



# Simulation of precipitate evolution in Fe–25 Co– 15 Mo with Si addition based on computational thermodynamics



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## ABSTRACT

Multi-component nucleation theory is applied to decipher the precipitate evolution of solution-treated and quenched Fe–25Co–15Mo (mass%) with Si addition during continuous heating and isothermal aging. For computer simulation of the nucleation and growth kinetics of precipitates, we optimize thermodynamic model parameters of the Fe–Co–Mo system with experimental data and enthalpies of formation of ternary ferrite phase determined by density functional theory analysis. Si-solubility in the precipitation-hardening  $\mu$ -phase is considered in the thermodynamic modeling. The body-centered cubic (bcc) ferrite phase reveals a metastable miscibility gap between Fe- and Mo-rich phase below 1033 K. Based on thermodynamic modeling of the Fe–Co–Mo system, it is shown that the alloy Fe–25Co–15Mo is located outside the spinodal region, which is in contrast to some previous work on this system. Thermo-kinetic simulations, which are validated on experimental data from atom probe tomography, propose that during aging, the first microstructures form by means of nucleation and growth of metastable bcc-precipitates before the formation of rhombohedral  $\mu$ -phase. For the thermokinetic analysis, we evaluate and utilize theoretically predicted nucleus compositions of bcc-precipitates from the minimum nucleation barrier concept.

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## 1. Introduction

Solution-treated and quenched Fe–25Co–15Mo-alloys (compositions in mass% unless stated otherwise) with Si addition of about 0.2% (FCM) show remarkable increase in hardness during aging at elevated temperature [1–3]. The observed precipitation strengthening potential has been attributed to finely dispersed semi-coherent  $\mu$ -phase particles with a stoichiometry of  $(\text{Co,Fe})_{7-8}\text{Mo}_6$ . 3D-AP tomography revealed the development of a modulated microstructure of Mo-enriched and -depleted zones prior to  $\mu$ -phase formation during aging [3–5]. The shape and spatial distribution of  $\mu$ -phase precipitates resembled to the microstructures of these Mo-enriched zones. In two early studies of Fe–Mo and Fe–Co–Mo alloys [6,7], similar microstructures with Mo-rich, chain-like regions along elastically soft crystallographic  $x\langle 100 \rangle$ -directions were observed and interpreted as spinodal

decomposition. In the framework of spinodal decomposition, these periodic striations reflected typical concentration fluctuations due to spontaneous decomposition. In contrast, CALPHAD thermodynamics suggested that metastable coherent bcc particles could form in Fe–Mo alloys by the nucleation and growth mechanism [8,9]. These nano-scale bcc-structured nuclei are Mo-rich due to the metastable miscibility gap between the Fe-rich and Mo-rich bcc-phase and form quasi-periodical morphological patterns. These are a consequence of coherency strain due to the lattice mismatch between precipitates and matrix [8–11].

In the first part of this paper, the thermodynamics of the Fe–Co–Mo system is established and formulated in terms of an optimized set of CALPHAD parameters. These are implemented into the thermodynamic database 'mc\_fe', version 2.011. Based on these data, the spinodal is calculated as a function of composition and temperature. The spinodal separates the region of spinodal decomposition from the region of phase separation by homogeneous nucleation and growth of Mo-rich bcc-phase of the miscibility gap in the bcc phase of the Fe–Co–Mo system. An energetically most favorable composition of the nucleus is determined at the minimum energy barrier for the nucleation event. This particular nucleus

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composition is used in thermo-kinetic simulations of precipitation within the kinetic framework of the MatCalc software [12–16].

## 2. Mechanisms of matrix decomposition

Spinodal decomposition [17] describes the spontaneous phase separation of a supersaturated solid solution phase due to random concentration fluctuations. In an alloy that exhibits a miscibility gap, spinodal decomposition occurs in the unstable region inside the miscibility gap. This region is confined by the chemical spinodal, which is the inflection point of the Gibbs energy  $G(x)$  curve at  $\partial^2 G/\partial x^2 = 0$ .

