Diffusional Phase Transformations on the Atomic Scale :Experiment and Modelling

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Abstract

In the early stages of phase transformations, microstructures are generated with the dimensions of only a few atomic spacings. Investigation of structures on such a fine scale poses severe difficulties, not only for experimental studies, but also for conventional theories based on continuum models. In this paper we report on a combination of atomic-scale microanalysis using the position-sensitive atom probe and atomistic simulations using the dynamic Ising model. Three phase transformations have been studied : spinodal decomposition in Fe-Cr alloys, nucleation and growth in dilute Cu-Co alloys and finally a conditional spinodal reaction in Ti-Al. The model provided a good quantitative match to the kinetics of spinodal decomposition observed in Fe-45%Cr, and nucleation and growth in Cu-1%Co. It also predicts the development of coupled ordering and phase separation in Ti-15%Al.

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1. Introduction

Many technologically important alloys used in service are thermodynamically metastable or unstable against some form of phase separation at the atomic scale. These alloys include duplex stainless steels used in power generating systems [1], copper-cobalt and iron-chromium multilayers whose giant magnetoresistance is being used for high density magnetic read heads, and low density titanium-aluminium based alloys used in the aerospace industry [2-4]. Conventional theories for phase separation have been developed using continuum approximations in which the local alloy concentration can be explicitly defined. However, in each of the alloy systems mentioned above, concentration modulations on a sub-nanometre scale generated during the early stages of phase separation have a dramatic effect on the physical properties of the alloy. Recent advances in microscopy now enable the examination of materials with near atomic resolution. Results show that structures on this fine scale cannot be adequately described by continuum approximations, and alternative atomistic microstructural models must be developed and compared with three-dimensional experimental information.

In this paper an atomistic model based on the dynamic Ising model is described. With suitable choice of interaction parameters, the model can predict spinodal decomposition, nucleation and growth and also a conditional spinodal reaction. To facilitate a detailed comparison with experimental results, binary model alloys based on technologically relevant materials have been chosen for study. The model predictions are compared with experimental results obtained from the position-sensitive atom probe [5, 6]. In this paper all concentrations are defined in atomic %.

2. The Position-Sensitive Atom Probe

The position sensitive atom probe is an instrument used for ultra-high resolution 3D microscopy. A specimen in the form of a sharp needle is held in a vacuum chamber and subjected to a high positive potential. If the potential is increased sufficiently, the field at the tip apex will be high enough to field evaporate individual atoms from the specimen surface. These ions are projected approximately radially towards a detector giving a desorption image with a magnification of the order of a million times. Time of flight mass spectrometry is used to determine the chemical identity of each ion. The position of impact on the detector is used to determine the approximate position of field evaporation. Thus an atomic map is built up of the distribution of elements on the specimen surface. Continued removal of material allows a full three-dimensional reconstruction of the atomic positions and thus local variations in chemical composition. The atomic scale structure of the ferrite phase of a duplex stainless steel in which spinodal decomposition has generated a two phase microstructure with a wavelength less than 10 nm is shown in Fig. 1.

3. The Dynamic Ising Model

The driving force for phase separation is the reduction of free energy. At a microscopic level this is achieved by the stochastic process of diffusion of atoms through the microstructure. The dynamic Ising model can be used to simulate this process. A Hamiltonian is defined in terms of bond energies either between pairs of atoms or over small clusters of atoms and summed over all possible interactions. The change in enthalpy (ΔH) on swapping a nearest neighbour pair of atoms is then calculated and the probability of acceptance determined. If only nearest neighbour interactions are considered, the change in energy, ΔH , will be a multiple of the interaction parameter, $\epsilon = E_{AA} + E_{BB} - 2E_{AB}$, where E_{AA} , E_{BB} and E_{AB} are the energies associated with a A-A, B-B and A-B nearest neighbour interactions respectively. Provided that the ratio of the probability of accepting a swap with energy change ΔH to a swap with energy change $-\Delta H$ is $e^{-\Delta H/kT}$, then the free energy of the system will tend towards equilibrium. The simplest acceptance criteria is given by the Metropolis algorithm [7], in which the new configuration (x') is always accepted if the enthalpy decreases and accepted with probability $P = e^{-\Delta H/kT}$ if the enthalpy increases (equation 1).

