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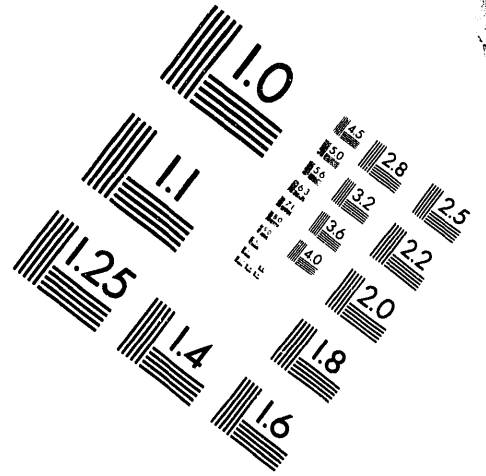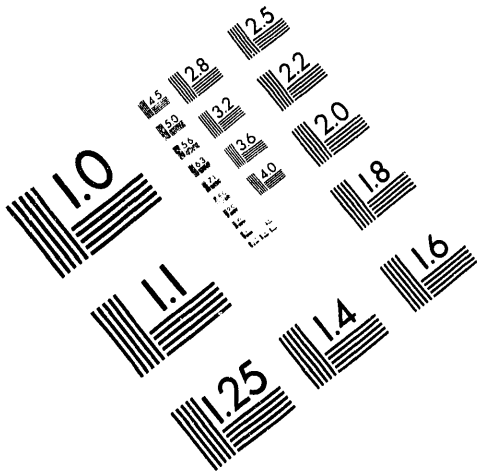
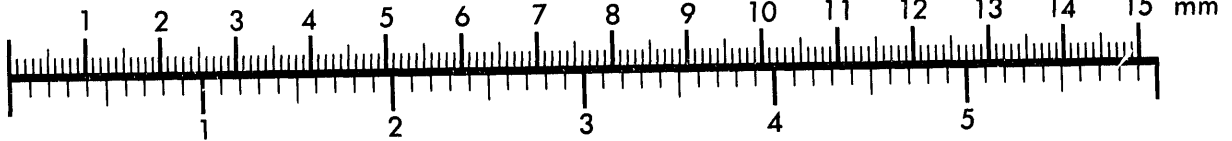**Association for Information and Image Management**
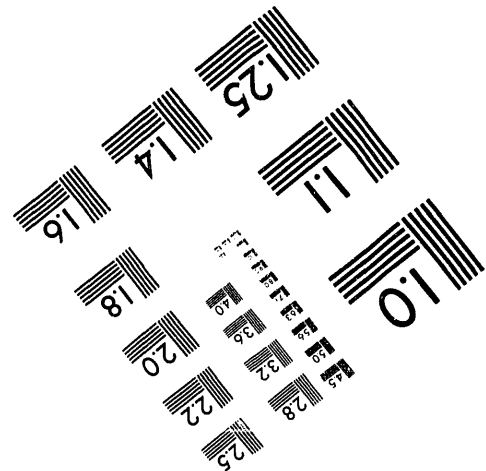
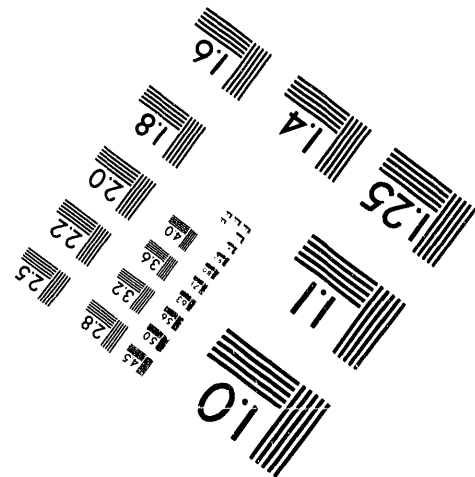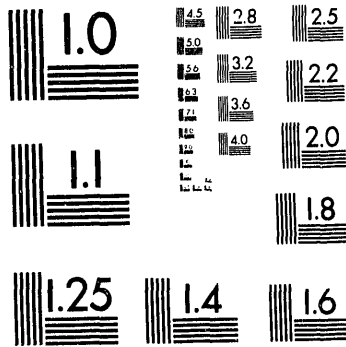1100 Wayne Avenue, Suite 1100
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DYNAMICAL ISING MODEL SIMULATIONS OF NUCLEATION AND GROWTH IN COPPER-COBALT ALLOYS

