Ostwald ripening in high magnetic field: analytical and numerical approach of polarized diffusion

E Beaugnon\textsuperscript{1,2} and E Arras\textsuperscript{2}

\textsuperscript{1}CNRS/CRETA-LdC, BP166, 38042 Grenoble Cedex 9, France
\textsuperscript{2}Université Joseph Fourier, BP53, 38041 Grenoble Cedex 9, France
beaugnon@grenoble.cnrs.fr

Abstract. Recent experiments in the Co-B eutectic alloy have evidenced the anisotropic growth of Co precipitates at high temperature in the solid state when an external magnetic field up to 16 Tesla is applied. Two mechanisms are considered in this study. Firstly, the magnetic forces around the poles of a ferromagnetic Co particle can locally trap the diffusing Co ions in the matrix. An analytical approach demonstrates that, although weak, this mechanism is comparable to the curvature driving force in the Ostwald ripening. Secondly, the external magnetic field can affect the motion of the diffusing charged ions. Assuming a magnetically induced anisotropy of diffusion, Monte Carlo simulations show that the precipitates first elongate in a direction perpendicular to the fast diffusion axis and then recover a spherical shape for long annealing times.

1. Introduction

High magnetic fields are known to modify the microstructure of materials during their processing at high temperature. Such effects have been recently studied for the solid state transformations. In the Co-B eutectic alloy, it has been shown that the magnetic field induces an anisotropic microstructure during the annealing of the alloys quenched after melting \cite{1}. Starting from a very fine submicron lamellar eutectic structure, Cobalt particles are growing through the Ostwald ripening mechanism during the high temperature annealing. As compared to zero field processed samples, the growth of cobalt particles in magnetic fields up to 16 Tesla is anisotropic and aligned along the field direction. In addition, it was observed that the elongation phenomenon was not saturated in a 7 Tesla magnetic field and that a larger field alignment and elongation was measured in 16 Tesla.

As the magnetic annealing was processed at a temperature below the Curie temperature of the cobalt phase, different mechanisms could account for the observed anisotropic microstructure. Considering a ferromagnetic particle itself, its shape should elongate along the field direction to minimize the demagnetizing field energy, or the longest length of a particle should align along the field to accommodate a magnetic torque. In both cases, the driving force is limited by the saturation of the magnetization so that no more effect should be observed between 7 and 16 Tesla, in contradiction with preliminary observations \cite{1}.

Other field dependent mechanisms must then be considered, acting not in the ferromagnetic particle itself but in the surrounding paramagnetic matrix. The growth of the particle is governed by the diffusing Cobalt ions and the diffusion can be influenced by the magnetic field, either by the local magnetic forces applied on the paramagnetic cobalt ions or through the Lorentz force acting on these diffusing ions.

2. Magnetic trapping and curvature stabilization

Near a ferromagnetic Cobalt particle saturated by a large external field, the field distortion generated by the magnetization creates strong magnetic forces and locally attract or repulse paramagnetic cobalt ions in the matrix. For a spherical particle with a radius $r_0$ and a magnetization $M$, the magnetic field in polar coordinates (with $\theta=0$ corresponding to the magnetization direction) is given by:

$$B_r = \frac{2\mu_0 M}{3(r/r_0)^3}\cos(\theta)$$

for the radial component;
\[ B_\theta = \frac{\mu_0 M}{3(r/r_0)^3}\sin(\theta) \] for the orthoradial component.

The magnetic energy of a single cobalt ion in the matrix will be given by:

\[ E_M = -\frac{\chi_a B_{\text{tot}}^2}{2\mu_0}, \]

with \( \chi_a \) the atomic susceptibility of a single ion and \( B_{\text{tot}} \) the sum of the external applied field \( B_{\text{ext}} \) and the local field \( (B_r, B_\theta) \) generated by the particle.

