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Kinetic Monte Carlo simulation of phase-precipitation versus instability behavior in short period FeCr superlattices

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ABSTRACT

The structural evolution of FeCr superlattices has been studied using a quasi-atomistic Object Kinetic Monte Carlo model. Superlattices with different spatial periods have been simulated for anneal durations from few hours to several months at 500 °C. Relatively-long period superlattices stabilize into Fe-rich and Cr-rich layers with compositions close to those of bulk α and α′ phases. In contrast, superlattices with very short periods (4, 5, 6 nm) are observed to undergo instability and, for long annealing times, evolve into three-dimensionally decomposed regions, in qualitative agreement to recent experimental observations. The instability onset is delayed as the spatial period increases, and it occurs via interface roughness. This evolution can be explained as a minimization of the free-energy associated to the α/α′ interfaces. A comprehensive description of the evolution dynamics of FeCr-based structures is obtained with our model.

1. Introduction

Iron-chromium (FeCr) alloys are materials of high technological and fundamental interest [1]. From the technological point of view, they have been selected as structural materials for advanced nuclear applications [2]. From the fundamental side, they exhibit a rich phenomenology with a miscibility-gap leading to phase nucleation for moderated Cr content and spinodal decomposition for the medium composition range, and these processes are accelerated by radiation [3–5]. The composition-dependence of the alloy mixing energy has been subject of active discussions, and some uncertainties are still remaining for the phase diagram [6].

Phase decomposition in nominally homogeneous alloys is triggered by random composition fluctuations. Such phase decomposition can be also induced artificially in composition-modulated superlattices (SLs), with Fe-rich and Cr-rich regions acting as seeds for phase nucleation [7]. Thus, Fe-rich layers would precipitate into a bulk-like Fe-rich phase (α-phase) whereas Cr-rich layers would precipitate into a bulk-like Cr-rich phase (α′-phase), with metastable α/α′ interface regions [8]. In this way, the layers are expected to stabilize and the modulation amplitude of FeCr SLs may increase under anneal. This behavior is opposite to usual SL interdiffusion.

Recently, Atom Probe Tomography (APT) measurements revealed that very thin-layer FeCr SLs, with spatial period of 6 ± 1 nm, undergo instability, instead of stabilization, at 500 °C. In particular, composition profiles become irregular after few days anneals, losing the original periodicity. For longer anneals, the system is observed to evolve toward three-dimensional morphologies [9]. These results have been interpreted in terms of a critical layer thickness on the light of a one-dimensional Mean Field Model [9]. Nevertheless, it would be desirable to count on a comprehensive model including the whole phenomenology: random nucleation of homogeneous alloys, phase-stabilization of thick-layer SLs, instability for thin-enough layers, and evolution toward three-dimensional morphologies for advanced stages.

Atomistic-like Object Kinetic Monte Carlo models (OKMC) are promising candidates to simulate the structural evolution of crystal alloys, reaching the required time scales of typical experiments, while preserving a direct connection to atom-scale processes [10–12]. Recently, a defect-based OKMC model has demonstrated to provide an accurate description over time of phase nucleation and spinodal decomposition in FeCr alloys [8], while offering improved computational efficiency respect to more detailed models [13].

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In this work, the above mentioned OKMC model has been extended to simulate the evolution of FeCr-based SLs, including ultra-thin SLs. Our purpose is to provide a unified picture for the structural evolution of iron-chromium alloy systems, including regular phase-separation and short-period superlattice instability. The paper is organized as follows. After this introduction, the model and methods used in the simulations are sketched out. Subsequently, the simulation results are presented and the corresponding discussion is developed. Finally, some conclusions are wrapped up.

2. Model and methods

We have used the OKMC model described by *Dopico* et al. [8] and we have applied it to FeCr alloys with initial periodic one-dimensional composition modulation (FeCr superlattices, SLs). In that model, mobile point-defects are treated as atomistic particles whereas lattice atoms (Fe or Cr) are described by integer counters in each local region [10]. With this aim, the simulation domain is divided into nanometer-sized cells. Material properties in each cell are assumed to depend on its own Cr-molar fraction (composition) and on the composition of neighbor cells having atomic bonds to this, with weights derived from a simple crystallographic bond model and accounted in terms of an effective composition [8]. Composition dependence of formation energy of point-defects, migration energy of point-defects, tracer diffusivity ratio between Cr and Fe atoms, and alloy mixing energy are included in the model.

Point-defects moving from a cell to another may induce the movement of Cr or Fe atoms, with probabilities depending on the tracer diffusivity ratios and on the mixing energies of the cells. Within our model, point-defect induced atom movements are accounted by an efficient exchange algorithm. Near equilibrium conditions, point-defect concentrations depend on their formation energies. Moreover, in metals near equilibrium, vacancies are dominant over self-interstitials [14]. The model has been implemented into the MMonCa simulator [15,16].