If the involved species have different molar volumes, the decomposition process is accompanied by coherency strains. The Gibbs energy of a coherent solid solution is increased by the reversible elastic work, which is needed to accommodate the lattice mismatch [18]. Thus, the thermodynamic definition of the so-called 'coherent spinodal' includes an additional term describing the energy contribution of elastic strain [19] with

$$\frac{\partial^2 G}{\partial x^2} + \frac{aE(\varepsilon)^2}{(1-\nu)} = 0 \quad (1)$$

$E$  is the Young's modulus,  $\varepsilon$  is the linear misfit strain, which is 1/3 of the transformation volume change or volumetric lattice mismatch, and  $\nu$  denotes the Poisson's ratio. Elastic anisotropy of the matrix causes a reduction of the total strain energy by the factor  $a$ . Microstructurally, this is reflected in the alignment of the precipitates with respect to the elastically soft  $\langle 100 \rangle$ -directions [9].

In the 30ies of the last century, Borelius [20] already considered decomposition of an unstable alloy due to concentration fluctuations. Later, Hillert [21] gave a theoretical explanation of periodicity. Starting with a regular solution model, he derived a flux equation for one-dimensional diffusion on a discrete lattice, which yields a periodic variation of composition with distance inside the spinodal. At the same time, Cahn [17] developed a continuum model for spinodal decomposition, which is based on the Cahn–Hilliard equation for the free energy of a solid solution [22], and which includes coherency strain effects.

Between the coherent spinodal and the binodal line, which separates the one-phase from the two-phase region, theory predicts that periodic concentration fluctuations are unstable and will decay spontaneously. On the other hand, in this composition range, homogeneous nucleation of precipitates can occur. This is most often described by classical nucleation theory (e.g. [23]). In contrast to the process of spinodal decomposition, which occurs spontaneously, an activation barrier  $G^*$  must be overcome in the nucleation process with

$$G^* = \frac{16}{3} \pi \frac{\gamma^3}{(\Delta G_{\text{nuc}})^2}, \quad (2)$$

where  $\gamma$  is the specific interfacial free energy and  $\Delta G_{\text{nuc}}$  is the total volume free energy change associated with the nucleation event. Eq. (2) is valid for spherical shape of the nucleus.

## 3. Modeling of small coherent nuclei

The possibility that the composition of an embryo may deviate from the composition of a macroscopic precipitate during nucleation was already discussed in the mid of the last century [24,25]. Recently, this concept of a 'most likely' nucleus composition has been applied to the nucleation of homogeneous bcc Cu–Fe precipitates in a ferritic matrix [26], and in multi-component precipitation-hardened steel [27]. Following the concept of Hobstetter [24], the most likely composition of the nuclei is given at the composition where the nucleation barrier  $G^*$  shows a minimum. This procedure is applied in the present work to the bcc-precipitate phase, since this phase is modeled as a solution phase allowing for a gradual variation of all element contents. Taking into account the energy contribution from misfit strain also in the critical energy expression, the nucleation barrier of homogeneous bcc nuclei in Fe–Co–Mo-based alloy is evaluated as:

$$G^* = \frac{16}{3} \pi \frac{\gamma^3}{\left(\Delta G_0 - \frac{aE\varepsilon^2}{(1-\nu)}\right)^2} \quad (3)$$

$\Delta G_0$  is the chemical bulk free energy change on nucleus formation.

The term  $aE\varepsilon^2/(1-\nu)$  accounts for the contribution of coherency strain per unit volume of precipitate to the critical nucleation barrier. The effect of strain becomes more important for  $G^*$ , the larger the composition difference between the homogeneous nucleus

and the matrix is, i.e. the larger the lattice mismatch becomes. For evaluation of the composition and temperature dependent specific interfacial energy,  $\gamma$ , the generalized broken bond (GBB) model [28] is used.

$$\gamma = \frac{n_s \cdot z_s}{N \cdot z_l} \cdot \Delta E_{\text{sol}}, \quad (4)$$

where  $N$  is the Avogadro constant,  $n_s$  is the number of atoms per unit area of interface,  $z_l$  is the coordination number, and  $z_s$  is the number of nearest neighbor broken bonds.  $\Delta E_{\text{sol}}$  in Eq. (4) is the solution enthalpy of precipitate in the matrix, which is evaluated on basis of the CALPHAD optimization of matrix and precipitates. The idea of a sharp distinction between spinodal decomposition and nucleation regime was rejected by Binder et al. [29]. According to his argumentation, the calculated singularity of the spinodal would be only valid in an artificial system with infinitely weak long-range forces and no short-range forces. Since the dynamics of phase separations is only controlled by the diffusion of atoms in a chemical potential gradient, in a real system, gradual transition between nucleation and spinodal decomposition is expected.