ALFRED CEREZO*, JONATHAN M. HYDE*, MICHAEL K. MILLER**, ROHAN P. SETNA* AND GEORGE D. W. SMITH*
*Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, U.K.
**Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6436.

ABSTRACT

A simple dynamical Ising model on a fixed lattice with a single bond energy parameter has been used to simulate the kinetics of diffusion during solid-state phase transformations in binary metallic alloys. The results of these simulations are compared with direct real-space measurements of the atomic distributions of elements in alloys, obtained with the position-sensitive atom probe. Despite the simplicity of the model, there is good quantitative agreement between the development of microstructure in the simulation and the nucleation and growth of cobalt-rich precipitates in copper-cobalt alloys.

INTRODUCTION

When an alloy is aged at temperatures below the solvus, it is possible for phase separation to occur by a process of diffusion. Conventional theories of diffusional phase transformations are based on continuum models, an approach which appears reasonable given the number of atoms in even a modest amount of material.[1, 2] However, advances in microscopy and microanalysis have extended the study of phase decompositions to the earliest stages, when composition fluctuations are on the scale of only a few atomic spacings. In many engineering alloys, important properties result from microstructural features on the nanometre scale, generated by phase separation during heat treatment. Understanding the early stages of phase decomposition is therefore important not only at a fundamental level, but also for predicting the long-term stability of engineering alloys and in the design of new materials. At these size scales, continuum representations of the composition variations are no longer valid, and this leads to a breakdown of conventional models in predicting the kinetics of the reactions. This paper describes a statistical, atomic-scale simulation of the ageing of materials, using a dynamical Ising model. The modelling work is being performed in conjunction with an experimental programme of atomic-scale studies of the early stages of phase transformations, using ultra-high spatial resolution atom probe field-ion microscope (APFIM) techniques [3, 4]. With APFIM microanalysis, composition-depth profiles can be obtained with 1-2nm lateral resolution, and a depth resolution of a single atomic layer. In a more recent variant of the technique, the position-sensitive atom probe (PoSAP) [5], this microanalysis capability is extended to a full three-dimensional reconstruction of the distribution of atoms originally present in a volume approximately 20nm x 20nm x 20nm in the solid, with sub-nanometre spatial resolution. It is now possible to make direct comparisons between the results of simulations and the atomic-scale chemical measurements.

DYNAMICAL ISING MODEL

The simulation of a binary alloy uses a fixed lattice to represent the positions of both types of atoms in the material. An appropriate lattice type is used to match the material being modelled (body-centred cubic for iron-chromium alloys, face-centred cubic for copper-cobalt) although it is found that the results for the simulation of spinodal decomposition are not affected by the choice of lattice type. A typical simulation would use a crystal of either $50 \times 50 \times 50$ or $100 \times 100 \times 100$ unit cells. The crystal is then 'aged' by random nearest neighbour exchanges (Kawasaki dynamics). The probability of two atoms being swapped is related to the change of energy, ΔH. In the simple model, the energy of the crystal is defined only in terms of nearest

neighbour bonds, but second nearest neighbour bonding has also been used in the modelling of the body–centred cubic lattice in iron–chromium alloys. The exchange probability used is the Metropolis algorithm: [6]

$$P(X_i \rightarrow X_{i+1}) = \begin{cases} 1 & \Delta H \leq 0 \\ e^{-\Delta H/kT} & \Delta H > 0 \end{cases}$$