Near the ferromagnetic particle, the ion concentration will increase with the field value, following a Boltzmann statistic. If \( C_0 \) is the equilibrium concentration far from a particle and \( \Delta C = C - C_0 \) the local concentration variation near a particle, then:

\[ \Delta C = C_0 \exp \left( \frac{\chi_a (B_{\text{tot}}^2 - B_{\text{ext}}^2)}{2\mu_0 kT} \right) - 1 \]

With \( B_{\text{tot}}^2 - B_{\text{ext}}^2 = \frac{2\mu_0 MB_{\text{ext}}}{3(r/r_0)^3}(3\cos^2\theta - 1) + \frac{1}{9}\frac{(\mu_0 M)^2}{(r/r_0)^6}(3\cos^2\theta + 1) \)

The susceptibility of a single Co++ ion can be estimated from its Bohr magneton number \( \mu = 4.8 \). At 900 °C (the temperature actually used for the experiments) \( \chi_a \) is then about \( 5 \times 10^{-32} \) SI. The saturation magnetization \( \mu_0 M \) of pure Cobalt is about 1.4 Tesla at room temperature and is certainly decreased at 900°C, since it is only 190° below the Curie point of the Cobalt phase which also contains some Boron. For an order of magnitude estimation, \( \mu_0 M = 1 \) Tesla was used in this model. The local \( \Delta C/C \) around a spherical particle was then calculated and plotted as seen on figure 1.

Near the magnetic poles of the particles, the local concentration is increased by about \( 3 \times 10^{-5} \) while it is decreased by about \( 1.5 \times 10^{-7} \) near the equator plan of the particle. As for the curvature driven Ostwald ripening, these local concentration variations, even low, may enhance the growth along the magnetic axis and decrease it on the perpendicular direction, leading to particles elongated along the applied field.

Figure 1: relative variation of the local Cobalt ion concentration in the matrix around a ferromagnetic Cobalt particle immersed in a 16 Tesla static field at 900°C. The arrow indicates the magnetization axis. Some isovales are projected on the base as a guide for the eye.
To confirm this possible effect, it is necessary to estimate the concentration variation due to curvature effects themselves. The local equilibrium concentration near a sphere of radius $r$ with interfacial energy $\gamma$ is given by the Gibbs-Thomson relationship:

$$C_r = C_0 \exp \left( \frac{2\gamma_{\text{m}}}{rRT} \right)$$

with $R$ the gas constant and $V_m$ the molar volume.

$\gamma$ is unknown in this study, but we used a typical value of 0.1 J/m$^2$. The molar volume of Co is about 6.6 $10^{-6}$ m$^3$/mol. For a sphere with a 1 $\mu$m radius (a typical size we observed for Co precipitates during their growth), then the local concentration change is about 1.3 $10^{-4}$, a value not far from the concentration shifts estimated for the magnetic force effect.

These estimations suggest that the local magnetic forces can indeed play an important role in the growth mechanism. In the Ostwald ripening analysis, the concentration increase at the interface with a small radius particle induces a concentration gradient in the matrix that tends to dissolve the small radius particles in favour of the growth of large radius particles. However, near the magnetic poles, the local magnetic forces can trap this excess concentration and prevent from the dissolution. Near the equatorial plane the effect is reversed, so that the regular evolution of the particle shape should give a small radius on the magnetic pole and a larger one the equatorial plane. Each particle should then elongate along the magnetic field direction.

A critical stabilisation radius $r^*$ on the magnetic poles can then be calculated by equating the two exponential terms in the magnetic concentration shift and in the Gibbs-Thomson relationship, thus giving:

$$r^* = \frac{4\gamma_{\text{m}}}{\mu_0 N \chi_{\text{at}} (B_{\text{tot}}^2 - B_{\text{ext}}^2)}$$

Above $r^*$, the local magnetic forces will counteract the particle dissolution and then promote sharp tips and hence elongated shapes on the growing particles.

3. Anisotropic diffusion

Besides the possible effects of the magnetic forces exerted on the paramagnetic ions, the external magnetic field can also modify the diffusion by the application of Lorentz forces.

Youdelis et al. [2] studied the diffusion of Copper in Aluminium in a 3 Tesla external field. They measured a 25 % damping of the diffusion in a direction perpendicular to the applied magnetic field. They proposed a model based on the Lorentz force acting on the electronic cloud moving with the diffusing ion. Later, Nakajima et al. [3] observed no field effects on the diffusion of Nickel in Titanium. Recently, the diffusion of Carbon in Iron was found to be decreased in the direction parallel to the applied field [4].

These contradictory results suggest a complex coupling between the magnetic field and the diffusing species. Besides the demonstration of the magnetic field effect on atomic diffusion, it is still required to evidence any effect of an anisotropic diffusion on the microstructure of particles growing in an external high magnetic field. The aim of this study is to numerically probe the effect of anisotropic diffusion on the shape anisotropy of growing precipitates.

