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Atomic ordering in Cu-Al-Ni: Point approximation and Monte Carlo simulations

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ABSTRACT

Long range ordering in the bcc phase of the Cu-Al-Ni alloy is modelled through the analytical Bragg-Williams approximation and by means of numerical Monte Carlo simulations. The interchange energies that govern the ordering reactions are determined by fits to experimental ordering temperatures. A satisfactory agreement with the experimental data is obtained within both models, using slightly different sets of interchange energies. It is found that ordering in first neighbours is driven by the Ni-Al interactions, whereas the ordering in next nearest neighbours occurs by a reordering of Cu-Al pairs. Monte Carlo simulations enable a reinterpretation of the experimentally observed ordering reactions. Further details of the ordering process, such as the existence of tricritical points as the Ni content is reduced, and the evolution of sublattice occupancies as the ordering proceeds are also discussed: the site occupation probabilities at low temperatures agree with the experimental values.

1. Introduction

Cu-Al-Ni, as other Cu-Al based alloys, has shape memory properties associated with a martensitic transformation. This transformation takes place from a high temperature β phase, with bcc structure, to a low temperature martensitic phase. At temperatures above the martensitic transformation, the β phase can be in different states of long range order (*lro*). For instance, in the range of experimentally investigated compositions, the Cu-Al-Ni alloy undergoes a two stages ordering process: first from a disordered (or short range ordered) bcc structure, called *A*2, to a *B*2 structure ordered in first neighbours, and then to a $L2_1$ phase with order in first and second neighbours [1,2]. The type and degree of order in the β phase modifies the properties associated with the martensitic transformation [3]; thus, the understanding of the ordering processes is of interest from both basic and applied points of view.

The description of the different superstructures can be made with the help of Fig. 1, which shows the general bcc lattice and the four interpenetrating fcc sublattices (I to IV) in which it is subdivided. In the *A*2 structure all the sites have the same probability of being occupied by any of the atomic species, $p_A^I = p_A^{II} = p_A^{III} = p_A^{IV}$ (*A* = Cu, Al, Ni). In the *B*2 structure (ClCs type), the occupation of the center of the cubes differs from that of the corners, $p_A^I = p_A^{II} \neq p_A^{III} = p_A^{IV}$. In the $L2_1$ configuration (Heusler type structure), there is an additional ordering in second neighbours, $p_A^I = p_A^{II} \neq p_A^{III} \neq p_A^{IV} \neq p_A^I$.

The most comprehensive experimental assessment of critical order-disorder temperatures in Cu-Al-Ni is the work by Recarte et al. [4]. These authors measured critical order-disorder temperatures along three lines of compositions with fixed 13.2 wt% Al, 13.7 wt% Al, and 4 wt% Ni, respectively. For all the investigated samples, two ordering reactions were observed, that the authors identified with A2 → B2 and B2 → $L2_1$ ordering processes.

From the theoretical side, there have been three previous attempts to model the temperatures of atomic long range ordering in Cu-Al-Ni [4–6]. These studies were based on mean field approximations. In Ref. [4], expressions derived from the point (Bragg-Williams, BW) approximation [7] were used. It was assumed that the chemical interactions between *AB* pairs were determined by constant (composition and temperature independent) pair interchange energies in first and second neighbours, $W_{AB}^{(k)}$ (*AB* = CuAl, CuNi or AlNi, *k* = 1, 2 for first and second neighbours, respectively). The values for $W_{\mathrm{CuAl}}^{(1,2)}$ were taken from [8], $W_{\mathrm{AlNi}}^{(1,2)}$ from [9], and it was assumed that $W_{\mathrm{CuNi}}^{(1,2)} = 0$. In Ref. [5], the BW model, as modified by Inden [7] was used to model the *A*2 + *B*2 and *B*2 + *B*2 coexistence regions observed experimentally at low temperatures. The interchange energies in first and second neighbours for Cu-Al and Ni-Al were obtained from the (extrapolated) order-disorder temperatures in the corresponding binary alloys, whereas for Cu-Ni pairs they were assumed to be zero. More recently, a model based

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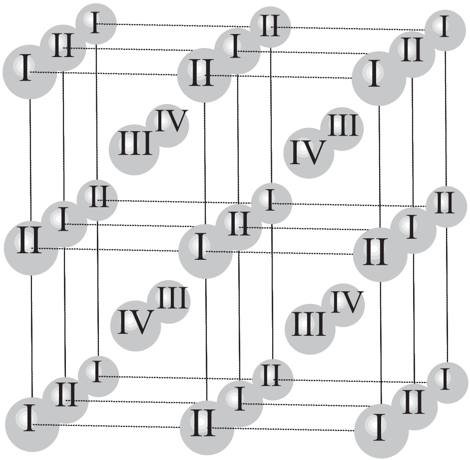

Fig. 1. The bcc lattice and the four interpenetrating sublattices in which it is subdivided.

in the irregular tetrahedron approximation of the cluster variation method (IT-CVM) [10] was employed by Pelegrina [6] to determine a new set of interchange energies from a fit to the experimental critical temperatures.

Despite these previous theoretical efforts, there are some issues that still remain unclear. One of them is the fact that, in all the range of compositions experimentally studied, Cu-Al-Ni displays a two-steps ordering process even for very low Ni contents (2.73 at.%, [4]). This contrasts with the behaviour of other Cu-Al-X ternary alloys (X = Zn, Be, Mn), which, for low contents of the third element X (below ≈8 at.%), display a single $A2 \leftrightarrow L2_1$ transition [27–31], consistently with the fact that Cu-Al with compositions close to Cu_3Al has also a single ordering transition [23]. The different behaviour of Cu-Al-Ni could be attributed, in principle, to a high binding energy for Ni-Al pairs. One of the objectives of the present work is the construction of realistic model which can clarify this and other points.