The use of a swapping algorithm means that ΔH is always a integral multiple of $2E_{ab} - E_{aa} - E_{bb}$, where E_{ab}, E_{aa}, and E_{bb} are the bond energies between an A–B pair of atoms, between two A atoms and between two B atoms respectively. This leaves only a single energy parameter in the model:

$$\alpha = \frac{2E_{ab} - (E_{aa} + E_{bb})}{kT}$$

The value of this parameter for a given simulation is obtained by comparing the phase diagram of the Ising model with that of the alloy system being modelled, thus providing a temperature scale for the model. In alloys with simple miscibility gaps, the phase diagram of the Ising model (which represents a regular solution) can be directly matched. Iron–chromium has a particularly simple phase diagram at low temperatures, with a wide miscibility gap and a clear spinodal. At higher temperatures there is also a sluggish sigma phase reaction, not seen in most circumstances, but it is possible to predict the phase diagram in the absence of this reaction by using a thermodynamic modelling package such as the ThermoCalc database [7]. The critical parameter of the Ising model, $\alpha = 0.625$, is equated with the critical temperature of $T_c = 900$ K calculated for the alloy in this way. Any other ageing temperature can be simulated in the model by scaling the value of α accordingly. This model has been found to provide a very good fit to PoSAP data on the spinodal decomposition in Fe–Cr alloys aged at 773 K [8].

NUCLEATION AND GROWTH

Just as the iron–chromium system represents a good model alloy for the study of spinodal decomposition, cobalt alloys have been widely used for studies of nucleation and growth processes. A thorough review of the data on the early stages of precipitation in copper–cobalt alloys, and a number of other systems, has been given by Aaronson and LeGoues.[9] The phase diagram for the copper–cobalt system is not as simple as that of iron–chromium, due to an intervening eutectoid reaction, so matching with the Ising model is not so straightforward.
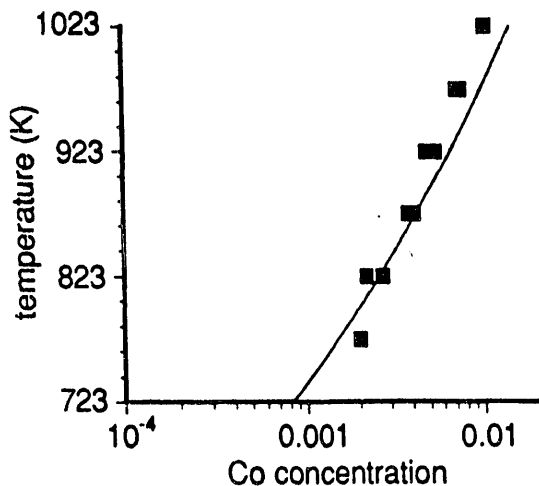

Figure 1. Experimental solubilities for cobalt in the copper–cobalt system, from the work of Nishizawa and Ishida (points) together with the fit to this data using a sub-regular solution model (curve).
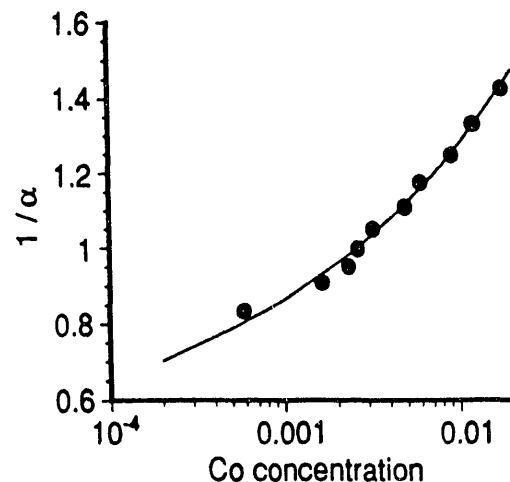
Figure 2. Phase diagram for the dynamical Ising model for a face–centred cubic lattice (points) and the phase diagram predicted using a mean–field approximation (curve).