## 4. Thermodynamic modeling

For the CALPHAD-type thermodynamic modeling, the ternary model parameters of the following phases are assessed in order to obtain the thermodynamic basis for calculations of the spinodal line, interfacial energies, the nucleus compositions with minimum nucleation barrier, and the entire precipitate evolution during aging: Body-centered cubic (bcc) ferrite, with the sublattice description [30,31]  $(\text{Co,Fe,Mo,Si})_1(\text{Va})_3$ , face-centered cubic (fcc) austenite described by  $(\text{Co,Fe,Mo,Si})_1(\text{Va})_1$ , and the rhombohedral  $\mu$ -phase with the sublattice (sl) description  $(\text{sl1}[\text{CN12}])_6(\text{sl2}[\text{CN12}])_1(\text{sl3}[\text{CN14}])_2(\text{sl4}[\text{CN15,CN16}])_4$  [32]. CN denotes the coordination number. The smaller constituents Fe, Co, Si are preferentially filling [CN12] and [CN14] sites. The larger Mo atom is preferentially located on [CN15] and [CN16] sites [32]. Va in the formulas denotes vacancies.

The thermodynamic model parameters of the unary [34] and binary phases [33,35,36] are adopted from the given literature, with the exception of the binary Fe–Mo compound of  $\mu$ -phase. The 4sl description is clearly a simplification of the structural-chemical situation as sites CN15 and CN16 are combined in one sublattice. Even so, the 4sl description chosen in the present study qualitatively reproduces the site preferences obtained by first principles analyses [37].

### 4.1. Alloy phases

Eq. (5) describes the molar Gibbs energies of the ternary fcc and bcc solid solution phases:

$$\begin{aligned} G_m = & {}^\circ G_{\text{Fe}} y_{\text{Fe}} + {}^\circ G_{\text{Co}} y_{\text{Co}} + {}^\circ G_{\text{Mo}} y_{\text{Mo}} + {}^\circ G_{\text{Si}} y_{\text{Si}} \\ & + RT(y_{\text{Fe}} \ln y_{\text{Fe}} + y_{\text{Co}} \ln y_{\text{Co}} + y_{\text{Mo}} \ln y_{\text{Mo}} + y_{\text{Si}} \ln y_{\text{Si}}) \\ & + G_{\text{mag}} + y_{\text{Co}} y_{\text{Fe}} L_{\text{CoFe}} + y_{\text{Co}} y_{\text{Mo}} L_{\text{CoMo}} + y_{\text{Co}} y_{\text{Si}} L_{\text{CoSi}} \\ & + y_{\text{Fe}} y_{\text{Mo}} L_{\text{FeMo}} + y_{\text{Fe}} y_{\text{Si}} L_{\text{FeSi}} + y_{\text{Mo}} y_{\text{Si}} L_{\text{MoSi}} \\ & + y_{\text{Co}} y_{\text{Fe}} y_{\text{Mo}} (y_{\text{Co}} L_{\text{Co}} + y_{\text{Fe}} L_{\text{Fe}} + y_{\text{Mo}} L_{\text{Mo}}) \end{aligned} \quad (5)$$

where  ${}^\circ G_A$  is the Gibbs energy of pure element A relative to its reference state at 298 K, and  $y_A$  is the site fraction of species on the sublattice.  $G_{\text{mag}}$  is the magnetic contribution to the molar Gibbs energy and it is described in detail elsewhere [35,36]. The  $RT$ -term describes the configurational entropy of ideal mixing. Non-ideal binary interaction energies between two different elements are defined in the second-last line of Eq. (5). The last line represents non-ideal ternary interactions between Co, Fe, and Mo. Ternary interaction parameters in fcc and bcc are optimized with experimental

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