$$P(x \rightarrow x') = \begin{cases} e^{-\Delta H/kT} & \Delta H > 0 \\ 1 & \Delta H \leq 0 \end{cases} \quad (1)$$

The absence of a pre-exponential factor to take into consideration the attempt frequency and activation energy shows that this algorithm does not simulate exact microscopic behaviour. However, provided that this factor is independent of local atomic configuration, and is the same for both species, it simply scales the time and so can be ignored. Moreover, inclusion of a pre-exponential factor would necessitate many millions of steps in which no swaps were accepted and unnecessarily increase the required computing power. Direct swapping of nearest neighbour atoms is unphysical in that phase separation is more accurately represented by vacancy diffusion. However, the two methods produce similar results provided that the vacancy migration attempt frequency is independent of local atomic configuration [8]. In this paper, only direct swapping of atoms has been considered because introducing a vacancy to the simulations also necessitates introducing unknown 'vacancy-atom' interactions.

The precise choice of interaction energies will determine the mode of phase transformation. If like bonds are more favourable than unlike bonds, the alloy will tend to phase separate at temperatures and concentrations within the miscibility gap (Fig. 2). As the alloy temperature is increased, the probability of accepting an 'unfavourable' swap increases and so the width of the miscibility gap decreases. At high temperatures the alloy tends towards a random solid solution. If unlike bonds are favoured, ordering will occur. In many alloys, interactions between atoms further apart are important. The choice of interaction energies for each of the three phase transformations reviewed in this paper will be discussed in the relevant sections. The phase diagram will depend on the choice of interaction parameters, but can easily be determined by simulation and matched to the alloy phase diagram.

Time in the model is defined in terms of Monte Carlo steps (MCS). If there are N atoms in the simulation then one MCS corresponds to N attempted swaps. Time in the model is directly proportional to real time assuming that the vacancy concentration in the real alloy is constant. The constant of proportionality is most easily determined by matching microstructural parameters such as the scale between experimental data and model data.

4. Spinodal Decomposition in Fe-Cr alloys

4.1 Introduction

In a spinodal alloy there is no thermodynamic barrier to phase separation [9]. Any random fluctuations in local composition reduce the free energy and will therefore be amplified. Spinodal decomposition in the ferrite phase of duplex stainless steels increases the alloy hardness and can lead to an increase in the ductile-to-brittle transition temperature. Since these alloys are used for heavy engineering applications such as the cooling pipes in pressure vessel reactors, it is important to be able to predict the development of phase separation and, from that, the resulting change in physical properties. During decomposition the atoms in the ferrite unmix to form a fine scale microstructure consisting of Fe-rich and Cr-enriched veins. The Fe-Cr is an ideal system to study because it is a model alloy for the ferrite phase of duplex stainless steels and because its phase diagram is similar in shape to the dynamic Ising model miscibility gap as shown in Fig. 2 [10-13]. The only competing phase transformation is the sluggish formation of sigma phase which can be ignored. Moreover the lattice mismatch is small and so it is not necessary to consider the effect of lattice strain in the computer model.

4.2 Experimental Alloys

An Fe-45%Cr alloy was made from high purity elemental Fe (>99.99% purity) and Cr (>99.996% purity) by arc-melting in a dry argon atmosphere. Wires of diameter 0.25 mm were fabricated from the master ingot by swaging and wire drawing operations. The wires were then solution treated in argon (0.4 atm) for 2 h at 1273K, water quenched and isothermally aged at 773 K for various times up to 500 h and water quenched. Each specimen was analysed in a position-sensitive atom probe (PoSAP).

The change in microhardness as a function of ageing time was determined from the ends of the wires with the use of a Shimadzu hardness tester with a 200 g load. An increase in hardness from 210 to 470 VHN was observed clearly demonstrating that a phase transformation was occurring [14]. Fig. 3 shows reconstructions of the Cr-enriched regions from PoSAP analyses. As thermal ageing proceeds the scale of the Cr-enriched and Fe-rich regions increases. After 500 h of ageing at 773 K the mean width of the domains had increased to approximately 5 nm.

