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Structure and stability of binary metal alloys. Precipitation treated via ab-initio calculations

STEFAN MÜLLER[*]

Universität at Erlangen-Nürnberg, Lehrstuhl für Festkörperphysik Staudtstr. 7,
D-91058 Erlangen, Germany

Theoretical studies of substitutional ordering phenomena in binary metal alloys demands the consideration of both huge parameter-spaces (e.g. for ground-state searches) and systems containing more than a million atoms (e.g. for precipitation). The combination of density functional theory calculations (DFT) with cluster expansion methods (CE) and Monte-Carlo (MC) simulations fulfills these requirements. They can be applied to study properties of a metal alloy which possess a delicate temperature-dependence without any empirical parameters, but with such accuracy that quantitative prediction of experimental data becomes possible. The concept is applied to study the structure and distribution of coherent precipitates in binary metal alloys.

Key words: *cluster expansion; density functional theory; Monte-Carlo simulation; metal alloys; precipitation*

1. Introduction

The keyword "Computational Materials Science" includes a huge number of different theoretical approaches reaching from continuum theory and semi-empirical models to so-called first-principles methods, mostly based on the density functional theory (DFT) [1, 2]. Although the latter would be the most elegant solution for describing material properties, because it is based on the rules of quantum mechanics and, therefore, has a predictive power, it is restricted to model systems containing no more than about 200 atoms, i.e. the concept allows studying material properties on an atomic scale only. Moreover, the description of many ordering phenomena in alloy systems demands the consideration of exchange processes between atoms. In other words, the configurational entropy has to be taken into account which is not the case in DFT calculations. These two problems are summarized in Fig. 1.

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[*] E-mail: stefan.mueller@physik.uni-erlangen.de

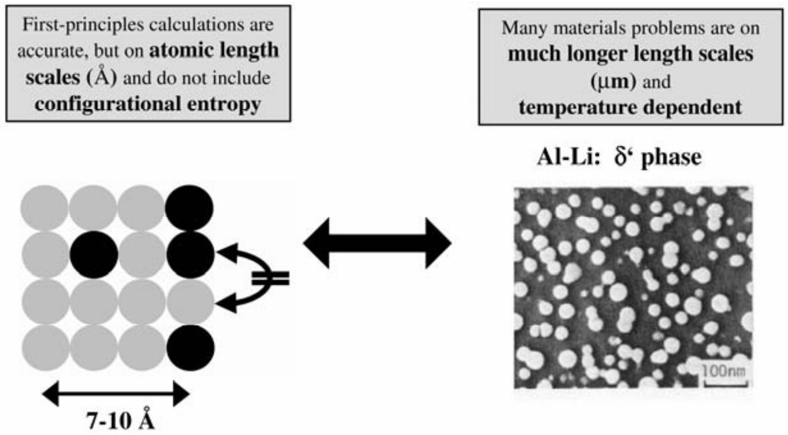

Fig. 1. While DFT calculations allow for a quantitative description of alloy properties on the atomic scale, they fail to describe material properties demanding a mesoscopic scale and exchange processes. As example, the right side shows a TEM picture [3] of the δ′ phase in Al–Li alloys

The transmission electron microscopy (TEM) image on the right [3] shows the so-called δ′ phase of an Al-rich fcc-based Al–Li alloy. Spherical precipitates can be observed possessing the famous $L1_2$ structure (Al_3Li) which does not exist as an intermetallic compound in the Al–Li phase diagram. Indeed, precipitates define an important part of the microstructure of many alloy systems and have practical importance, as they act to impede dislocation motion. A quantum-mechanical based treatment of phases as the precursor phase in Fig. 1 represents a big challenge, because the theoretical concept applied must be able to: (i) deal with model systems containing millions of atoms and (ii) allow a temperature-dependent description of the alloy's properties.

In the following, it will be shown that these problems can be solved by combining DFT with concepts from statistical physics. A central role is played by the so-called Cluster Expansion (CE) method [4] which permits the gap between the atomic and the mesoscopic scale by the construction of characteristic interactions based on first -principles calculations to be bridged. The extension to finite temperatures is then achieved by using these interactions in Monte-Carlo (MC) simulations. This will be briefly described in section 2. The concept will be applied to study one of the most important decomposition reactions in binary metal alloy systems, namely precipitation (section 3). It is shown that the results even allow a quantitative prediction of the size –shape–temperature relationships for coherent precipitates.

2. Methods

Firstly, formation enthalpies for a set (about 15–20) of geometrically fully relaxed intermetallic compounds with typically 2–16 basis atoms are calculated via DFT.