Although it is possible to predict the critical temperature in the absence of the eutectoid, the available solubility data does not match a regular solution model. It is not therefore possible to provide a direct temperature scaling of α on the basis of the critical temperature for copper–cobalt. Instead, a temperature calibration can be obtained by comparing the solid solubility of cobalt from the model with that which is experimentally observed for the alloy. Solid solubility data for the copper–rich side of the copper–cobalt phase diagram is shown in figure 1, from the work of Nishizawa and Ishida.[10] By fitting this data to a sub–regular solution model, it is possible to extrapolate the solid solubility of cobalt to lower temperatures (as shown by the line in figure 1). The equivalent section of the phase diagram for the Ising model is shown in figure 2, compared with the phase boundary expected in the regular solution model using the mean field approximation. Although the mean field approximation does not match the behaviour of the Ising model at high concentrations, due to the non–randomness introduced by clustering above the miscibility gap, the fit is good at these low concentrations. In the sub–regular model [1], the binding between atoms effectively varies as a function of temperature, so that α no longer scales as $1/T$ in a simple manner. Nonetheless the solid solubility does provide a direct correlation, so that at 723 K (at which temperature the solubility of cobalt in copper is 0.082 at.%) $\alpha=1.178$ from the Ising model, and for the mean–field approximation $T/T_c = 0.281$ and $\alpha=1.186$. This value for the energy parameter can be used to make an estimate for the effective surface energy within the model, from a bond–breaking argument. On a (100) surface between pure A and B phases there would be four A–B bonds per interface atom, each bond contributing $\alpha/2$ to the internal energy. The interface energy on this basis, without taking excess entropy into account, would be 0.26 Jm^{-2}, which is in reasonable agreement with reported values of 0.19 Jm^{-2} and 0.165 Jm^{-2}.[11, 12]

The results of a simulation using $\alpha=1.178$ are given in figure 3, which shows the distribution of cobalt atoms in part of a modelled crystal of $100 \times 100 \times 100$ unit cells for a simulated Cu–1 at.% Co alloy. Each part of the figure shows a single snapshot in the ageing sequence, where the ageing times are given in Monte carlo steps (MCS). A single step has been performed when, on average, each atom has been selected once. For comparison, the cobalt distributions from the PoSAP analysis of Cu–1 at.% Co aged at 723 K for 10 minutes, 1 hour and 24 hours are shown in figure 4. It can be seen that the match between the simulation and the experimental results is good. In previous simulations by Chisholm and Laughlin, nucleation events had to be initiated by seeding the lattice in the model with cobalt clusters.[13] The need to do this was perhaps brought about by the use of a critical temperature (1680 K), calculated from a sub–regular solution model, which was inappropriate for the Ising model and gave a reduced level of supersaturation. A size effect is also observed at lower supersaturations, whereby a $50 \times 50 \times 50$ lattice aged with a parameter of $\alpha=1.0$ (supersaturation of 400%) will remain stable, whereas nucleation does occur in a $100 \times 100 \times 100$ lattice. This effect seems to be due both to the reduced number of cobalt atoms present in the smaller system, and the effect on the free energy of the system of a reduced matrix volume. Determination of critical nucleus sizes in the simulation are also made difficult by this effect, so that large lattices are essential if critical sizes are to be measured from the model.

The matrix cobalt concentration and cluster density from the simulation is shown in' figure 5. Any cluster of cobalt atoms larger than 10 was taken to be a particle, and used to calculate the cluster density, while the remaining cobalt atoms were assumed to be part of the matrix and used to calculate matrix composition. The simulation shows a clear change over between the nucleation regime, where the cobalt concentration in the matrix remains relatively constant and the cluster density increases, and coarsening, when the matrix cobalt level has decresed significantly and the cluster density decreases. Measurements of mean cluster sizes from the simulation show a similar change in behaviour. Up to 3000 MCS, the nucleation stage, the mean cluster diameter increases as $\sqrt{t}$., showing diffusion limited growth. After 3000 MCS, the diameter increases much more slowly ($t^{0.19}$) as the particles coarsen.

