](\text{Ni,Cu})_6$.

For a real solid solution alloy, as the measured short-range-order parameters indicated, disordering is present at any sites, including the 1st and the 2nd nearest neighbors which are always mix-occupied by both Cu and Ni. For instance, Warren-Cowley short-range-order parameters $\alpha_{110} = +0.058$ (for the first neighboring shell), and $\alpha_{200} = -0.058$

(for the second neighboring shell) were obtained using diffuse neutron scattering on single-phase FCC alloy $\text{Cu}_{80}\text{Ni}_{20}$ [19]. The composition of the first and second shells with respect to the Cu center is calculated to be $\text{Cu}_{9.74}\text{Ni}_{2.26}$ and $\text{Cu}_{4.73}\text{Ni}_{1.27}$, which gives the overall chemical composition within the second shell region of $\text{Cu}-\text{Cu}_{9.74}\text{Ni}_{2.26}-\text{Cu}_{4.73}\text{Ni}_{1.27} = \text{Cu}_{15.47}\text{Ni}_{3.53} = \text{Cu}_{81.42}\text{Ni}_{18.58}$, which is very close to the alloy composition of $\text{Cu}_{80}\text{Ni}_{20}$. Due to the quite weak α parameters, this formula is not much different from the average composition, and in practice, a composition formula enclosed within the first two neighboring shells can always be constructed for any alloy using the average composition, such as $\text{Cu}_{0.8}\text{Ni}_{0.2}-\text{Cu}_{9.6}\text{Ni}_{2.4}-\text{Cu}_{4.8}\text{Ni}_{1.2} = \text{Cu}_{15.2}\text{Ni}_{3.8} = \text{Cu}_{80}\text{Ni}_{20}$ in this case.

In order to match the atomic interaction between Cu and Ni atoms, the Ni atoms in the first shell should be moved to the second shell, and Cu atoms in the second shell vice versa. The final formula covering the 1st and 2nd nearest neighbors is then $[\text{Cu}-\text{Cu}_{12}](\text{Cu}_{2.5}\text{Ni}_{3.5})$ for the short-range-order formula and $[\text{Cu}-\text{Cu}_{12}](\text{Cu}_{2.2}\text{Ni}_{3.8})$ for the average composition formula, which is quite close to an ideal cluster formula $[\text{Cu}-\text{Cu}_{12}](\text{Cu}_2\text{Ni}_4)$. This chemical composition, $\text{Cu}_{15}\text{Ni}_4 = 80.2\text{Cu}-19.8\text{Ni}$ (wt.%), coincides exactly with that of the C71000 alloy, 80Cu-20Ni (wt.%).

From the aforementioned composition analysis, it can be seen that a cluster formula describes an ideal atomic configuration covering only the center and its 1st and 2nd neighborhoods. For a real alloy, as the measured short-range-order parameters indicated, these nearest neighboring sites are mix-occupied and the disordering extends outwards into outer shells as well. The formulated structural unit is just an idealization of the real disordered short-range-order states, and can be obtained by exchanging the atoms between the first two neighboring shells. However, as far as the composition is concerned, the atoms enclosed within the first two neighboring shells well represent the overall composition as indicated by the analyzed example. Therefore the local unit gives a satisfactory composition explanation for the stable solid solutions, even quite disordered.

Next, the stability issue of the local units will be dealt with. It will be seen that a stable solid solution adopts the formulated composition only when its electronic structure is also favorable, as evidenced by specific valence electron rules.