Thereby, the formation enthalpy $\Delta H_f(\sigma)$ per atom of a compound σ consisting of m A and n B atoms per a unit cell is defined by the energy gain or loss with respect to the bulk constituents at their equilibrium lattice constants a_A and a_B

$$\Delta H_f\,(\sigma, A_m B_n) = \frac{1}{m+n}\left[E^{\mathrm{tot}}\,(\sigma, A_m B_n) - mE_A^{\mathrm{tot}}\,(a_A) - nE_B^{\mathrm{tot}}\,(a_B)\right] \tag{1}$$

with $E_A^{\mathrm{tot}}\,(a_A)$ and $E_B^{\mathrm{tot}}\,(a_B)$ being the total energies of the elements A and B in bulk form. Since all total energy values are negative, a positive sign of ΔH_f stands for phase-separation, while a negative sign of ΔH_f means ordering.

These DFT based formation enthalpies are now used to construct so-called effective cluster interactions in order to bridge the gap between atomistic and mesoscopic scale. The basic idea by Sanchez, Ducastelle and Gratias [4] is called “Cluster Expansion” (CE): for a given underlying lattice, the crystal structure is divided into characteristic figures such as pairs, triangles, etc. Then, the energy of any configuration σ on this lattice can be uniquely written [4] as a linear combination of the characteristic energies J of the individual figures. The construction of the so-called effective interactions J is realized by an inversion method [5] with the goal of finding that set of values for the interactions, $\{J\}$, which minimizes the deviation between the formation enthalpies resulting from CE and DFT for all input structures σ. In practice, the predictive power of $\{J\}$ plays the most important role, i.e. the ability to predict the formation enthalpy of an arbitrary structure which was not used for the construction of the interactions (for details, see e.g. ref. [6] and references therein). Mostly, the effective cluster interactions on average only causes a prediction error of no more than 1–3 meV/atom compared to the direct DFT energies.

Moreover, as first shown by Laks et al. [7], any CE in real space fails to predict the energy of long periodic coherent superlattices – a prerequisite for studying precipitation on a mesoscopic scale from first-principles. In principle, this problem can be solved by transforming a group of interactions to the reciprocal space, which is easiest to do for the pair interactions and considering the long-periodic limit separately [8]. Finally, this leads to the Hamiltonian of the “Mixed-Space Cluster Expansion (MSCE)” [7, 8]. Here, any configuration σ is defined by specifying the occupations of each of the N lattice sites by an A atom (spin-index $\hat{S}_i = -1$) or a B atom ($\hat{S}_i = +1$). The formation enthalpy of any configuration σ at its atomically relaxed state is then given by

$$\begin{aligned}\Delta H_{CE}\,(\sigma) = {} & \sum_k J_{\mathrm{pair}}\,(k)\left|S\,(k,\sigma)\right|^2 \\ & + \sum_f^{MB} D_f\, J_f\, \bar{\Pi}_f\,(\sigma) + \frac{1}{4x-1}\sum_k \Delta E_{CS}^{eq}\,(\hat{k},x)\left|S\,(k,\sigma)\right|^2\end{aligned} \tag{2}$$

The first two terms represent the chemical energy, E_{chem} (often referred to as *interfacial energy*). Here, the first sum describes all possible pair figures. $J_{\mathrm{pair}}(k)$ is the lattice Fourier transform of the real space pair interactions, and $S(k, \sigma)$ are structure factors. The second sum describes many-body figures, such as triangles, tetrahedra, etc. J_f is the reAl–space effective many-body interaction of figure f, D_f stands for the number of equivalent clusters per lattice site and $\Pi_f(\sigma)$ are spin products. The third term, the constituent strain, E_{CS} (often referred to as coherency strain), describes the strain energy necessary to maintain coherency between bulk element A and B along an interface with orientation k. It can be calculated by deforming the bulk elements from their equilibrium lattice constants a_A and a_B to a common lattice constant a perpendicular to k. The constituent strain is a function of composition x and direction k only, but does not include information about the strength of chemical interactions between A and B atoms.

Figure 2 gives a survey about our concept which demands neither empirical parameters nor simplifications in the quantum-mechanical based Hamiltonian in order to get access to huge system sizes and finite temperatures.