The variation of matrix composition measured by PoSAP analysis for the Cu–1 at.% Co alloy aged at 723 K for up to 24 hours is shown in figure 6. Also shown is the variation in measured particle density. The observed change in matrix composition follows a very similar curve to that obtained from the simulations, and shows that the 1 hour ageing at 723K, on the knee of the curve, is approximately equivalent to 1200 MCS in the simulation. The observed peak cluster density of $8 \times 10^{24} m^{-3}$ at this stage also agrees well with the value of $2 \times 10^{24} m^{-3}$ given by the simulation. Given the simple nature of the model, the agreement is remarkable. A mean cluster diameter of 1.5 nm measured after 24 hour ageing matches well with the value of
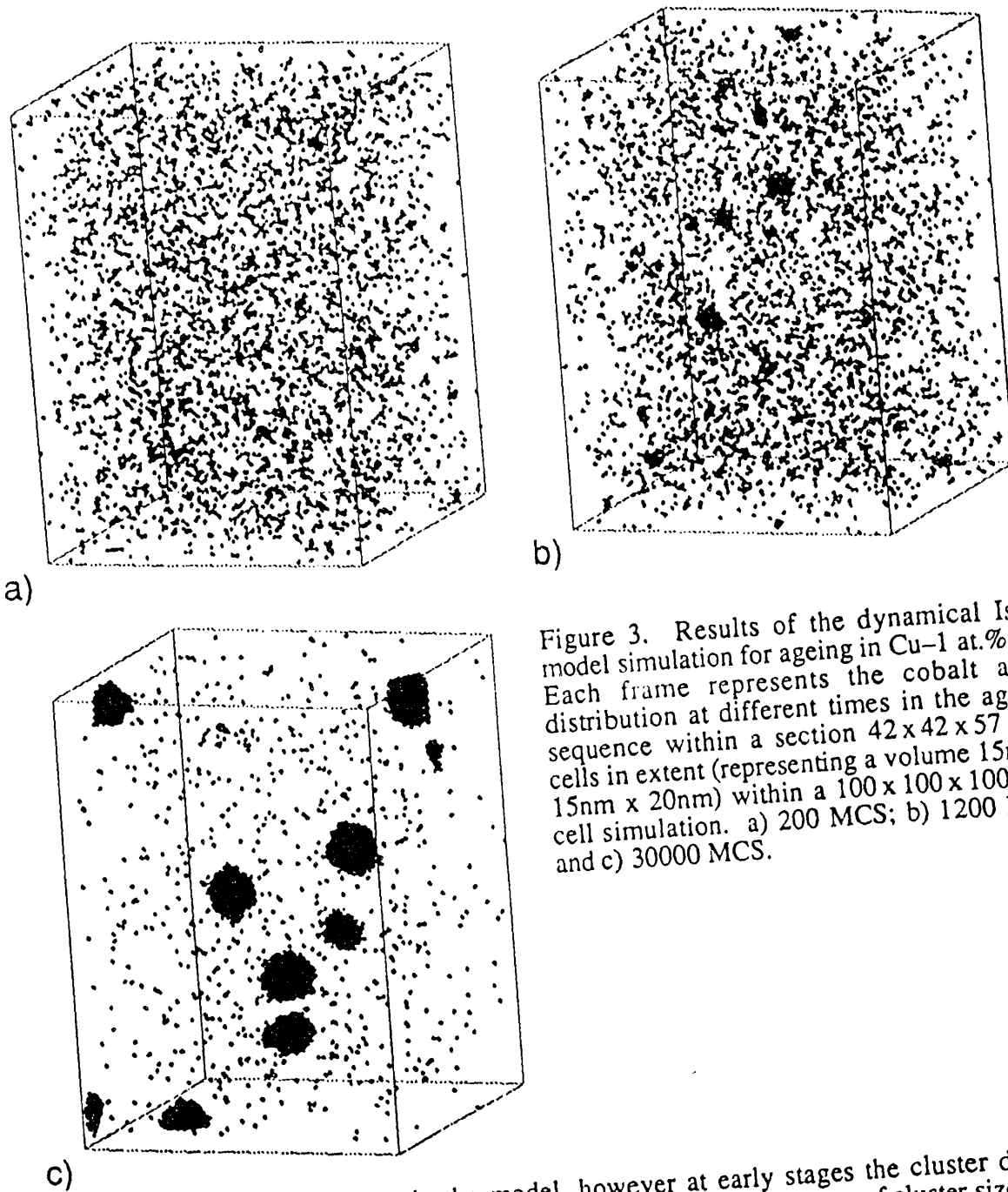
a)