3.1. Numerical modelling of growth with anisotropic diffusion

A Monte Carlo method (Potts model) has been implemented for the simulation of the Cobalt particles growth taking into account an anisotropic diffusion. In the Potts model, P-atoms (solute leading to precipitates) are diffusing in a M-atoms matrix. The energy of the system is the sum of all neighboring pair energies $E_{\text{MM}}$, $E_{\text{PM}}$ and $E_{\text{PP}}$. In addition to a classical Ising model, the Potts model allows Q different orientations of the P-atoms for describing different P-atoms grain orientations [5]. As a result, the $E_{\text{PP}}$ binding energy can be differentiated between similar or different Q-oriented P-P* atom pairs. The simulation is held on a periodic square grid. Only the P sites are probed, and one time step (MCS, Monte Carlo Step) consists of $n_p$ trials with $n_p$ the number of P atoms. The complete algorithm is as follows:

- randomly select a P site;
randomly select a new possible orientation amongst the Q possibilities for this site;
accept the change if the energy change $\Delta E$ ($\Delta E = \text{Pair energy after} - \text{pair energy before}$) is negative;
possibly accept the change with a probability equal to $\exp(-\Delta E/kT)$ if $\Delta E$ is positive;
select one of the 8 first neighbors (selection probability depends on the anisotropy of the diffusion, see below);
allow the atoms swap between the two sites if the energy change is negative;
possibly accept the change with a probability equal to $\exp(-\Delta E/kT)$ if $\Delta E$ is positive.

If $Q=1$ (no grain orientation degeneracy), only the difference $\Delta E_0 = E_{MM} + E_{PP} - 2E_{MP}$ is needed for the calculation of all pair energy differences. If $Q\geq 1$, it occurs that all energy differences are linear combinations of $\Delta E_0$ and $\Delta E_0^* = E_{MM} + E_{PP} - 2E_{PM}$.

To take into account an anisotropy of the diffusion, the probability for the selection of one of the 8 first neighbors is pondered as presented on figure 1. The probability weight is 1 along a particular direction while it is $A$ along the perpendicular one ($A > 1$ meaning a faster diffusion along this direction). For the four corner neighbors, a probability weight following the geometry of an ellipse (see figure 1) is applied, the weighted diffusion probability being proportional to the 45° radius length of the ellipse:

\[ D = \frac{A\sqrt{2}}{\sqrt{A^2 + 1}} \]

Figure 2: weighing probabilities for neighbour exchange direction selection as a function of $A$, the anisotropy factor ($A > 1$ means a faster diffusion along the above horizontal direction). The corner probability $D$ is calculated as the 45° radius of an ellipse.

The microstructure of the P-atoms distribution after a given simulation is analyzed by the intercepts method: the resulting image is low-pass filtered to remove isolated P-atoms (dissolved ions) or M-atoms (vacancies in precipitates); the M to P (and P to M) transitions are then counted for all vertical columns (sum = $I_v$) and for all horizontal rows (sum = $I_h$) of the simulation grid. An anisotropy factor $ANIS$ is then defined as the ration $I_v/I_h$. In the figure 2 configuration, $ANIS > 1$ means a longer size along the $A$ factor diffusion.

3.2. Anisotropic growth

Typical results of anisotropic growth are presented figure 2. Simulations up to 80 000 MCS were performed on a 256x256 grid, starting from a random P and M atoms distribution. The P atoms concentration was 42 %, $kT=2.1$, $\Delta E_0=-4$, $\Delta E_0^*=-2$ and $Q=25$. The resulting microstructures are given after 8000 MCS and 80000 MCS for an isotropic diffusion ($A=1$) and an anisotropic diffusion ($A=10$). With $A=1$, a regular isotropic microstructure is observed while with $A=10$, a remarkable anisotropic
structure is evidenced, with the grains elongated perpendicularly to the fast diffusion axis (horizontal axis on figure 3).

![Isotropic diffusion (A=1) vs Anisotropic diffusion (A=10)](image)

Figure 3: microstructures of the P atoms distributions after 8 000 MCS (top images) and 80 000 MCS (bottom images). The left images correspond to an isotropic diffusion and the right images are calculated for an anisotropic diffusion with a faster coefficient A=10 along the horizontal direction. Each rectangular image consists of two joined square parts, unfiltered on left and filtered on right. The continuity between the two parts reflects the periodicity of the computation grid. The different colours or grey levels on the left parts correspond to different Q-orientations.