VALENCE ELECTRON RULES IN THE CLUSTER FORMULAS FOR STABLE Cu-Ni SOLID SOLUTIONS

It is generally believed that solid solutions are electron phases satisfying specific valence electron rules, which was

first advocated by Hume-Rothery [22]. According to Xie *et al.* [23], the valence electron contributions of Cu and Ni are respectively 1 and 0 in Cu-rich alloys containing less than 40 at.% Ni. This is because the s-d electron state in Ni and Cu atoms is completely merged into a uniform band structure. The Ni 3d electron state is filled and the electrons of unified 4s orbital only come from Cu 4s¹. Thus, the Cu-rich composition formulas $[\text{Cu}-\text{Cu}_{12}](\text{Cu},\text{Ni})_6 = [\text{Cu}-\text{Cu}_{12}]\text{Cu}_{6-N}\text{Ni}_N = \text{Cu}_{19-N}\text{Ni}_N$ give integer electron number per unit cluster formula, e/u , ranging from 13 ($N=6$) to 18 ($N=1$). Although the meaning of these electron numbers is still not fully explored, they can be tentatively explained with reference to the spherical jellium model for clusters [24–26], which states that the valence electrons of stable clusters such as icosahedra Al_{12}X correspond to stable molecular orbital configurations of $1s1p1d2s1f2p$, etc., with the stable clusters possessing special valence electron numbers, 40 for the icosahedra corresponding to fully filled electronic orbital structure $1s^21p^61d^{10}2s^21f^42p^6$. The stability of a cluster is issued from the electron shell filled by the valence electrons of the cluster. In the same way, the electron number e/u of one cluster formula might also follow certain stable electron orbital structure, and the electron numbers of 13 up to 18 can well correspond to outer electron orbital configurations of $1s^21p^61d^{5-10}$. The most popular specification in the Cu-rich side is 70Cu-30Ni, which can be explained with cluster formula $[\text{Cu}-\text{Cu}_{12}]\text{Ni}_6$ with $e/u = 13$ and a relatively stable electron orbital configuration $s^2p^6d^5$, where the d orbital is half-filled.

In the alloys containing more than 40 at.% Ni, the valence electron contribution from Ni is composition dependent. The valence electron structure of pure Ni is supposed to be $3d^{9.44}4s^{0.6}$ [23], where the 3d orbital is only partially occupied and the extra 0.6 electron goes to the 4s orbital. This makes the electron contribution from pure Ni to be 0.6. With Cu atom being added into the Ni base, the Cu 4s¹ electron preferentially fills the Ni unfilled 3d orbital, while at the same time, the Ni 4s^{0.6} electrons are equally transferred to the unfilled Ni 3d orbital. The valence electron number of Ni is then equal to 0.6 minus Cu 4s¹, the latter value being equal to the atomic fraction of Cu. Assuming the atomic fraction of Ni to be β , the average valence electron number per Ni atom in alloy $\text{Cu}_{1-\beta}\text{Ni}_\beta$ is $0.6-(1-\beta) = \beta-0.4$, and the average valence electron number per atom is $(e/a)_{\text{Cu}_{1-\beta}\text{Ni}_\beta} = (1-\beta) \times 1 + \beta \times (\beta-0.4) = \beta^2 - 1.4\beta + 1$, with the minimum value being obtained at $\beta = 0.7$, corresponding exactly to Monel alloy. [23] This means that Monel alloy has the lowest electron number in this binary system, with its structural stability being enforced by the coupling between Cu's s¹ and Ni's s-d electrons. The transfer of s electrons to the unfilled Ni d orbital, on one hand, decreases the energy level of the s electrons and hence makes the electron releas-

ing difficult, and on the other hand, the increasingly filled d orbital reduces the capacity of electron absorption. For this reason the Monel alloy has better corrosion resistance than Cu in the oxidizing environment (releasing electrons) and Ni in the reducing environment (absorbing electrons). The recent work by Mizutani *et al.* [27] confirmed that, though being lack of direct treatment of Cu-Ni alloys, the valence electron number of Ni was zero in Ni-lean systems, whereas in Ni-rich alloys it was close to 0.5. These conclusions are similar to those by Xie *et al.* [23] as used in our discussion. In fact, in Ni-rich alloys, the valence electron number of Ni is 0.6 as given by Xie *et al.* [23], and with increasing Cu contents, the value decreases, such as $(e/a)_{\text{Ni}} = 0.5$ in $\text{Cu}_{10}\text{Ni}_{90}$, and $(e/a)_{\text{Ni}} = 0.3$ in $\text{Cu}_{30}\text{Ni}_{70}$.