The BW model has the advantage of its relatively easy application to the problem of atomic ordering, and, in particular, provides analytical expressions for the determination of interchange energies by fitting to experimental order-disorder temperatures. However, since this model neglects short range order correlations, the thermodynamical quantities obtained within this approach considerably differs from the results obtained with more realistic methods [11]; this has been shown to occur, for instance, in the related ternary Cu-Al-Zn system [12]. A more sophisticated approach is the Monte Carlo (MC) method, which allows obtaining quasi-exact results from calculations made on finite systems [13]. However, due to the numerical character of this technique, it may become difficult determining the interaction parameters from a fit to experimental data, such as order-disorder transition temperatures. A plausible solution, which will be employed in the present work, is to use the interchange energies obtained within the BW model as initial guesses for the MC simulations [11]. This initial values should be optimized in order to obtain an adequate description of the experimental order-disorder temperatures.

The purpose of the present work is the construction of a model for the description of ordering phenomena in Cu-Al-Ni. The interchange energies are determined by fitting to the experimental order-disorder temperatures from Ref. [4]. The BW formalism, as described in Section 2.1, is used as first approximation, and the values are further optimized for their use in MC simulations (described in Section 2.2). Two types of MC simulations are performed: first, canonical ensemble simulations with direct atomic interchanges are used to optimize the energetic parameters and to analyze the predicted atomic distributions. Then, the phase equilibrium around the compositions of interest is studied by means of simulations in the grand-canonical ensemble. The rest of this paper is organized as follows: in Sections 3.1 and 3.2 we present and discuss the results obtained with BW and MC, respectively; the validity of the MC model is analyzed by comparing with other experimental information not included in the fitting. The main conclusions are drawn in Section 4.

2. Theory

2.1. Bragg-Williams model

The Bragg-Williams (BW) [7] model is the lowest step in a hierarchy of successive approximations to the free energy of an alloy known as the Cluster Variation Method (CVM) [10]: In this approximation, the configurational free energy is written in terms of the probabilities p_i^α for a site in sublattice α ($\alpha = I - IV$) to be occupied by an atom of specie i. Since probabilities of larger clusters (for instance, pair probabilities) are given just in terms of the p_i^α's, this is also known as the *point* approximation of the CVM [11,14]. For a bcc ternary alloy A-B-C with atomic fractions c_A, c_B and c_C, and considering constant pair interactions extended to first and second neighbours, the configurational free energy per atom, F/N, takes the form [15]:

$$\frac{F}{N} = \frac{U - TS}{N} = \sum_{ij}\left[4x_i x_j W_{ij}^{(1)} - 3\left(x_i x_j - \frac{1}{2}(y_i y_j + z_i z_j)\right)W_{ij}^{(2)}\right] + \sum_{ij} c_i c_j\left(-4W_{ij}^{(1)} - 3W_{ij}^{(2)}\right) + \sum_i c_i\left(4V_{ii}^{(1)} + 3V_{ii}^{(2)}\right) + \frac{k_B T}{4}\sum_{\alpha=I}^{IV} p_i^\alpha \cdot \ln\left(p_i^\alpha\right) \qquad (1)$$

In the above expression, U is the internal energy, T is the absolute temperature and S the entropy; $V_{ii}^{(k)}$ is the interaction between a pair of $i - i$ atoms placed as first ($k = 1$) or second ($k = 2$) neighbours; $W_{ij}^{(k)} = -2V_{ij}^{(k)} + V_{ii}^{(k)} + V_{jj}^{(k)}$ are the so-called *interchange energies*, which determine the tendency to ordering or segregation between the components i and j. The parameters x_i are linear combinations of probabilities and quantify the degree of order in first neighbours

$$x_i = \frac{p_i^I + p_i^{II} - p_i^{III} - p_i^{IV}}{4} \qquad (2\text{-a})$$

whereas y_i and z_i are linear combinations that describe the ordering between second neighbours,

$$y_i = \frac{p_i^I - p_i^{II}}{2} \qquad (2 \text{ - b})$$

$$z_i = \frac{p_i^{III} - p_i^{IV}}{2} \qquad (2\text{-c})$$

Due to the conditions $\sum_i p_i^\alpha = 1$, and $\sum_\alpha p_i^\alpha = 4c_i$, only six among the twelve occupation probabilities are independent; the description of the type and degree of *lro* is then more conveniently performed through the six independent parameters x_i, y_i and z_i ($i = A$, B; $x_C = -x_A - x_B$, $y_C = -y_A - y_B$, $z_C = -z_A - z_B$). Thus, in absence of *lro* (structure $A2$), is $x_i = y_i = z_i = 0$; in a $B2$ configuration, ordered in first neighbours, is $x_i \neq 0$, $y_i = z_i = 0$; and for an $L2_1$ structure is $x_i \neq 0$, $z_i \neq 0$, and $y_i = 0$.

In Eq. (1), the first term accounts for the energy due to ordering, the second one is the energy due to mixing, the third one is the internal energy of the pure components, and the last one is the configurational entropy (k_B being the Boltzmann's constant). The summations run over $i = A$, B, and C, or over $ij = AB$, AC, BC.