The elongation of the particles perpendicularly to the fast axis diffusion can be justified by the following simple model: as the P atoms can move faster along a horizontal axis (as for figure 1 and figure 2), they are more likely to encounter each other, to join and to form stable vertical pairs which increase the growth of vertically aligned bulk particles. Such an argument becomes obvious if the slow diffusion on the vertical axis goes to zero.

In previous experiments on the annealing of melted and quenched Co-B eutectic alloys, cobalt particle were elongated parallel to the external field. According to the results of these simulations, under magnetic fields, the diffusion constant is lowered along the direction of the applied field or enhanced perpendicularly to it.

In order to study the relation between the diffusion anisotropy A and the shape anisotropy factor ANIS, simulations were calculated for 17 different A values ranging from 1 to 10. For each A value, 10 different simulations were processed. For each simulation, the shape anisotropy factor ANIS was measured every 500 MCS and the mean value from 500 to 10000 MCS was calculated to reduce the noise resulting from the structure fluctuations. Finally, the mean of the 10 results for each A value was also determined to even better filter the results. For these simulations, a 512x512 computation grid was used with a 42% P atoms concentration, $kT=2.1$, $\Delta E_0=-4$, $\Delta E_0^*=-2$ and $Q=25$.

All results are quite well fitted by a logarithmic law. For different experimental conditions (150x150 grid, $Q=1$, $kT=2.2$ and 200000 MCS), it was found that a similar law was obeyed but with a different slope. Others experiments are required to investigate the effect of initial conditions and time on the slope of this logarithmic law.
Figure 4: the shape anisotropy factor ANIS calculated from the intercepts method is plotted against the anisotropy diffusion coefficient A. The mean value (from 500 to 10000 MCS) for each simulation is marked by a cross. The averages of these values for each A are in solid black. All results are fitted by a logarithmic law (solid line).

3.3. Isotropic recovery
To study the stability of the shape anisotropy with time, simulations starting from a single vertically elongated ellipse were performed for A=0.33, A=1 and A=3. The initial concentration was 3%, the calculation grid 256x256 and all other parameters as above. For each A value, the average resulting shape anisotropy was calculated from 5 different runs, up to 100000 MCS. As seen on figure 5, whatever the diffusion anisotropy, the shape always evolve to a regular disk. This result suggests that the shape anisotropy observed in the previous experiments is transitory, and that the equilibrium shape should become isotropic for very long time calculations.
Figure 5: evolution of the shape anisotropy factor of a single vertically elongated ellipsoid. Whatever the diffusion anisotropy A, a circular shape is always obtained as a stable shape.

4. Conclusion
Two possible models are presented to take into account the magnetic field effects on the diffusing ions near growing precipitates.

In the first model, the local magnetic forces are expected to counteract the curvature driven dissolution so that sharp tips on the magnetic pole and hence elongated particles are expected.

In the second model, assuming the magnetic field induces an anisotropic diffusion, the resulting microstructure is studied by Monte Carlo simulations (Potts model). For a given faster diffusion axis, the particles are elongated perpendicularly to this axis. Experimentally, a dependence on the logarithm of the diffusion coefficient ratio is found.

Both models are not limited by the saturation of the magnetization of the particles and are then expected to make larger effects in very high magnetic fields: the Lorentz forces, which are assumed to polarize the atomic diffusion, can be increased by the external field; similarly, the local magnetic forces can also be increased by the external field as the paramagnetism of the ions is not yet saturated.

References
[1] Gaucherand F and Beaugnon E 2004 Magnetic texturing in ferromagnetic cobalt alloys Physica B 346-347 262-6
RHMF 2003, Toulouse, 20-23 July 2003.
[2] Youdelis W V, Colton D R and Cahoon J 1964 On the theory of diffusion in a magnetic field Canadian J. of Physics 42 2217-37
[3] Nakajima H, Maekawa S, Aoki and Koiwa M 1985 Diffusion of nickel in titatnium in a magnetic field Trans. JIM 26-1 1-6
[4] Hao X and Ohtsuka H 2005 Measurement of phase transformation temperature and carbon diffusio in Fe-C alloys in a high magnetic field Proceedings of International Symposium on Magneto-Science Yokohama November 2005
[5] Tikare V and Cawley J D 1998 Application of the Potts Model to Simulation of Ostwald Ripening Journal of the American Ceramic Society 81-3 485-91