The ideal short-range-order structural model for the Cu-Ni stable solid solution alloys, characteristic for a weakly positive enthalpy of mixing of Cu-Ni, is summarized as follows:

1) The first nearest neighbors are occupied by the same kind of atoms as the central one, forming cuboctahedral clusters expressed as $[\text{Cu-Cu}_{12}]$ or $[\text{Ni-Ni}_{12}]$;

2) The second nearest neighbors are mix-occupied by Ni and Cu glue atoms, located between the clusters, forming a local unit covering the 1st and the 2nd neighbors only, expressed by cluster formulas $[\text{Cu-Cu}_{12}](\text{Cu,Ni})_6$ and $[\text{Ni-Ni}_{12}](\text{Cu,Ni})_6$;

3) The cluster formulas, addressing the stable solid solution configurations, satisfy specific electron number rules per unit cluster formula.

The proposed cluster formulas indeed explain the compositions of all the Cu-Ni alloy specifications, as shown in Table 1.

COMPOSITION INTERPRETATION OF INDUSTRIAL Cu-Ni ALLOY SPECIFICATIONS USING CLUSTER FORMULAS

In the following, all the alloy specifications were analyzed in terms of the cluster-plus-glue-atom model for stable solid solutions. For each composition, firstly its average composition formula within the first two shells was given, ignoring any short-range-order (i.e., the atomic distribution is treated as random). Then a local structural unit and its corresponding composition formula was obtained by exchanging the atoms between the 1st and 2nd neighboring shells to satisfy the ideal atomic interactions. Finally the composition of the closest integer cluster formula was obtained and was compared with that of the specification. The valence electron number e/u was also pointed out.

1) C70400 (95Cu-5Ni, wt.%) has an averaged composition formula within the first two shells, $[\text{Cu}_{0.95}\text{Ni}_{0.05} - \text{Cu}_{11.35}\text{Ni}_{0.65}]\text{Cu}_{5.68}\text{Ni}_{0.32}$. After exchanging the atoms between the 1st and 2nd neighboring shells, the local structural unit becomes $[\text{Cu-Cu}_{12}]\text{Cu}_{4.95}\text{Ni}_{1.05}$, being extremely close to the integer cluster formula $[\text{Cu-Cu}_{12}](\text{Cu}_5\text{Ni}_1) = \text{Cu}_{18}\text{Ni}_1 = \text{Cu}_{94.7}\text{Ni}_{5.3}(\text{at.}\%) = \text{Cu}_{95.1}\text{Ni}_{4.9}(\text{wt.}\%)$. The valence electron number of this cluster formula $(e/u)_{[\text{Cu-Cu}_{12}]\text{Cu}_5\text{Ni}_1} = 18 \times 1 + 1 \times 0 = 18$, which can be interpreted by the fully occupied stable electron orbital configuration $s^2p^6d^{10}$.

2) C70600 (90Cu-10Ni, wt.%) has a composition formula covering the 1st and 2nd neighborhoods of $[\text{Cu}_{0.89}\text{Ni}_{0.11} - \text{Cu}_{10.71}\text{Ni}_{1.29}]\text{Cu}_{5.36}\text{Ni}_{0.64}$. The composition formula after exchanging atoms of the first and second neighboring shells is $[\text{Cu-Cu}_{12}]\text{Cu}_{3.96}\text{Ni}_{2.04}$, being close to the integer cluster formula $[\text{Cu-Cu}_{12}]\text{Cu}_4\text{Ni}_2 = \text{Cu}_{17}\text{Ni}_2 = \text{Cu}_{89.5}\text{Ni}_{10.5}(\text{at.}\%) =$

