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Influence of a magnetic field on the precipitation behaviour of nano-scale cobalt particles in a copper matrix

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ABSTRACT

The influence of a magnetic field on the microstructural evolution of nano-scale cobalt particles precipitated in a Cu–Co alloy during annealing at 973 K has been investigated using transmission electron microscopy (TEM). TEM observations revealed that an external field of $\sim$0.9 T accelerated precipitation and that the coherent–incoherent transition consequently occurred at an earlier time. The presence of the field, however, resulted in no significant change in the shape of the individual particles. A two-dimensional Monte Carlo simulation with the Ising spin model was also carried out to investigate the influence of an external magnetic field on the precipitation behaviour. These Monte Carlo simulations take both the chemical and magnetic interactions between solute atoms/clusters in the alloy into account, and successfully reproduced the qualitative features of the precipitation behaviour under a magnetic field seen in the experiments.

1. Introduction

A copper-based Cu–Co alloy has been investigated from the practical viewpoint of precipitation hardening in previous studies [1–3]. However, the focus of more recent work has been on the magnetic properties of dilute Cu–Co alloys, in the context of spin- or cluster-glass phenomena. Moreover, the discovery of giant magneto-resistivity (GMR) has invoked new scientific interest in the physical properties of fine magnetic particles formed in Cu–Co alloy (i.e., a granular magnetic material), not only from a fundamental but also from a practical point of view [4–8]. In previous studies [1–3] the precipitation behaviour of this alloy has been treated as a typical alloy, following a simple Ostwald ripening scheme. However, more detailed studies have revealed that the microstructural evolution proceeds with features differing from the conventional scheme [9–14]. It is widely recognised that the magnetic properties of nano granular magnetic materials are influenced by microstructural factors, such as the crystallographic structure, grain size, and distribution of nano-scale particles. Although a close correlation between the properties and the structure is expected, most past studies have dealt separately with the microstructure and the properties of solute particles. A few studies currently in progress are attempting to consider the relationship between the physical properties and the microstructure in detail. Our research team has investigated the microstructural evolution of Cu–Co alloy by transmission electron microscopy and by Monte Carlo simulations of the microstructures, and has pointed out the possibility that pairs of cobalt precipitates which appear in an isothermal annealing process form as an antiferro-coupling magnet [11,13]. Although previous research papers dealt with the precipitation phenomena of cobalt atoms in a copper alloy exclusively using elasticity theory [e.g., 15–17], cobalt particles may interact magnetically with other particles or atoms, since the Curie temperature of cobalt is much higher (approximately 1403 K [18]) than the annealing temperature. It therefore seems worth investigating in detail the relationship between microstructure and magnetic properties in Cu–Co alloys containing fine granular magnetic particles. We may conclude that microstructural evolution is subject to magnetic interaction with cobalt particles if the microstructure of the alloy is changed by application of a magnetic field. The present work particularly aimed at examining the influence of a magnetic field on the evolution of nano-granular ferromagnetic solute clusters formed in an alloy. For this purpose, we have carried out annealing experiments both in the presence of a magnetic field and with no applied field. We discuss the results of transmission electron microscopy observations, referring to Monte Carlo simulations to help elucidate the physical processes which occur in the precipitation process.

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2. Experimental

TEM observations: The alloy specimens used in this work were taken from a Cu–3at%Co alloy ingot. Disk-shape specimens (200 μm thick with a diameter of 30 mm) were punched out of polycrystalline sheets. Then the specimens were individually sealed in evacuated silica tubes. The tubes containing the alloy specimens were kept in a furnace at 1073 K for 3600 s. No magnetic field was applied during the solution treatment in this stage. After the solution treatment, the specimens were quenched in ice water. The specimens were subsequently annealed at 973 K for 3000 s, 6000 s, and 9000 s, respectively, under either (i) a zero magnetic field or (ii) an external magnetic field of approximately 0.9 T applied by an electromagnet. The influence of the magnetic field on the precipitation behaviour was experimentally studied using a 200 kV HITACHI H-800 transmission electron microscope.

Monte Carlo simulations: The Monte Carlo (MC) simulations which were carried out were based on a two-dimensional Ising spin model (Kawasaki dynamics), and were designed to consider qualitatively the influence of the magnetic field. The simulations employed the major framework of the calculation algorithm developed in our earlier study [19], but the ratio of the two spin states was altered in the initial distributions in order to take into account the influence of the magnetic field.