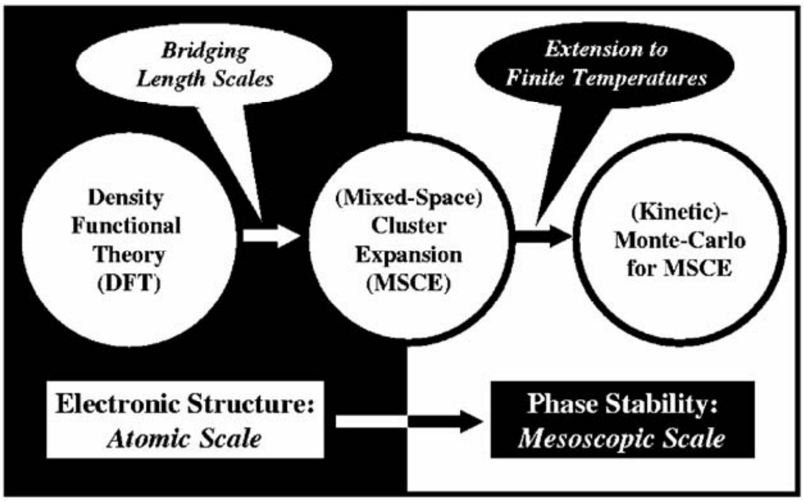

Fig. 2. The combination of DFT plus MSCE [8] plus MC [11] allows for a description of phase stability of metal alloys on a mesoscopic scale without any empirical parameters

For the latter, the MSCE Hamiltonian (Eq. (2)) is used in Monte-Carlo (MC) simulations. The field of applications to dynamic processes can be extended by switching from thermodynamic MC to kinetic MC [9]. For this, activation barriers for individual exchange processes between neighbouring atoms have to be calculated via DFT. This can be rather complicated and time consuming, because the calculation of diffusion coefficients demands the consideration of vacancies. In the case of precipitation, the number of different structural environments considered for exchange processes can, however, often be restricted by the fact that the alloy typically only contains a few percent of the precipitates-forming solute material (here called B atoms).

Then, the dominant process is the temperature-dependent diffusion of a B atom in material A. In many cases, as e.g. Al-rich Al–Zn alloys, this apparently rough approximation already allows a prediction of realistic precipitate distributions as function of ageing time, as will be discussed in the next section. Furthermore, first-principles based simulations of precipitation demand the possibility to consider long ageing times (many hours or days). Since precipitation is a phase-separating process, the probability that any atom of the precipitate forming species will ever diffuse from the precipitate to which it is already attached, back into the solid solution, becomes very low. Consequently, in standard MC algorithms most of such exchange processes are practically never performed which makes the simulation rather inefficient. Here, advantage is taken from the fact that the CE is able to calculate the probabilities for *all* possible exchange processes (even many thousands) within a few seconds which permits the concept of the so-called "residence time algorithm" [10] to our simulations to be applied: since now the time corresponding to each individual exchange process is known a priori, atoms can be forced to switch their sites (for details, see ref. [11]).

3. Precipitation

Quenching a solid solution of a metal alloy deep into the two phase-region of the phase diagram, followed by sample ageing, leads to the formation of so-called precipitates which comprise an important part of the microstructure of many alloy systems. The early stage of these reactions typically involves the formation of coherent precipitates that adopt the crystallographic lattice of the alloy from which they emerge [12]. Coherent precipitates have practical relevance, as they impede dislocation movement, and thus lead to "precipitation-hardening" in many alloys [12–14]. Thus, their size versus shape distribution as a function of temperature and ageing time is of special interest. Despite their importance, it is only recently [15] that, precipitate microstructures have been amenable to first-principles theories, since their description requires "unit cells" containing 103–106 atoms or more. The concept presented in section 2 gives access to such huge model systems.

The shape of precipitates is controlled by two competing energies [14]: interfacial or chemical energy E_{chem} and strain energy E_{CS}. While the former leads to a compact shape, the latter leads to a flattening along the elastically soft direction of the precipitate. Our MSCE Hamiltonian allows for a separation into these two characteristic energy parts: as already mentioned in section 2, the first two terms of Eq. (2) include information about strength and importance of the indvidual pair and multibody interactions and therefore, represent the chemical energy of the system. The last term, however, reflects the elastic properties of the alloy. This separation is used to analyse the ratio between chemical energy E_{chem} and strain energy E_{CS} as a function of the precipitate size. As examples, the focus is on Al-rich fcc-based Al–Li and Al–Zn alloys. Their precipitate distributions for a given ageing time and temperature are shown in the upper part of Fig. 3, whereby only the Li and Zn atoms are shown. The MC cell used for the simulations consists of 56×56×56 = 175 616 atoms in order to achieve sufficient statistics.