Table 1 Cu-Ni industrial alloys as listed in ASTM standard specifications and their corresponding cluster formulas

ASTM specification, wt.%	Composition range, wt.%	Cluster formula, wt.% Cu	e/u
C70400, 95Cu-5Ni	4.8 to 6.2 Ni+Co, 0.05 Pb max, 1.3 to 1.7 Fe, 1.0 Zn max, 0.3 to 0.8 Mn, 0.02 S, 0.02 P, bal Cu	$[\text{Cu-Cu}_{12}](\text{Cu}_5\text{Ni}_1)$, 95.1 wt.% Cu	18
C70600, 90Cu-10Ni	9.0 to 11 Ni+Co, 0.05 Pb max, 1.0 to 1.8 Fe, 1.0 Zn max, 1.0 Mn, bal Cu	$[\text{Cu-Cu}_{12}](\text{Cu}_4\text{Ni}_2)$, 90.2 wt.% Cu	17
C70900 85Cu-15Ni, (inactive)	13.5 to 16.5 Ni, 0.05 Pb max, 0.6 Fe, 1.0 Zn max, 0.6 Mn, bal Cu	$[\text{Cu-Cu}_{12}](\text{Cu}_3\text{Ni}_3)$, 85.2 wt.% Cu	16
C71000, 80Cu-20Ni	19.0 to 23.0 Ni+Co, 0.05 Pb max, 0.5 to 1.0 Fe, 1.0 Zn max, 1.0 Mn, 0.02 S, 0.02 P, bal Cu	$[\text{Cu-Cu}_{12}](\text{Cu}_2\text{Ni}_4)$, 80.2 wt.% Cu	15
C 71300, 75Cu-25Ni	23.5 to 26.5 Cu, 0.05 Pb max, 0.2 Fe max, 1.0 Zn, 1.0 Mn, bal Cu	$[\text{Cu-Cu}_{12}](\text{Cu}_1\text{Ni}_5)$, 75.2 wt.% Cu	14
C 71500, 70Cu-30Ni	39.0 to 33.0 Ni+Co, 0.05 Pb max, 0.4 to 1.0 Fe, 1.0 Zn max, 1.0 Mn, bal Cu	$[\text{Cu-Cu}_{12}]\text{Ni}_6$, 70.1 wt.% Cu	13
Monel400, 30Cu-70Ni	63 to 70 Ni, 0.3 C, 0.5 Si, 2.0 Mn, 2.5 Fe, 0.024 S, bal Cu	$[\text{Ni-Ni}_{12}](\text{Cu}_5\text{Ni}) \sim [\text{Ni-Ni}_{12}](\text{Cu}_6)$, 27.9~33.3 wt.% Cu (70.1~66.7 wt.% Ni)	~10

90.2Cu-9.8 Ni (wt.%), with $(e/u)_{[\text{Cu-Cu}_{12}]\text{Cu}_4\text{Ni}_2} = 17$. Its electron orbital configuration would be $s^2p^6d^9$.

3) C70900 (85Cu-15Ni, wt.%) has a composition formula covering the first two nearest neighbors of $[\text{Cu}_{0.84}\text{Ni}_{0.16}\text{Cu}_{10.08}\text{Ni}_{1.92}]\text{Cu}_{5.04}\text{Ni}_{0.96}$, which leads to $[\text{Cu-Cu}_{12}]\text{Cu}_{2.96}\text{Ni}_{3.04}$ after atomic exchanges. This formula is close to the integer formula $[\text{Cu-Cu}_{12}](\text{Cu}_3\text{Ni}_3) = \text{Cu}_{16}\text{Ni}_3 = \text{Cu}_{84.2}\text{Ni}_{15.8}$ (at.%) = 85.2Cu-14.8Ni (wt.%), with $(e/u)_{[\text{Cu-Cu}_{12}](\text{Cu}_3\text{Ni}_3)} = 16$, whose possible electronic configuration would be $s^2p^6d^8$.