b)

Figure 3. Results of the dynamical Ising model simulation for ageing in Cu–1 at.% Co. Each frame represents the cobalt atom distribution at different times in the ageing sequence within a section $42 \times 42 \times 57$ unit cells in extent (representing a volume 15nm x 15nm x 20nm) within a $100 \times 100 \times 100$ unit cell simulation. a) 200 MCS; b) 1200 MCS and c) 30000 MCS.

c)

2nm after 30000 MCS ageing in the model, however at early stages the cluster diameters measured from the PoSAP do not seem to fall below 1nm. Measurement of cluster sizes at 1nm or less using the PoSAP is made difficult by the presence of ion trajectory aberrations which limit the ultimate spatial resolution achieveable in the instrument.[4] However, this observation may also be further indication that diffuse clusters exist at the earliest stages of precipitation in copper–cobalt alloys.[9] Such diffuse clusters are not predicted in models with short range interactions, as are currently used in the dynamical Ising model shown here, but the technique has the ability to make use of more accurate *ab initio* interatomic potentials. Use of such potentials will help to clarify the issue of diffuse clustering in these alloys.

REFERENCES

1. J. W. Christian, The Theory of Transformations in Metals and Alloys, Part I (2nd Edition), Pergammon, Oxford, 1975.
2. Materials Science and Technology, Volume 5: Phase Transformations in Materials, (eds. R.W. Cahn, P. Haasen and E.J. Kramer), VCH, New York, 1991.
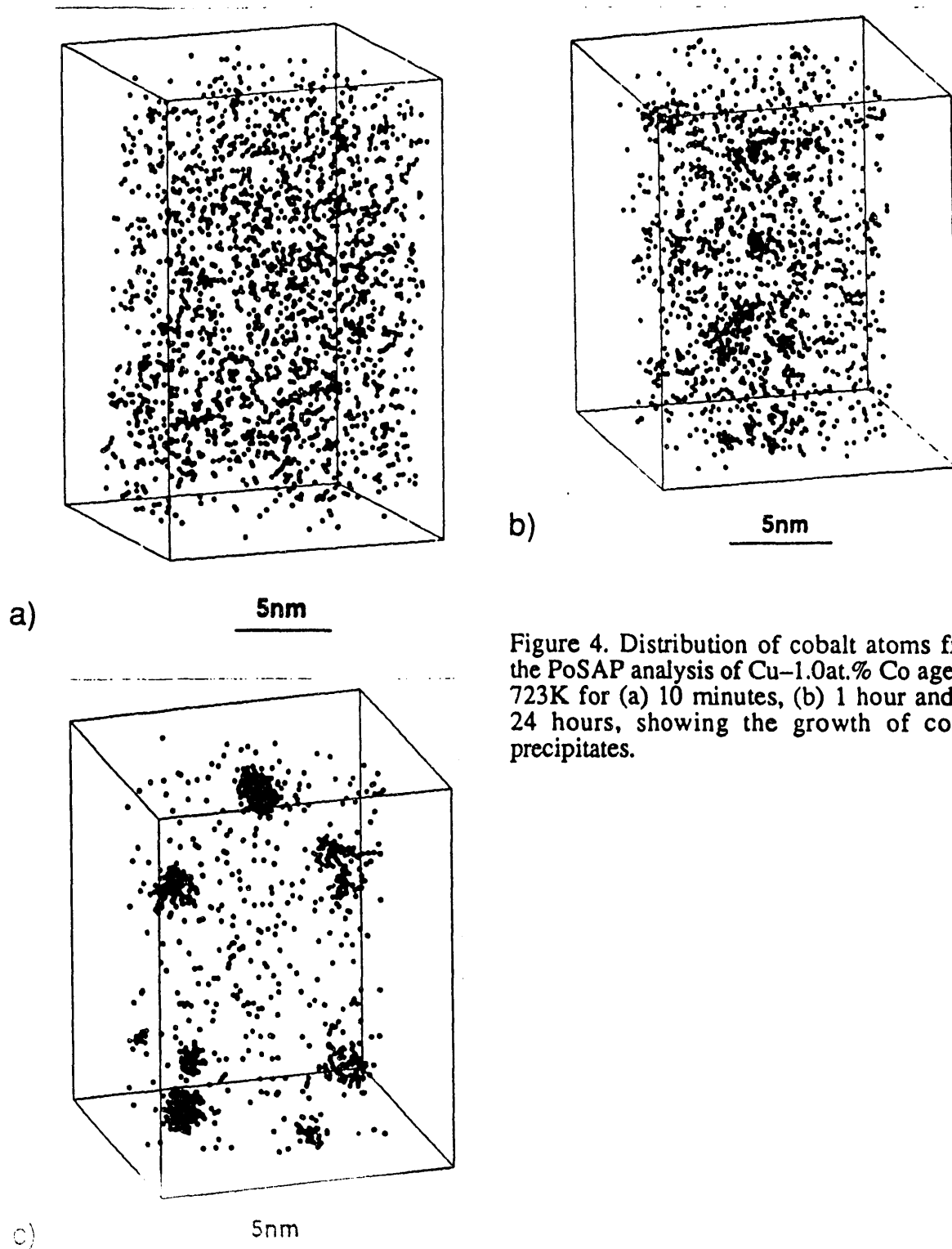
a)

5nm

b)

5nm

c)

5nm

Figure 4. Distribution of cobalt atoms from the PoSAP analysis of Cu–1.0at.% Co aged at 723K for (a) 10 minutes, (b) 1 hour and (c) 24 hours, showing the growth of cobalt precipitates.