4.3 Simulations

On a bcc lattice, the six second nearest neighbours are not much further away than the eight nearest neighbours and they are poorly screened. Therefore both first and second nearest neighbour interactions must be used, and weighted according to how the interatomic potentials vary as a function of distance (s). In the 3d transition metals, the binding potential falls approximately as s^{-5} [15]. In the simulations of spinodal decomposition in Fe-Cr second nearest neighbours interactions were therefore weighted by a factor of 0.5.

Because the Fe-Cr phase diagram is slightly asymmetric, simulations were performed on an A-50at.%B lattice. Temperature was introduced into the dynamic Ising model simulations by setting the critical temperature to that observed in the Fe-Cr system (~ 900 K). Simulations were performed on a bcc grid ($80 \times 80 \times 80$ lattice units) with both first and second nearest neighbour interactions for times up to 10,000 MCS at 750 K. For the time scales examined in this paper the development of phase separation was not influenced by the simulation size.

Isosurface reconstructions are shown in Fig. 4 from the dynamic Ising model. The volume shown is a cylindrical sub-volume of the simulation which has approximately the same dimensions as analysed during a typical PoSAP experiment. As the simulation proceeds, the scale of the microstructure gradually increases.

4.4 Discussion

The development of scale with ageing from both the experimental data and simulations was determined using the zero crossing point and first minimum of the three-dimensional autocorrelation function [16]. The first minimum of the autocorrelation function is a measure of the mean domain width or half of the mean distance between domains. The results, shown in Fig. 5, indicate that in both cases no incubation period exists before the onset of phase separation. Moreover the autocorrelation analyses suggest that a time scaling regime for the development of domain size exists. A best fit to the experimental results yielded a time exponent of 0.22 ± 0.05 . The dynamic Ising model results fitted a power law relationship with a time exponent of 0.25 ± 0.02 which is within the error bounds of the experimental results and demonstrates the linear relationship between real time and MCS during the time regimes studied. In contrast, simulations using Cahn-Hilliard-Cook model [16] for spinodal decomposition predict that a dominant wavelength will form during the early stages of decomposition, followed by a coarsening regime in which power law behaviour is observed with a time exponent close to the value of $1/3$ predicted by the LSW theory for the coarsening of isolated precipitates [17, 18].

The concentration amplitude of the phase separation (concentration difference between the Fe-rich regions and Cr-enriched regions) was analysed as a function of time for both the experimental results and the dynamic Ising model. In both, the concentration amplitude was observed to increase with ageing. In order to make a comprehensive comparison between experimental data and computer simulated results, the limitations of the experimental method must be taken into account. The concentration amplitude as a function of mean domain width (first minimum of the autocorrelation function) for the dynamic Ising model correction for the finite detector efficiency and spatial resolution is shown in Fig. 6 [14]. A fairly good correlation with the experimental data is achieved, demonstrating that the dynamic Ising model not only models the kinetics of domain growth but also the development of domain concentration in the Fe-Cr system.

5. Nucleation and Growth in dilute Cu-Co alloys

5.1 Introduction

A random solid solution outside the spinodal limits but within the miscibility gap is metastable and may phase separate by nucleation and growth [9]. Small composition fluctuations are unstable and will decay, however it is energetically favourable for a sufficiently large second phase nucleus to grow. Conventionally, the free energy of the nucleus is considered to consist of a favourable volume term, due to the bonding between like atoms and an unfavourable surface term due to bonding across the interface. When the precipitates are small, the surface term dominates and the precipitates are unstable. However above a critical size, the volume term will dominate and the precipitates will tend to grow. The nucleation barrier is the free energy required to form a nucleus of critical size at which stage the precipitate is equally likely to grow or shrink. In practice the

transition between spinodal decomposition and nucleation and growth is blurred because near the spinodal limits both the critical size and nucleation barrier are small.