4) C71000 (80Cu-20Ni, wt.%) has an average local unit of $[\text{Cu}_{0.79}\text{Ni}_{0.21}\text{Cu}_{9.44}\text{Ni}_{2.56}]\text{Cu}_{4.72}\text{Ni}_{1.28}$, which turns to $[\text{Cu-Cu}_{12}]\text{Cu}_{1.95}\text{Ni}_{4.05}$ after exchanging atoms. This formula is close to the integer cluster formula $[\text{Cu-Cu}_{12}]\text{Cu}_2\text{Ni}_4 = \text{Cu}_{15}\text{Ni}_4 = \text{Cu}_{78.9}\text{Ni}_{21.1}$ (at.%) = 80.2Cu-19.8Ni (wt.%), with $(e/u)_{[\text{Cu-Cu}_{12}](\text{Cu}_2\text{Ni}_4)} = 15$, whose possible electronic configuration would be $s^2p^6d^7$.

5) C71300 (75Cu-25Ni, wt.%) has a local structural unit of $[\text{Cu}_{0.73}\text{Ni}_{0.27}\text{Cu}_{8.82}\text{Ni}_{3.18}]\text{Cu}_{4.41}\text{Ni}_{1.59}$. After exchanging atoms, the formula becomes $[\text{Cu-Cu}_{12}]\text{Cu}_{0.96}\text{Ni}_{5.04}$, being close to the integer cluster formula $[\text{Cu-Cu}_{12}](\text{Cu}_5\text{Ni}_5) = \text{Cu}_{14}\text{Ni}_5 = \text{Cu}_{73.7}\text{Ni}_{26.3}$ (at.%) = 75.2Cu-24.8Ni (wt.%), with $(e/u)_{[\text{Cu-Cu}_{12}](\text{Cu}_5\text{Ni}_5)} = 14$, whose possible electron orbital configuration would be $s^2p^6d^6$.

6) C71500 (70Cu-30Ni, wt.%), being the most popular owing to its thermal potential, notch impact toughness, thermal conductivity, and compositional insensitiveness, has a local unit formulated as $[\text{Cu}_{0.68}\text{Ni}_{0.32}\text{Cu}_{8.20}\text{Ni}_{3.80}]\text{Cu}_{4.10}\text{Ni}_{1.90}$. After exchanging the atoms, the obtained composition formula $[\text{Cu-Cu}_{11.98}]\text{Ni}_{6.02}$ is close to the integer cluster formula $[\text{Cu-Cu}_{12}]\text{Ni}_6 = \text{Cu}_{68.4}\text{Ni}_{31.6}$ (at.%) = 70.1Cu-29.9Ni (wt.%), with $(e/u)_{[\text{Cu-Cu}_{12}]\text{Ni}_6} = 13$. Its electron orbital configuration might be $s^2p^6d^5$.

7) Monel400, being the only industrial specification in the Ni-rich side and known for its good corrosion resistance, has the following composition requirements: Ni(Co) ≥ 63.0 , C ≤ 0.3 , S ≤ 0.024 , Cu28.0~34.0, Mn ≤ 2.0 , Fe ≤ 2.50 , Si ≤ 0.5 , all in wt.%. Using the average composition 31.0 wt.% Cu, the alloy composition is adjusted back to a pseudo binary composition 69(Ni,Co,Fe,Mn)-31Cu (wt.%) = $\text{Ni}_{70.7}\text{Cu}_{29.3}$, the composition known for the best corrosion resistance as shown in Fig. 1. This alloy also has the largest mass density [8] and the least valence electron concentration [23].