2. Materials Science and Technology, Volume 5: Phase Transformations in Materials, (eds. R.W. Cahn, P. Haasen and E.J. Kramer), VCH, New York, 1991.
3. E.W. Müller, J.A. Panitz and S.B. McLane, Rev. Sci. Instrum. 39, 83 (1968).
4. M.K. Miller and G.D.W. Smith, Atom Probe Microanalysis: Principles and Applications in Materials Science (MRS, Pittsburgh, 1989).
5. A. Cerezo, T.J. Godfrey, C.R.M. Grovenor, M.G. Hetherington, J.M. Hyde, J.A. Liddle, R.A.D. Mackenzie and G.D.W. Smith, EMSA Bulletin 20, 77 (1990).
6. N. Metropolis, A.W. Rosenbluth, A.H. Teller and E. Teller, J. Chem. Phys. 21, 1087 (1953)
7. B. Sundman, B. Janson and J. Andersson, Calphad 9 (2), 13 (1985).
8. J.M. Hyde, A. Cerezo, M.G. Hetherington, M.K. Miller and G.D.W. Smith, Surf. Sci. 266, 370 (1992).
9. H.I. Aaronson and F.K. LeGoues, Met. Trans. A 23A, 1915 (1992).
10. T. Nishizawa and K. Ishida, Bull. Alloy Phase Diagrams 5, 161 (1984).
11. I. Servi and D. Turnbull, Acta Metall. 14, 161 (1966).
12. G.J. Shiflet, Y.W. Lee and H.I. Aaronson, Scripta Metall. 15, 723 (1981).
13. M.F. Chisholm and D.E. Laughlin, in Phase Transformations '87 (ed. G.W. Lorimer), Institute of Metals, London (1987), p.17.
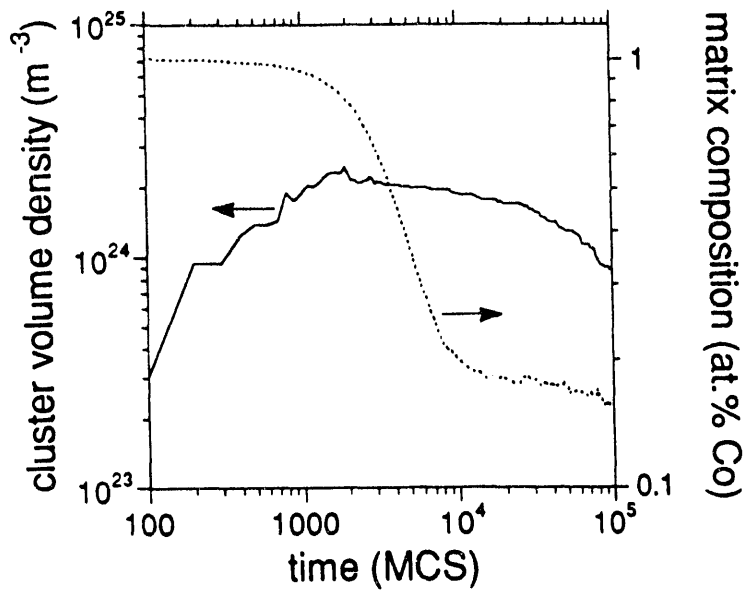
Figure 5. Variation in cluster density (solid curve) and matrix cobalt concentration (broken curve) for the dynamical Ising model simulation.
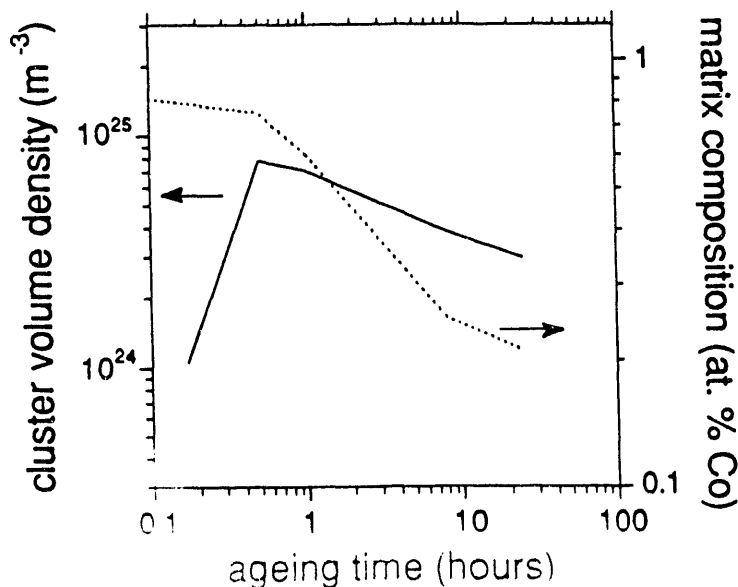

Figure 6. Measured cluster densities (solid line) and matrix cobalt concentrations (broken curve) from the PoSAP analysis of Cu–1.0 at.% Co aged at 723K.

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