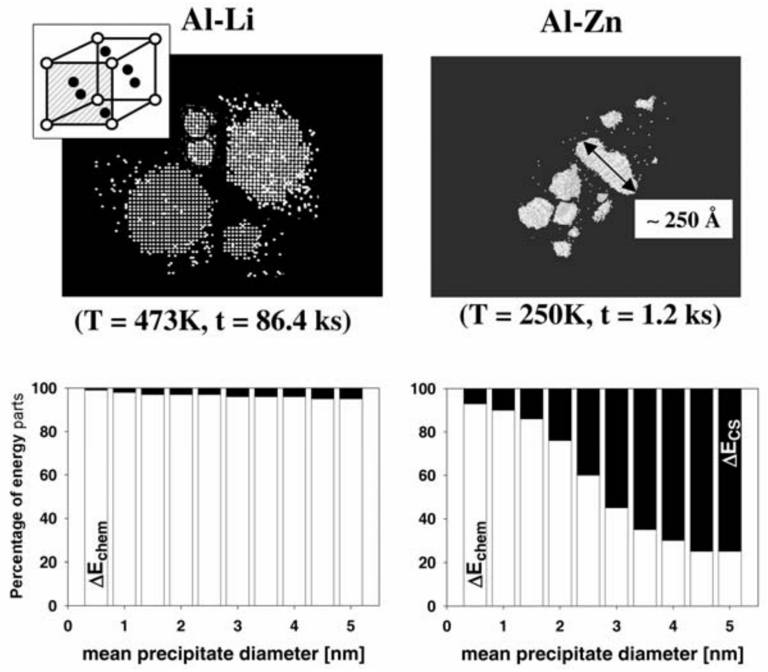

Fig. 3. Size-shape distribution of precipitates in Al-rich fcc-based Al–Li and Al–Zn alloys (no Al atoms are shown) and their corresponding percentage of strain and chemical energy as a function of the precipitate size. Precipitates of Al–Li form the $L1_2$ structure as shown in the top left corner

In the case of Al–Li, precipitates of the considered size up to 5 nm never flatten, but always possess a spherical shape, in excellent agreement with experimental results [3, 16]. This behaviour becomes understandable by analysing $E_{\mathrm{chem}}/E_{\mathrm{CS}}$ for different precipitate sizes as shown in the lower part of Fig. 3 for a sample containing 9.7% Li atoms: for all sizes the chemical energy E_{chem} (white bars) clearly dominates the strain energy E_{CS} (black bars). Following experimental results, it must be expected that this dominance of E_{chem} over E_{CS} even holds for precipitates of about 50 nm in diameter, because they still possess a spherical shape. The Li atoms seem to form a simple cubic lattice. This is due to the fact that the precipitates themselves show a Al_3Li stoichiometry forming the $L1_2$ structure sketched on the top left corner of Fig. 3: while all corners of the unit cell are occupied by Li atoms, all faces are occupied by Al atoms. Since only the Li atoms are displayed in the real space image, they form a simple cubic lattice. This observation also makes clear that there are practically no antiphase boundaries within the Al_3Li precipitates which would demand the occupation of Al sites by Li atoms.

Unlike Al–Li, for Al–Zn a strong size-dependence of the precipitate shape is found: Zn precipitates up to about 2.5 nm are more compact, i.e. chemically dominated, while larger precipitates become more and more ellipsoidal (strain dominated) [17]. It is interesting to note that for low temperatures a third component becomes important, namely the anisotropy of the chemical part which controls quantitatively the extent to which the precipitates facet at low temperatures. Figure 4 shows equilibrium shapes resulting from calculations considering the chemical part only: At low temperatures, when entropy is unimportant, the strong anisotropy of the chemical energy creates facets along planes of low interfacial energy.

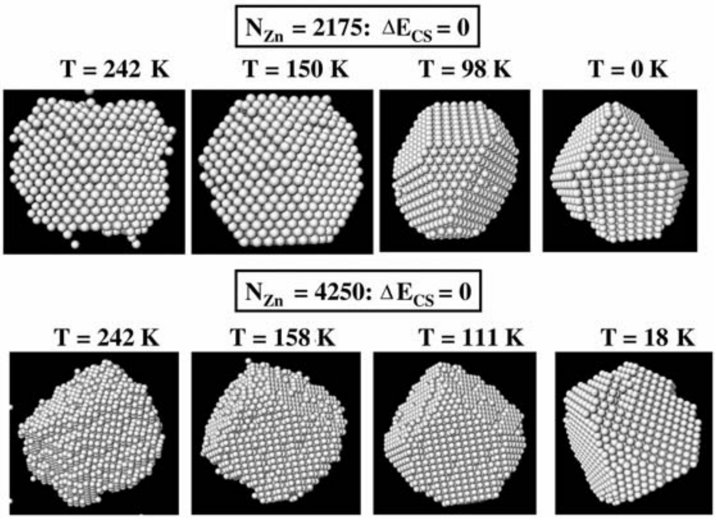

Fig. 4. Equilibrium precipitate shapes for different temperatures and sizes resulting from calculations where the constituent strain energy was neglected [6]. The size is given by the number of Zn atoms, N_{Zn}. For low temperatures, the faceting caused by the anisotropy of the chemcial energy in Al–Zn becomes visible