The average composition of Monel400, $\text{Ni}_{70.7}\text{Cu}_{29.3}$, is formulated as $[\text{Ni-Ni}_{12}](\text{Ni}_{0.43}\text{Cu}_{5.5})$ after constructing the local unit covering the first and second neighboring shells and then exchanging the atoms. Using the valence electron contribution of Ni of $(e/a)_{\text{Ni}} = \beta - 0.4 = 0.307$ [23], the total valence number per unit formula e/u is equal to 9.7, which is quite close to the filled $3d^{10}$ state. This is also the stable electron orbital structure with the least electron number for 3d transition metals. In this sense, the total number

of atoms per unit cluster formula cannot be less than 19, as decreasing the formula size would further decrease e/u below 10. Since the maximum number of atoms of cluster formulas for FCC lattice is 19 (twelve first neighbors, six second neighbors, plus one central atom), the cluster formula of Monel alloy can only take 19 atoms.

Supposing the least valence number of $e/u = 10$ for Monel alloy, the electron contribution of Ni needs to be modified accordingly. The integer cluster formulas, which are the nearest to the composition of Monel alloy, are $[\text{Ni-Ni}_{12}]\text{Cu}_6 = \text{Ni}_{13}\text{Cu}_6 = \text{Ni}_{68.4}\text{Cu}_{31.6}$ and $[\text{Ni-Ni}_{12}]\text{Cu}_5\text{Ni} = \text{Ni}_{14}\text{Cu}_5 = \text{Ni}_{73.7}\text{Cu}_{26.3}$. For the former formula, $e/u = 10 = 13 \times (e/a)_{\text{Ni}} + 6 \times 1$, which gives $(e/a)_{\text{Ni}} = 0.308 = \beta - 0.376$. For the latter one, $\beta = 0.737$, $e/u = 10 = 14 \times (e/a)_{\text{Ni}} + 5 \times 1$, $(e/a)_{\text{Ni}} = 0.357 = \beta - 0.380$. Then, for alloys near the Monel specification composition, $(e/a)_{\text{Ni}} = \beta - 0.378$. Thus the compositions between the two cluster formulas basically meet the requirements of $e/u = 10$, implying filled d^{10} orbital. The composition region of Monel alloy is then $\text{Ni}_{68.4}\text{Cu}_{31.6} \sim \text{Ni}_{73.7}\text{Cu}_{26.3}$ (66.7Ni-33.3Cu ~ 72.1Ni-27.9Cu, wt.%), with the average one being $\text{Ni}_{71.0}\text{Cu}_{29.0}$ (69.4Ni-30.6Cu, wt.%), which fall close to both the composition range of 28 ~ 34 wt.% Cu and the representative composition of Monel400, $\text{Ni}_{70.7}\text{Cu}_{29.3} = 69(\text{Ni}+\text{Co}+\text{Mn}+\text{Fe})\text{-}31\text{Cu}$ (wt.%).

For the Ni-rich side, the general cluster formulas $[\text{Ni-Ni}_{12}](\text{Cu}_{6-N}\text{Ni}_N)$ have their e/u values of 9.96, 10.00, 10.14, 10.39, 10.75, 11.21, 11.78 for $N = 0$ to 6. As already discussed, the first two e/u values, being close to 10, correspond to the Monel compositions; however, there are no other integer e/u values, which possibly explains why there is no more industrial specifications apart from Monel alloy in the Ni-rich side. From the above analysis, it can be seen that for a binary alloy system characterized by a weakly positive enthalpy of mixing and hence by a weak short-range-order, such as Cu-Ni, their alloy specification selection always falls on the integer forms of the cluster formulas containing 19 atoms. In the Cu-rich side, the general formula is $[\text{Cu-Cu}_{12}](\text{Cu}_6\text{Ni}_6)$. With the Ni number varying from 1 to 6, the corresponding atomic percentages of Ni are respectively 5.26, 10.53, 15.79, 21.05, 26.31 and 31.58, and the corresponding weight percentages are respectively 4.88, 9.80, 14.76, 19.76, 24.80, and 29.89 wt.% Ni, which explains perfectly the industrial alloy specifications C70400 (B5, 95Cu-5Ni), C70600 (B10, 90Cu-10Ni), C70900 (B15, 85Cu-15Ni), C71000 (B20, 80Cu-20Ni), C71300 (B25, 75Cu-25Ni), and C71500 (B30, 70Cu-30Ni). Their valence electron numbers per unit cluster formula e/u are all integers, ranging from 18 to 13. In the Ni-rich side, there is only one industrial specification, so-called Monel alloy (for instance, Monel 400), whose composition range is confined by two cluster formulas $[\text{Ni-Ni}_{12}]\text{Cu}_6$ and $[\text{Ni-Ni}_{12}]\text{Cu}_5\text{Ni}$ with their e/u being close to 10. The corresponding com-