The copper-cobalt system has been widely studied as a model for nucleation and growth [19, 20]. It exhibits a very wide miscibility gap with no intermediate phases [21]. The thermodynamics are well established and because the solid solubility limits at low temperatures are so small, dilute copper cobalt alloys nucleate almost pure cobalt particles. The precipitates are characterised by coherency, approximately spherical shape, and a lattice mismatch of less than 2%. In continuum models for phase separation the free energy is treated as a Lyapunov function. Continuum models can therefore never predict nucleation, because the free energy cannot increase. In contrast the diffusional changes in the dynamic Ising model occur through a *stochastic* algorithm involving only the probability of atomic exchanges. Therefore, in the dynamic Ising model, nucleation barriers can be traversed and the probability of overcoming a nucleation barrier decreases with increasing barrier size.

5.2 Alloys and Heat Treatments

The Cu-1.0%Co alloys had been prepared from oxygen-free high purity copper (5N) and electrolytic grade cobalt (4N) and homogenised at 1273 K for 48 h. The alloys were then directly quenched in a salt bath heated to the ageing temperature of 723 K and held for times up to 24 h before final water quenching. The alloys were then analysed in a position-sensitive atom probe. A series of atom maps showing the distribution of cobalt atoms observed from atom probe analyses of each specimen is shown in Fig. 7. In the earliest stages (10 min), the distribution of cobalt atoms appears to be random. After 0.5-1 h, regions clearly enriched in cobalt can be seen. After 24 h, approximately spherical precipitates 1.5nm in diameter containing over 90%Co have formed.

5.3 Dynamic Ising Model

In the Cu-Co system, both the Cu and Co-rich phases adopt a face centred cubic (fcc) lattice. In this system each atom has 12 nearest neighbours which effectively screen the second nearest neighbours. Simulations have therefore been performed using only nearest neighbour interactions. The phase diagram for the Cu-Co system is not as simple as that of Fe-Cr, due to an intervening eutectoid reaction, so matching with the Ising model is not as straightforward as for Fe-Cr. Instead, a temperature calibration can be obtained by comparing the solid solubility of cobalt from the model with experimentally determined data for the alloy. Solubility data from the copper rich side of the Cu-Co phase diagram are shown in Fig. 8a. The data have been fitted to a sub-regular solution model and extrapolated down to 723 K to estimate the solid solubility at the thermal annealing temperature of the experimental alloys. The equivalent section of the dynamic Ising model phase diagram is shown in Fig. 8b together with the phase boundary predicted by the mean field model. At low solid solubilities, the mean field is a good approximation to the Ising model because the effect of clustering outside the miscibility gap is small. A direct comparison

between Figs. 8a and 8b reveals that the appropriate interaction parameter divided by $kT \left(\frac{\epsilon}{kT} \right)$ is 1.178 for the dynamic Ising model simulations of Cu-Co at 723 K. Simulations have been performed on a fcc lattice containing 100x100x100 unit cells for a Cu-1.0%Co alloy aged at 723 K.

5.4 Discussion

The results of the simulation are shown in Fig. 9. In each part, the distribution of cobalt atoms from a subsection of the simulation corresponding to volume of 15x15x20 nm is displayed. A comparison with the experimental results in Fig. 7 shows that in both small concentration fluctuations form from an initially random solid solution and that after 30000 MCS, the cobalt clusters in the model are approximately the same size as observed in the experimental alloy after ageing for 24 h.

The matrix cobalt concentration and particle density from the experimental results and model are shown in Figs. 10a and 10b, respectively. Any cluster of cobalt atoms larger than 10 was taken to be a particle and used to calculate the cluster density. All remaining cobalt atoms were assumed to be in the matrix and used to calculate the matrix concentrations. During the nucleation regime, the matrix concentration remains approximately constant and the cluster density increases. After approximately 2000 MCS, coarsening begins to dominate and so both the cluster density and matrix concentration decrease. The experimental results show similar behaviour. The observed