These are mostly (100) and (111) planes whose interfacial energies are lowest and nearly degenerated. In contrast, at high temperatures, where many configurations coexist due to entropy, the chemical anisotropy is largely averaged out and therefore, the precipitates become spherical. Another remarkable feature of the coherent Zn precipitates is the fact that their short axis is always along the [111] (and symmetric equivalent) directions. Indeed, at first glance, this appears a little surprising, because most fcc elements are elastically soft along the [100] direction, and consequently hard along [111]. However, it should not be forgotten that it is necessary to inquire about the stability and elastic properties of an unusual phase: fcc-Zn: while Zn is stable in the hcp structure, fcc-Zn shows an instability when deformed rhombohedrally along [111] [18]. As a consequence, fcc-Zn precipitates flatten along this direction [17]. This feature allows the definition of a *c/a* ratio and therefore, a quantitative measure for the description of the precipitate shape as used in many experimental studies and schematically shown on the left side of Fig. 5. While *a* represents the long axis of the ellipsoid (perpendicular to [111]), *c* is its thickness (parallel to [111]). The size is given by the radius of the associated sphere having the same volume as the corresponding precipitate.

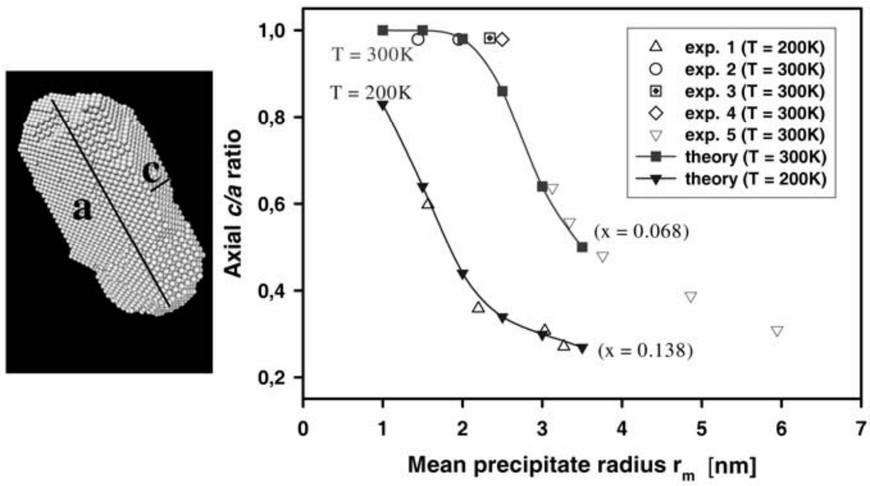

Fig. 5. Shape (*c/a*) vs. size relation of Zn precipitates for two different temperatures. The lines denote the results from our calculations [24], the open points are taken from different experimental studies (exp. 1–5 correspond to ref. [19–23])

Figure 5 compares the experimental size-shape relation for two different ageing times and concentrations [19–23] with those predicted by this method. For both temperatures, the agreement is excellent, i.e. the method allows for a quantitative prediction of the size versus shape versus temperature relation of coherent precipitates [24].

4. Conclusions

The combination of DFT with MSCE and MC is probably one of the most successful approaches to study binary alloy properties without any empirical parameters. At the moment, the limitation of the presented access is given by the underlying lattice which does not, for example, permit the study of melting processes. Regarding ordering phenomena in the solid phase, the method allows a quantitative prediction of experimental data. This paper has focussed on just one important example: precipitation in binary metal alloys. Here, there is profit from the fact that the approach applied allows study of configurations consisting of millions of atoms. In the case of Al–Zn, it was demonstrated that the prediction even goes through a quantitative comparison of the size-shape-temperature relation with experimental results. The presented method is by no means restricted to the two characteristic ordering phenomena, but it can also be applied for example to surface problems such as adsorbate systems [25] or surface segregation [26].

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