position range is $\text{Ni}_{68.4}\text{Cu}_{31.6} \sim \text{Ni}_{73.7}\text{Cu}_{26.3}$ (at.%) = 66.7Ni-33.3Cu $\sim$ 72.1Ni-27.9Cu (wt.%).

This work confirms that behind the empirical industrial specifications, there are simple composition rules reflecting the short-range-order local structures of solid solutions with certain stabilities. The cluster formula approach might serve an important practical tool to guide the alloy interpretation and eventually design of new alloy.

CONCLUSIONS

By using the cluster-plus-glue-atom model for the description of chemical short-range-order in stable solid solution, the composition rules of FCC Cu-Ni industrial alloy specifications are fully analyzed. The seemingly continuous Cu-Ni solid solution, in fact, possesses special short-range-order local structural units that arise from atomic interactions between solute and solvent atoms. The corresponding cluster formulas are composed of a first-neighbor cuboctahedral cluster $[\text{Cu-Cu}_{12}]$ (Cu-rich side) or $[\text{Ni-Ni}_{12}]$ (Ni-rich), plus six glue atoms mix-occupied by Cu and Ni atoms in the second neighborhood. The industrial Cu-based Cu-Ni alloys are explained with cluster formulas $[\text{Cu-Cu}_{12}]$ $(\text{Cu,Ni})_6$ with total valence number per unit formula with e/u ranging from 13 to 18, and the only Ni-rich specification Monel alloy is explained by cluster formulas $[\text{Ni-Ni}_{12}]$ Cu_6 and $[\text{Ni-Ni}_{12}](\text{Cu}_5\text{Ni})$ with their e/u being close to 10. This work, together with our previously studies in a variety of alloy systems [28–30], shows that simple composition formulas reflecting the short-range-order structural characteristics of solid solution alloys lie behind the complex industrial alloy specifications.

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Author contributions Hong H collected the composition and property data and helped with composition interpretation. Wang Q analyzed the

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Conflict of interest The authors declare that they have no conflict of interest.

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中文摘要 工业合金牌号成分一般满足简单的成分式, 我们认为该成分式源自其固溶体中的化学近程有序. 本文通过引入用于描述近程有序结构的团簇与连接原子模型, 进一步详细阐述面心立方结构Cu-Ni合金的工业牌号成分解析. 我们提出的团簇成分式只涉及第一近邻的十二配位立方八面体团簇(方括号部分)和第二近邻的八面体(连接原子部分), 理想满足元素间相互作用: 富铜端的白铜对应于 $[\text{Cu-Cu}_{12}](\text{Cu}, \text{Ni})_6$ 团簇式, 在富镍端只有蒙乃尔一种工业牌号合金, 用团簇式 $[\text{Ni-Ni}_{12}]\text{Cu}_6 \sim [\text{Ni-Ni}_{12}](\text{Cu}_5\text{Ni})$ 来解析. 我们还指出, 团簇式对应着特定的价电子总数规律. 本工作进一步证实, 工业合金牌号背后隐藏着体现固溶体近程有序本质的成分规律.