peak cluster density of $8 \times 10^{24} \text{ m}^{-3}$ agrees well with the value of $2 \times 10^{24} \text{ m}^{-3}$ given by the simulation. Two further simulations were performed at temperatures of 673 K and 773 K on a Cu-1.0%Co alloy. The distribution of cobalt clusters at peak cluster density is shown in Figs. 11a and 11b, respectively. Reducing the temperature increases the supersaturation and reduces the critical nucleation size. As a result, many critical nuclei form and grow. At higher temperatures, the reduced supersaturation reduces the probability of forming critical nuclei. Furthermore, once a critical nucleus has formed and begins to grow, the matrix becomes further depleted in solute. A comparison between Fig. 11 and experimental results at peak cluster density (Fig. 7a) indicates that the energy parameter determined for use in the dynamic Ising model was approximately correct.

The results show that this simple model can reproduce an incubation period, nucleation barrier and Ostwald ripening which we expect to see in homogenous nucleation and growth. Moreover, a good quantitative agreement for cluster densities, matrix concentration and mean cluster sizes was observed. The match would appear to support the view that short-range interactions are sufficient in modelling this alloy system.

6. Conditional Spinodal in Ti-15%Al

6.1 Introduction

The pressure to improve the efficiency of aerospace engines has led to a considerable research effort in the understanding of low density Ti-Al based alloys. For instance, the composition of near- α Ti alloys has been optimised for creep and fatigue strength by the addition of elements such as Sn, Zr, Mo, Ni, Si and C. One method of maximising the strength of these alloys is to allow limited formation of the ordered Ti_3Al α_2 phase to occur [4, 22]. Diffraction studies show superlattice reflections before clear microscopic evidence of phase separation which suggest that a conditional spinodal (i.e. concurrent ordering and decomposition) [23] mechanism may be involved. Since the phase transformation is driven by atomistic diffusion and ordering occurs rapidly, the conditional spinodal in near- α Ti-Al alloys is a further type of phase transformation suitable for study using the dynamic Ising model.

6.2 Implementation of the Dynamic Ising Model

In the simulations of spinodal decomposition in Fe-Cr and nucleation and growth in dilute Cu-Co alloys, only a single energy parameter was required to define the miscibility gap. In both, phase separation occurred because the bonds between like atoms were more favourable than those between unlike atoms. However, a single interaction parameter is not sufficient to predict a conditional spinodal on a hexagonal close packed (hcp) lattice, therefore, determining the range and strength of interactions is an important issue. First principles calculations using the full-potential linear muffin tin orbital method [24] have been used to calculate the heat of formation of Ti-Al hcp super-structures at zero temperature [25, 26]. From these, volume-dependent effective cluster interactions (ECIs) can be defined which parameterise the total energy of any Ti-Al structure [25, 26]. Only nine clusters (including the empty cluster) were needed to accurately characterise the formation energies of the hcp structures predicted by ab initio calculations [26]. Third and fourth neighbour pair interactions are not important, but linear triplets and clusters containing first and second-nearest neighbour pair interactions are important. Since the range of volumes observed in Ti-Al alloys is not too great the volume dependence of the ECIs can simply be expanded to a quadratic form on the average atomic volume [27]. In theory, after each swap an energy minimisation should be performed to calculate a more accurate value of the average atomic volume. However, it is found in practice that performing the minimisation after each MCS is sufficient during the early stages and less frequent energy minimisations are required during the later stages of phase separation as the mean atomic volume of the alloy tends towards its equilibrium value.

6.3 Simulations

Simulations have been performed by quenching a random solid solution containing 15 at. %Al in to a supersaturated state at 700 K that can decompose to give a two phase microstructure consisting of a coherent ordered Ti_3Al α_2 phase and a disordered α phase [28]. The DO₁₉ structure of the α_2 phase is shown in Fig. 12. Each unit cell contains 2 Al atoms and 6 Ti atoms. There are four possible positions for the pair of aluminium atoms within the unit cell as shown in Fig. 11. The simulations were performed on a 200x200x100 regular hcp lattice with periodic boundary conditions.