3. Results and discussion

TEM observations: Fig. 1 shows TEM images of the microstructure of the Cu–3at%Co alloy isothermally annealed at 973 K either with or without a magnetic field. To compare the evolution of the microstructure, TEM images were taken at three different annealing times: (a) 3000 s, (b) 6000 s, and (c) 9000 s. At the early stage of annealing at 3000 s, Fig.1(a), similar small coherent cobalt particles were observed in the specimens treated both with and without the field. At this stage of annealing, the sizes of the coherent cobalt particles that were formed in the presence of the field seemed to be only slightly larger than those observed in the specimens annealed with no applied field. The number density of the precipitates formed in the applied field also seemed to be only a little higher.

Thus, in the early stage of precipitation the effect of the applied field is not large, so that the field is not likely to have a potent effect on the nucleation of cobalt clusters. However, examination of the micrographs recorded at longer annealing times (Fig. 1 (b) and (c)) reveals a clear trend that growth of cobalt particles was accelerated by the external field. Moreover, the micrographs recorded at 9000 s shows that the particles annealed in the field, but not those annealed in the absence of the field, are now incoherent. Thus, the applied field has resulted in the coherent–incoherent transition occurring earlier.

Fig. 2 shows quantitatively the change in the mean radius of the cobalt particles with annealing time. The curve lying above corresponds to the mean radii of the precipitates formed in the applied field, while the curve below shows the mean radii of precipitates in specimens annealed without applying a field. In previous TEM observations of our research team, it was found that cobalt particles lost their lattice coherency to the copper matrix at a size larger than 60–70 nm [10]. Figs. 1 and 2 show that the coherent–incoherent transformation occurs at a similar size for precipitates under the field. This seems to be compatible with the fact that no shape difference was observed. Thus, the TEM observations led to the conclusion that the magnetic field which

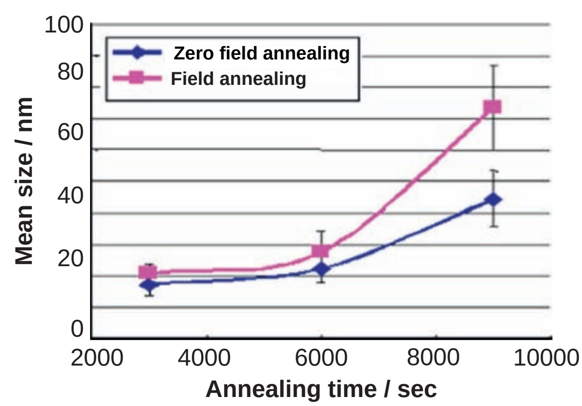

Fig. 2. Change in the mean radius of cobalt particles due to the presence of a magnetic field.

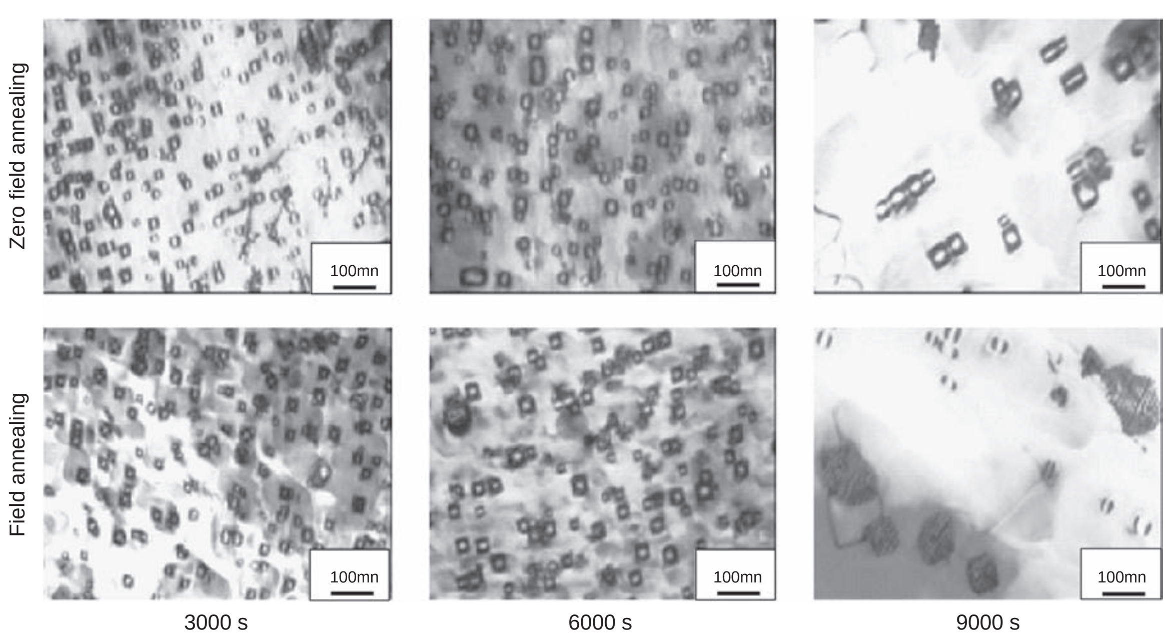

Fig. 1. TEM images of microstructural evolution in Cu–3at%Co alloys isothermally annealed at 923 K either with or without a magnetic field.

was applied to the Cu–Co specimen had a major influence on the precipitation growth kinetics, but not on precipitate nucleation or transformation.

