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Solubility and ordering of Ti, Ta, Mo and W on the Al sublattice in $L1_2$-Co_3Al

J. Koßmann [a, *], T. Hammerschmidt [a], S. Maisel [b], S. Müller [c], R. Drautz [a]

[a] *Interdisciplinary Centre for Advanced Materials Simulation, Ruhr-Universität Bochum, Bochum, Germany*
[b] *Max-Planck-Institute for Iron Research, Düsseldorf, Germany*
[c] *Institute of Advanced Ceramics, Hamburg University of Technology, Hamburg, Germany*

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ABSTRACT

Co–Al–W-based alloys are promising new materials for high-temperature applications. They owe their high-temperature strength to hardening by ternary $L1_2$-$Co_3(Al_{1-x}W_x)$ precipitates, which may form even though binary Co_3Al is not stable. In the current work, density functional theory calculations are performed to study the solubility and ordering of the transition metals W, Mo, Ti, and Ta at the Al sublattice in $L1_2$-Co_3Al. The sublattice disorder is modelled with a newly parametrised cluster expansion and compared to results using special quasi-random structures. Our results for W and Mo show that the mixing energy exhibits a minimum at approximately $x = 0.7$. However, the computed small values of the mixing energies indicate that W and Mo atoms are fully disordered with the Al atoms already at low temperatures. For Ti and Ta we find no sizeable driving force for ordering with the Al atoms. The computed solubilities on the Al sublattice obtained are in the range of 40–80 meV/atom for W and Mo and less than 25 meV/atom for Ti and Ta.

1. Introduction

The observation of the $L1_2$-ordered γ' phase that coexists with the disordered γ phase in Co–Al–W [1] has pushed the development of new Co-based superalloys. Since this discovery many Co–Al–W-based materials were shown to be promising materials for high-temperature applications [2–8]. Atom probe investigations suggest that Al and W both occupy the B sublattice in the $L1_2$-A_3B structure, while Co is located at the A sites [9–11]. Therefore, the ternary γ' phase is commonly identified as $L1_2$-$Co_3(Al_{1-x}W_x)$. While in earlier publications [3,12–14] an Al:W ratio of 1:1 has been assumed, recent studies suggest that a higher fraction of W may be incorporated in the (Al,W)-sublattice [11,15]. This gives rise to the question, if there are ordering effects in $L1_2$-$Co_3(Al_{1-x}W_x)$ that can explain the observed higher sublattice concentrations x. In the current work, we want to address this questions not only for substitutional W on the Al sublattice, but also for Mo, another group 6 element that partitions to the Al sublattice and stabilizes the γ' phase [10] and can act as a substitute for W in W-free Co-based superalloys [16]. In addition, Ti and Ta as strong γ'-formers in Co-base superalloys [11,17] that can occupy the Al sublattice are considered [10,13].

In Sec. 2 we will explain our methodology and specify computational details used in the current work. Our results are discussed in Sec. 3 and summarized in Sec. 4.

2. Methodology

We perform spin-polarised density functional theory (DFT) calculations using VASP [18–20] in combination with a high-throughput environment [21]. Our calculations are carried out with PAW potentials [22] and the generalised-gradient approximation functional PBE [23]. A plane-wave cutoff of 400 eV and a Monkhorst-Pack **k**-point mesh [24] with a density of 0.020 Å^3 is sufficient to converge formation energies to an error of less than 1 meV/atom. With the computed total DFT energies per atom (E) the mixing energies on the B sublattice

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[*] Corresponding author. Ruhr-Universität Bochum, Universitätsstr. 150, 44801, Bochum, Germany. Tel.: +49 234 32 29316.
E-mail address: joerg.kossmann@rub.de (J. Koßmann).

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$$\begin{aligned} E_{\mathrm{mix}} = {} & E(\mathrm{Co_3(Al_{1-x}TM_x)}) \\ & -xE(\mathrm{Co_3TM}) - (1-x)E(\mathrm{Co_3Al}) \end{aligned} \tag{1}$$

and formation energies

$$\begin{aligned} E_{\mathrm{f}} = {} & E(\mathrm{Co_3(Al_{1-x}TM_x)}) - \frac{3}{4}E(\mathrm{Co}) \\ & -\frac{x}{4}E(\mathrm{TM}) - \frac{1-x}{4}E(\mathrm{Al}) \end{aligned} \tag{2}$$

of a $\mathrm{Co_3(Al_{1-x}TM_x)}$ structure with a sublattice concentration x of a transition metal TM are obtained. The energies E of the elements were taken as the DFT total energies per atom of fcc-Al, hcp-Co, bcc-Ta, hcp-Ti, bcc-Mo and bcc-W. The energies $E(\mathrm{Co_3TM})$ and $E(\mathrm{Co_3Al})$ refer to the DFT total energies per atom of the $\mathrm{L1_2}$ binaries.