In our simulations, the initial composition has been set to be spatially modulated in one dimension. As the model is intrinsically three-dimensional, this initial condition does not impose a constraint for the subsequent evolution. Sinusoidal Cr molar fraction profiles with amplitude of 0.25 and average of 0.5 and an anneal temperature of 500 °C have been selected to reproduce the physical conditions of the experimental measurements [9]. Different SL periods (λ) have been used with the aim of studying layer stability/instability as a function of layer thickness. A simulation domain of $12 \times 60 \times 99\ \mathrm{nm}^3$, divided in cubic cells with side $L = 0.6$ nm, has been considered. This cell side is close to the lowest limit of the approach ($L \geqslant 2a \approx 0.57$ nm, with a being the lattice parameter). A free surface has been located at the domain front (0 nm depth), mirror boundary conditions have been assumed at the bottom (99 nm depth), and periodic boundary conditions have been set in the lateral (12 nm × 60 nm) directions [8].

Equilibrium vacancy concentration (with negligible self-interstitial contribution) is assumed in our simulations. This is established by the balance of vacancy emission and capture at the free surface, and by the probability of vacancy jumps between cells [8,10]. Therefore, simulation times would match to experimental conditions with low initial defect concentration. If extra defects are in the sample, either incorporated during epitaxial growth or generated by irradiation, experimental dynamics is expected to be accelerated with regard to the predicted one. Additionally, the presence of oxygen impurities, evidenced in the experiments of Ref. [9], has not been included in our simulations. The parameter set of Ref. [8] has been used, with the vibrational entropy parameter Θ tuned from 1400 K to 1300 K in order to compensate the discrepancies of precipitate compositions in Ref. [9] with respect to the original calibration.

Spatial composition maps and profiles, suitable to be compared to APT experiments, can be extracted from the simulated composition configurations. With this aim, the alloy composition is averaged within a volume analogous to the one probed by the experimental beam. In the reference experiment, a beam spot with a diameter of 0.5 nm and a probing profundity of 8 nm has been used [9] and it can be equated to a column of 7 cubic cells for our 0.6 nm spacing. Thus, simulated composition maps (or profiles) are built by scanning the simulation domain within a cell plane

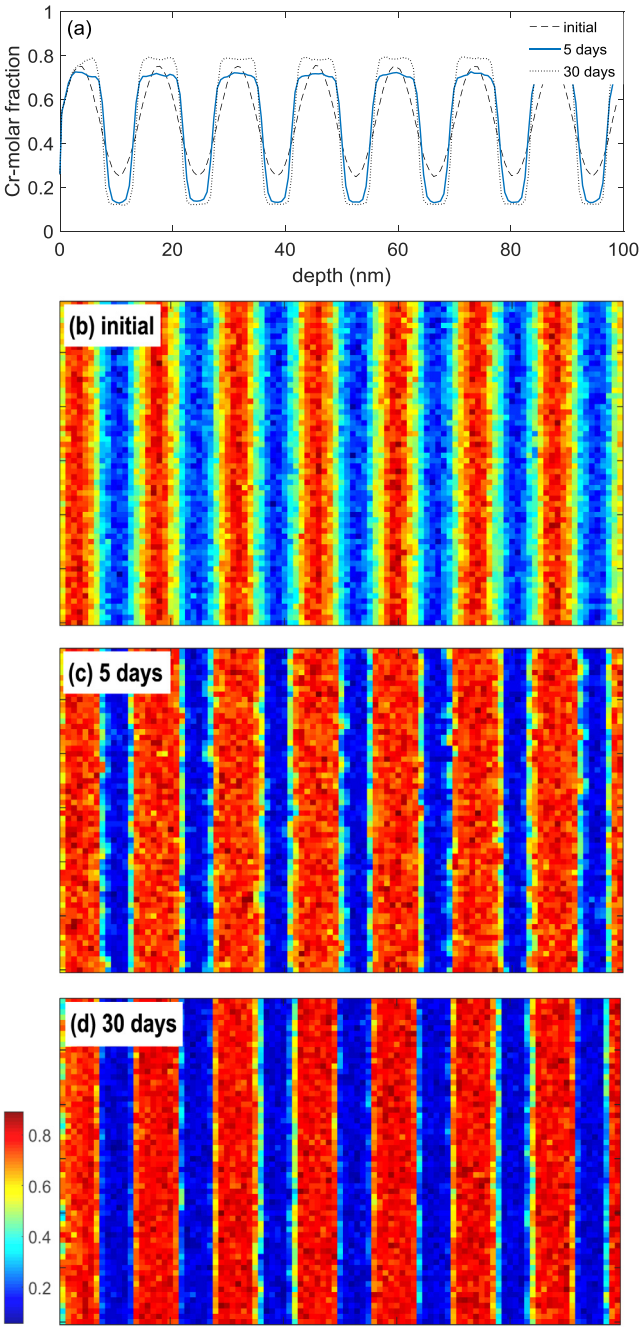

Fig. 1. Simulated spatial composition distribution, measured as Cr molar fraction, for a 14 nm-period FeCr superlattice with initial sinusoidal composition modulation annealed at 500 °C. (a) Initial and aged composition profiles. (b) Initial composition map. (c) and (d) Composition maps after annealing for 5 and 30 days, respectively.

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