Monte Carlo (MC) simulations: The TEM observations described above have confirmed that the applied field has an explicit influence on the precipitation behaviour. To examine the feasibility of the role of the magnetic field in the phase decomposition from a different viewpoint, we carried out Monte Carlo (MC) simulations to model the microstructural evolution of alloy decomposition. In the MC calculation, the external field is likely to have an influence on the microstructure as an effective term to an individual spin, since the field is homogeneously exerted on all cobalt atoms from the initial stage of phase decomposition.

We combined this assumption with the spin Hamiltonian which comprises the sum of the individual spins:

$$H = \sum_{i,j} J_{ij} S_i S_j + \sum_i h S_i$$

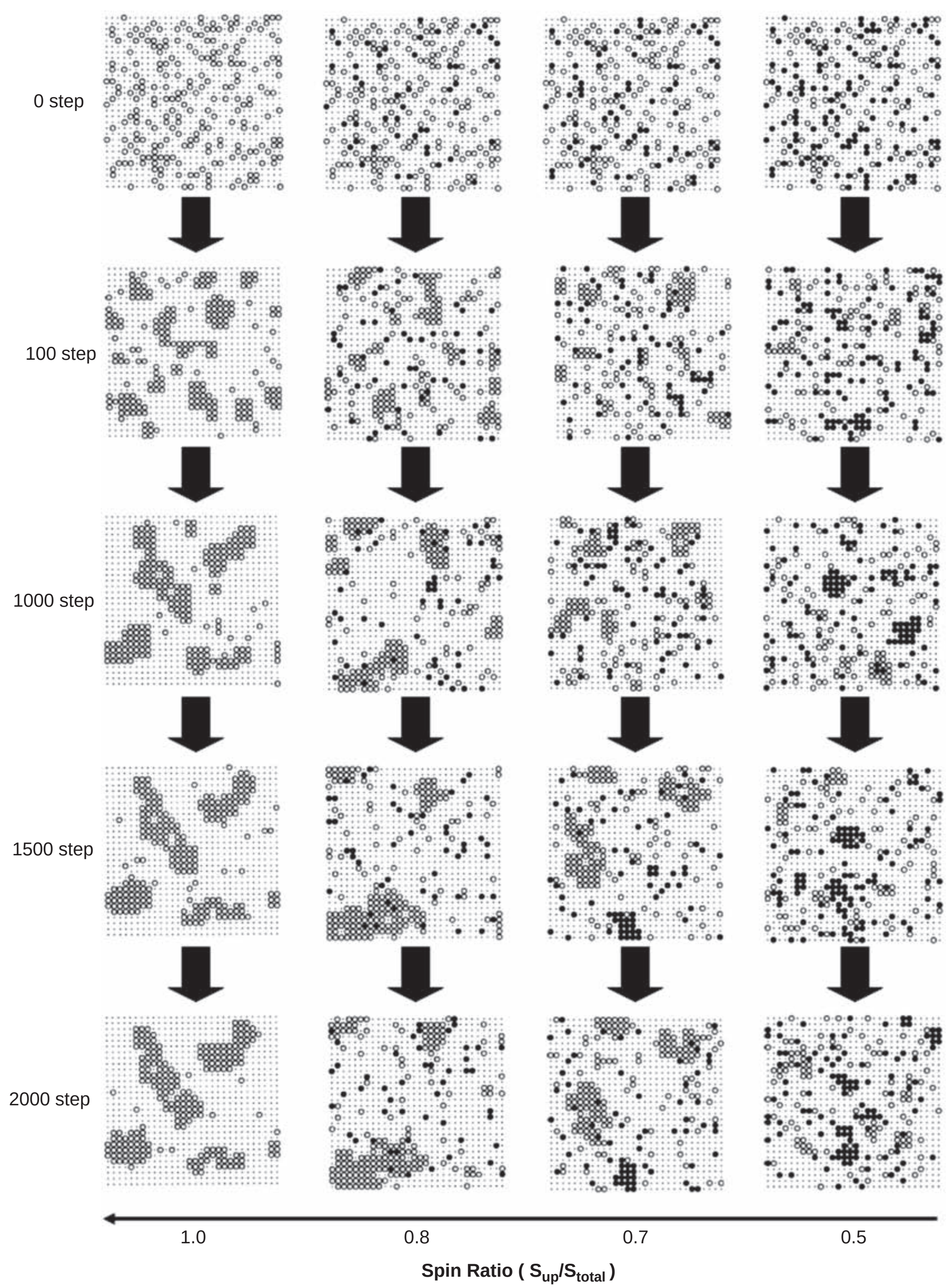

Fig. 3. Monte Carlo simulation of cobalt precipitation occurring in copper matrices with various strengths of chemical and magnetic interactions.