We use the cluster expansion (CE) method [25–27] to model the sublattice disorder in $\mathrm{Co_3(Al_{1-x}TM_x)}$. As we only study the B sublattice, we consider the ternary system as a pseudo-binary and therefore only include configurations and clusters of the B sublattice in our CE. A correlation function $\Pi_F(\sigma)$ along a cluster F at site l in B sublattice configuration σ is then given by the product of the occupation variables $s_j = \pm 1$ along the vertices of a cluster,

$$\Pi_F(\sigma, l) = \prod_{\text{vertices } j} s_j \, , \tag{3}$$

which are $+1$ if the sublattice site j is occupied by TM and -1 if it is occupied by Al. With the lattice average of the correlation function of a cluster F with the multiplicity D_F over all N sites in the B sublattice,

$$\overline{\Pi}_F(\sigma) = \frac{1}{ND_F} \sum_l \Pi_F(\sigma, l) \, , \tag{4}$$

the mixing energy of $\mathrm{Co_3\,Al_{1-x}\,TM_x}$ can be formulated in a CE as

$$\begin{aligned} E^{\mathrm{CE}}_{\mathrm{mix}}(x, \sigma) = {} & N \sum_F D_F J_F \overline{\Pi}_F(\sigma) \\ & -xE(\mathrm{Co_3TM}) - (1-x)E(\mathrm{Co_3Al}) \, . \end{aligned} \tag{5}$$

The expansion coefficients J_F are commonly referred to as effective cluster interactions (ECIs). In the current work, the optimal set of clusters $\{F\}^{\mathrm{opt}}$ and the corresponding ECIs $\{J_F^{\mathrm{opt}}\}$ are obtained using the DFT energies E_{mix} of ternary $\mathrm{L1_2}$-$\mathrm{Co_3(Al_{1-x}TM_x)}$ supercells (about 80 for each system) within the genetic fitting algorithm implemented in the UNCLE code [27]. We checked the convergence of the CE by predicting the CE mixing energy of more than 10,000 configurations and found no configuration with a smaller energy than the DFT ground state line (within an accuracy of 2 meV/atom). The root mean square energy difference of the DFT and CE mixing energies and the cross validation score were both ≤ 1 meV/atom in each case, which corresponds to the numerical precision of DFT calculations.

For the ideal random mixing of Al and TM on the B sublattice in $\mathrm{L1_2}$-$\mathrm{A_3B}$, the lattice average over the correlation functions depends, for a given set of clusters – e.g. $\{F\}^{\mathrm{opt}}$ with the ECIs J_F^{opt} as obtained by the CE fitting – only on the composition x

$$\begin{aligned} \overline{\Pi}^{\mathrm{R}}_F & = (x \cdot (+1) + (1-x) \cdot (-1))^{k_F} \\ & = (2x-1)^{k_F} \end{aligned} \tag{6}$$

where k_F is the number of vertices of a cluster F. Inserting Eq. (6) in Eq. (5) gives the ideal random mixing energy

$$\begin{aligned} E^{\mathrm{R}}_{\mathrm{mix}}(x) = {} & N \sum_F D_F J_F (2x-1)^{k_F} \\ & -xE(\mathrm{Co_3TM}) - (1-x)E(\mathrm{Co_3Al}) \, . \end{aligned} \tag{7}$$

We compute the ideal random mixing energies of all $\mathrm{Co_3(Al_{1-x}TM_x)}$ systems using the optimized set of clusters — i.e. $\{F\}^{\mathrm{opt}}$ with the ECIs J_F^{opt} obtained by the fitting to DFT.

Furthermore, we compare the CE mixing energies with DFT calculations for special quasi-random structure (SQS) supercells [28] that are particularly constructed to mimic the correlation functions of the random alloy. Here, a modified version [29] of the ATAT package [30] is used in order to identify SQS supercells that minimize the deviation $\varepsilon(\sigma)$ of the correlation functions from the ideal random state

$$\varepsilon(\sigma) = \sum_F \frac{D_F}{\left(k_F \overline{d_F}\right)^2} \left| \overline{\Pi}_F(\sigma) - \overline{\Pi}^{\mathrm{R}}_F \right| \, , \tag{8}$$

where $\overline{d_F}$ is the mean distance between the vertices of cluster F. For the construction of the 32-atoms SQS supercells with 8 intermixing atoms on the B sublattice, we include all 2-body clusters with edge length up to the 9th coordination shell, all 3-body figures with edge length up to the 6th coordination shell, all 4-body figures with edge length up to the 4th shell, and all 5-body figures with a maximum inter-vertex distance of 2 coordination shells. In contrast to the CE, all lattice positions are considered to compute $\varepsilon(\sigma)$. The constructed SQS are compiled in the appendix. The SQS supercells are fully relaxed within DFT calculations as described above. Some of these SQS supercells exhibit a tetragonal distortion during full relaxation and are not taken into account in this study.

The solubility of a transition metal TM on the Al sublattice in $\mathrm{L1_2}$-$\mathrm{Co_3Al}$ can be interpreted as the change of the mixing energy w.r.t. the TM concentration x on that sublattice, which can be analytically obtained for the random alloy by forming the derivative of Eq. (7) in the dilute limit, *i.e.* at $x = 0$

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}x} E^{\mathrm{R}}_{\mathrm{mix}}\Big|_{x=0} = {} & 2N \sum_{F, k_f > 0} D_F J_F k_F (-1)^{k_f - 1} \\ & -E(\mathrm{Co_3TM}) + E(\mathrm{Co_3Al}) \, . \end{aligned} \tag{9}$$

We compare these results with the solubility in the ordered state, obtained by numerical differentiation of the mixing energies of the CE ground-state line (GSL) configurations $\{\sigma^{GSL}(x)\}$ for small Δx values

$$\frac{\mathrm{d}}{\mathrm{d}x} E^{\mathrm{CE}}_{\mathrm{mix}}\Big|_{x=0} \approx \frac{E^{\mathrm{CE}}_{\mathrm{mix}}(\Delta x, \sigma^{\mathrm{GSL}}(\Delta x))}{\Delta x} \, . \tag{10}$$