6.4 Data Analysis

Several parameters need to be defined to enable the development of microstructure to be characterised. An ordered site is defined as either an aluminium atom surrounded by 12 titanium atoms or a titanium atom surrounded by 8 other titanium atoms and 4 aluminium atoms as shown in Fig. 12. A random solid solution contains ordered sites, however these do not constitute second phase ordered domains. To make the distinction, a working definition was used in which ordered domains (Ti_3Al) were defined as 10 or more adjacent ordered sites. Since any sites not belonging to an ordered region are considered to be matrix, it is possible to calculate the short range order in the matrix as

$$\text{SRO} = \frac{\text{Observed Ordered Sites in Matrix} - \text{Ordered Sites Expected in Random Solid Solution}}{\text{Maximum Ordered Sites in Matrix} - \text{Ordered Sites Expected in Random Solid Solution}}$$

In the analysis of spinodal decomposition in Fe-Cr and nucleation and growth in Cu-Co alloys, parameters such as domain concentration, scale and cluster density could be defined. The corresponding parameters for studying a conditional spinodal reaction are matrix concentration, and size and number density of ordered domains.

6.5 Results

Some ordered sites exist in the random solid solution immediately following the quench (Fig. 13a). Many of these act as nucleation sites for ordered domains. During the first MCS, the rapid increase in SRO is shown by the increased number of ordered sites (Fig. 13b) and the increase in the matrix SRO parameter from 0 to ~0.07 (Fig. 15). During the next four MCS, the matrix SRO parameter continues to increase as local rearrangements form many more ordered sites. At this stage there are only a few ordered domains and so the matrix concentration remains near the alloy composition (Fig. 15) and there is only a small increase in the mean cluster size (Fig. 14). The matrix SRO reaches a maximum after ~7 MCS. On further ageing up to 20 MCS, the mean size of the ordered domains begins to increase and there is a dramatic increase in the number density of ordered domains (Fig. 14). By this stage, the reduction in matrix solute concentration is apparent, reducing the supersaturation and therefore there is a rapid decrease in the rate of formation of new ordered regions. On further ageing, ordered domains grow in size and may begin to impinge upon each other. If the neighbours have the same orientation then the free energy will be reduced if they coalesce to form a larger ordered domain. If they have a different orientation then an APB will form. The result is a rapid increase in mean domain size and the formation of a ramified interconnected structure. Ostwald ripening behaviour is observed on further ageing as larger ordered domains grow at the expense of smaller ordered domains and the interface area between matrix and α_2 is reduced.

6.6 Conclusions

The simulations on Ti-15at.% Al quenched into the α - α_2 region predict the rapid development of SRO with no large scale composition modulations. Rapid growth in the ordered domains occurs when neighbouring domains begin to coalesce to form a complex interconnected microstructure. The simulations correspond only to the earliest stages of phase separation. After 400 MCS, the mean domain width is only 5 nm.

7. Summary and Conclusions

The position-sensitive atom probe technique is unique in giving three-dimensional real space compositional information on a sub-nanometre scale. The experimental results clearly demonstrate that important concentration variations can exist on a scale of only a few lattice spacings where the definition of a coarse-grained composition parameter becomes difficult. However, the small scale of the concentration variations makes these systems ideal for study using atomistic models.

The dynamic Ising model has been implemented to simulate three phase transformations: spinodal decomposition, nucleation and growth, and a conditional spinodal reaction. In each case the kinetics predicted by the dynamic Ising model have been analysed. Modelling spinodal decomposition in Fe-Cr was achieved by selecting the critical energy parameter of the model so that the miscibility gap from the model matched the Fe-Cr phase diagram. Modelling nucleation and growth in Cu-1.0%Co alloys was achieved by ensuring that the supersaturation in the model matched the supersaturation in the experimental alloy. More complex interaction potentials for the

conditional spinodal reaction in Ti-15%Al were obtained from published first principles calculations.