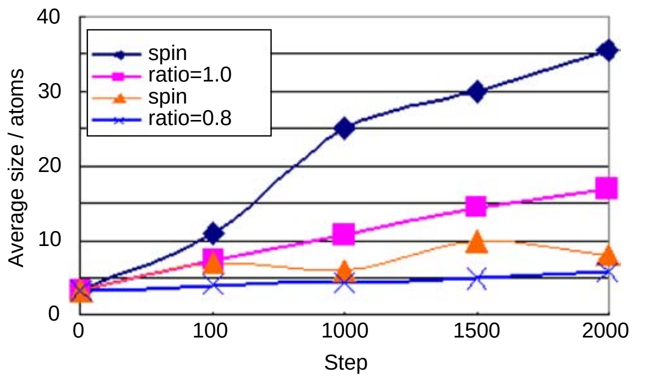

Fig. 4. Change in the average size of cobalt aggregates in the Monte Carlo simulations.

where J_{ij} represents the exchange coefficient, S_i (or S_j) a spin state (either $+1$ or -1 in the Ising model) for each cobalt atom at a position i (or j) and h a coefficient of molecular field. Since the purpose of the present MC calculations was to examine with a simple model whether a magnetic field affects the precipitation process or not, we assumed that the effect of the field could be modelled by an alteration of the spin distribution ratio at the starting state, which corresponds to the distribution at the zero-th MC step.

Fig. 3 shows several MC calculation sequences with different starting spin distribution ratios. The four sets of figures arranged in four columns were obtained using the statistical spin ratios at the zero-th MC step: spin $+$: spin $-$ $=$0.5:0.5, 0.7:0.3, 0.8:0.2 and 1:0, respectively.

The mean sizes of the resulting cobalt aggregates are plotted against each MC step in Fig. 4. The mean size represented by $<n>$ was estimated using the formula, $<n>=\sum n_i\ N_i/\sum N_i$, where n_i is the number of atoms comprising a cluster ($n_i \geqq 2$) and N_i is total number of particles of size n_i. The mean size shows a somewhat unsettled trend due to the instability of small particles with a spin ratio of $\sim$0.7. It may be noted that coalescence and separation of single cobalt atoms at the surface of a cluster occurs dynamically during the MC simulation and this sort of fluctuation gives a more significant influence on the calculated value of $<n>$ in an early stage of precipitation when the mean cluster size is small than in a later stage. Although such a complexity remains, it is clearly seen as a general trend that the mean cluster size increases as the initial $+/-$ spin ratio deviates more from equivalence, $+/-=$0.5:0.5. Thus, the MC simulations suggest that the precipitation behaviour in a Cu–Co alloy may be subject to magnetic interaction between atoms and precipitates.

The present study suggests that the magnetic interaction working between atoms/clusters increases as the cobalt particle grows and overcomes thermal turbulence. It is also expected that small cobalt particles show superparamagnetism in the precipitation process, as shown in a small MC step. The details of the initial stage of precipitation seem to be interesting and important for understanding the magnetic interaction of magnetic nano-particles, since precipitation follows the most energetically probable path in the reaction.

In the present experiments, the surface normals of the TEM specimens were not held perpendicular to the field during annealing. Accordingly, the effective field in the plane of the specimens was estimated to be 0.58 T at most. The effective value of the field may have an influence on the precipitation phenomena observed by TEM. The authors thus intend to carry out a further study on microstructural evolution under a stronger effective field. In addition, the present MC simulations were based on a simple scheme that included chemical and magnetic interactions affecting nearest neighbouring atoms only. Further consideration of the phenomenon will require more advanced MC simulations with less restrictive conditions.

4. Conclusions

The present study has revealed that an applied magnetic field has an influence on precipitation behaviour in a Cu–Co alloy. Specifically, cobalt clusters in specimens annealed in a magnetic field grew faster than the clusters in specimens annealed without a magnetic field, while the shape of the cobalt clusters was not significantly changed. The critical size at the coherent–incoherent transition was not different in specimens annealed in a field. The influence of the magnetic field was also confirmed in Monte Carlo simulations. The present results strongly suggest that a magnetic interaction occurs between cobalt atoms and particles in the precipitation process.

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