Despite the simplicity of the algorithm, the dynamic Ising model predicts the correct kinetics of phase separation for spinodal decomposition in Fe-Cr and shows that there is a linear relationship between real time and MCS. The dynamic Ising model also predicts the various phenomena observed during homogeneous nucleation and growth and there was good quantitative agreement with the experimental results from Cu-1.0%Co alloys. The model predicts a conditional spinodal reaction in Ti-15%Al alloys at low temperatures. An analysis of the results shows the rapid development of SRO with no large-scale composition modulations followed by growth of ordered regions to form a complex interconnected microstructure. On further ageing, large ordered domains grow at the expense of smaller ordered domains and form equiaxed ordered regions.

With suitable choices of interaction potentials it should be possible to model other, more complicated, alloy systems and, with improvements in computational algorithms it will be possible to study later stages of phase separation.

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FIGURES.

Fig. 1 Position-sensitive atom probe microanalysis of the ferrite phase in a CF3 duplex stainless steel aged for 10^4 hours at 400°C . In (a), each sphere represents the position of a Cr atom located within a slice of material 2nm in depth. In (b) the shaded regions represent those areas enriched in Cr. The volume of material analysed is 15 nm in diameter and 10 nm deep.

Fig. 2 The solid state miscibility gap in the Fe-Cr phase diagram. The dotted lines represent thermodynamic calculations and the symbols are from experimental investigations. The solid line is from the dynamic Ising model with a critical temperature of 900 K.

Fig. 3 Isosurface reconstructions from PoSAP analyses showing the morphology of the Cr-enriched regions from an Fe-45%Cr alloy after thermal ageing at 773 K for (a) 24 h, (b) 100 h and (c) 500 h.

Fig. 4. Isosurface reconstructions showing the developing Cr-enriched regions from the dynamic Ising model of spinodal decomposition in an A-50%B alloy aged at 750 K for (a) 10 MCS, (b) 100 MCS, (c) 1000 MCS and (d) 10000 MCS.

Fig. 5. Development of microstructural scale during spinodal decomposition determined from (a) PoSAP analysis of an Fe-45%Cr alloy and (b) dynamic Ising model of an A-50%B alloy.

Fig. 6. Development of composition amplitude as a function of microstructural scale for both the PoSAP results and dynamic Ising model.

Fig. 7. PoSAP atom map distributions for a Cu-1.0%Co alloy, showing the development of cobalt clusters with ageing at 723 K for (a) 30 min, (b) 2 h and (c) 24 h.

Fig. 8. Fits using the sub-regular solution model to (a) the experimentally determined solid solubility of Co in Cu at low temperatures and (b) the dynamic Ising model.

Fig. 9. Atom maps showing the positions of cobalt atoms from a $15 \times 15 \times 20 \text{ nm}$ section of a dynamic Ising model simulation of a Cu-1.0%Co alloy thermally aged at 723 K for (a) 600 MCS (b) 1200 MCS (c) 29000 MCS.

Fig. 10. Development of matrix composition and cluster density from (a) PoSAP analyses of thermally aged Cu-1%Co specimens and (b) dynamic Ising model simulation of nucleation and growth in Cu-1%Co alloys at 723 K.

Fig. 11. Atom maps showing the distribution of Co atoms at peak cluster density from dynamic Ising model simulations at (a) 673 K (1000 MCS) and (b) 773 K (5000 MCS).

Fig. 12. Structure of the α_2 phase (DO19). The unit cell consists of 2 Al atoms (dark spheres) and 6 Ti atoms (light spheres). Equivalent configurations could be achieved with the Al atoms positioned on the sites marked B, C or D.

Fig. 13. $20 \times 20 \times 20$ section of a simulation showing the development of ordered regions at 700 K after ageing (a) as quenched, (b) 1 MCS, (c) 4 MCS, (d) 15 MCS, (e) 60 MCS and (f) 240 MCS.

Fig. 14. Increase in mean ordered domain size and development of ordered domain density as a function of ageing.

Fig. 15. Decrease in matrix concentration and development of matrix SRO as a function of ageing.

a)

b)

5 nm

Fig. 1

Fig. 2.

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Fig. 3

Fig. 4

Fig. 5.

Fig. 6.

Fig. 7

Fig. 8

Fig. 9

Fig. 10

a)

b)

Fig. 11

Fig. 12

Fig. 13

Fig. 14.

Fig. 15.