Alignment of Iron Nanoparticles in a Magnetic Field Due to Shape Anisotropy

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During high magnetic field solidification processing there is evidence for the alignment of nanoscale metallic particles with elongated morphologies that nucleate from a liquid metal. Such alignment occurs well above the Curie temperature of the particle where the magneto-crystalline anisotropy energy and exchange energy contributions are negligible. The main driving force for alignment is the magnetic shape anisotropy. Current understanding of the phenomenon is not adequate to quantify the effect of particle size, aspect ratio, temperature and the magnetic field on particle alignment. We demonstrate a Monte Carlo approach coupled with a scaling law for the dipole-dipole interaction energy as a function of the particle size to identify the conditions under which such alignment is possible.

1. Background

Magnetic texturing of a precipitating second phase particle from a matrix using static or alternating external magnetic field has been exploited in many metallic alloys including cubic and non-cubic crystal structures, above or below the Curie temperature [1, 2]. The aligning of metallic phase particles using a strong magnetic field offers a unique approach to produce oriented structures in structural and functional materials with improved properties. The key to the alignment process is that the thermodynamic driving force for alignment should be significantly larger than the thermal energy. The magnetic energy contributions can be summarized through the following equations [3]:

$$E_{ext} = -H \cdot M \quad [1]$$

$$E_{exch} = -\sum J_{ij} e_i e_j \quad [2]$$

$$E_{dip} = m^2 \sum_{j=1}^n \sum_{k \neq j}^n \frac{a_j a_k - 3(a_j e_{jk})(a_k e_{jk})}{4\pi\mu_0 r^3} \quad [3]$$

$$E_{an} = K_1(m_1^2 m_2^2 + m_2^2 m_3^2 + m_1^2 m_3^2) + K_2 m_1^2 m_2^2 m_3^2 \quad [4]$$

In Eqn. 1, H is the external magnetic field strength and M is the magnetic moment vector of the atoms in the crystal and E_{ext} is the energy due to the presence of the external field. In Eqn. 2, E_{exch} is the spin exchange energy for each atom i where the e_i and e_j are the unit magnetic moment vectors of the i and j atoms where the j atoms included up to the fourth nearest-neighbors, and J_{ij} is the exchange interaction parameter between i and j atoms. In Eqn. 3, E_{dip} is the dipole-dipole interaction energy where a_j and a_k are the unit magnetic moment vectors of atoms j and k , e_{jk} is the unit vector of the displacement that connects an atom i with atom k , and μ_0 is the permeability of space. In Eqn. 4, K_1 and K_2 are the magneto-crystalline anisotropy constants for iron, and m_1 , m_2 and m_3 are the direction cosines of the total atomic magnetic moment vector with respect to the coordinate axes.

Below the Curie temperature (T_C) the contribution from E_{exch} that tends to align the magnetic moments in a ferromagnetic particle is significant compared to the entropic contribution to the free energy, and therefore the particle has significant net magnetic moment. The atomic moments within the particle can lower their energy not only by aligning with each other but also by collectively aligning with the easy magnetization direction. In the presence of an external field, the particle tends to align both their net moment and their easy magnetization direction with the field direction to the extent that they are free to rotate. In the case of alpha iron, the easy magnetization directions are the [100] directions, while in the case of Ni they are [111] directions. For bulk cubic crystals the strength of the magneto crystalline torque is controlled by the magnitudes of K_1 and K_2 in equation 4. While in materials with cubic crystal symmetry the anisotropy energy is small, it is significantly larger for materials with lower symmetry. In low symmetry materials the anisotropy is often uniaxial and the alignment of magnetization tends to occur along a single specific crystal axis. In a small particle with defects the anisotropy could be even greater than in low symmetry crystals. Above the T_C , both the exchange energy and the magnetic anisotropy energy are less than the entropic contribution to the free energy. The largest laboratory generated magnetic fields are small compared to the effective local fields that result from exchange. Therefore it is very difficult to achieve significant alignment except in very specific regimes and in the presence of the highest available magnetic fields.

Yet another factor that can contribute to alignment in the presence of external magnetic field is the magnetic shape anisotropy. The change in the magnetic energy due to shape anisotropy for a macroscopic elongated particle oriented perpendicular and parallel to an external magnetic field B is given by [4]

$$\Delta U = \frac{B^2 V}{2\mu_0} (\chi_p - \chi_m)(N_{\perp} - N_{\parallel}) \quad [5]$$

where χ_p and χ_m are the magnetic susceptibilities of the particle and the surrounding medium and V is the volume of the particle. In the case of solidification, the surrounding medium is the liquid metal from which the solid particles have nucleated. While Eqn. 5 gives an energy based criterion for alignment in an external field, it is quite difficult to quantify on the basis of Eqn. 5, the combinations of particle size, shape and the external field required for achieving alignment in a specific alloy. The difficulty arises due to two factors: (1) for a general non-spherical particle, especially in the case of a dendrite, it is very difficult to calculate the demagnetizing fields $N_{\perp}$ and $N_{\parallel}$; (2) magnetic susceptibilities for solids and liquids at high temperatures are not readily available for a complex alloy. Another detail that is missing in Eqn. 5 is the coupling between the magnetic susceptibility and the magnitude of the demagnetizing field. In other words, the quantity $(N_{\perp} - N_{\parallel})$ does not exist in the absence of magnetic susceptibility. The demagnetizing field is related to the dipole-dipole interaction energy and the particle aspect ratio. Furthermore, the scaling law for the dipole-dipole interaction energy cannot be obtained analytically for complex geometries. The objective of the present work is

to demonstrate a scaling law for the dipole-dipole interaction using a Monte Carlo (MC) simulation approach and quantify the conditions under which shape magnetic anisotropy can promote alignment of elongated particles in a magnetic field. The proposed simulations for iron nanoparticles can enable a multi-scale approach where the effect of solute concentration on magnetic energy contributions calculated using first-principles [5] could directly be used to simulate the magnetic field induced texturing in complex alloys.

Section 2 describes experimental work on a complex, multi-component Fe-based alloy that indicates alignment of nucleating particles by a magnetic field. Section 3 describes the modeling effort; after a brief description of thermodynamic modeling of the complex alloy, focus is shifted to pure Fe so that the dependence of alignment on the fundamental quantities: size, applied field, and temperature could be explored. Results are summarized in Section 4 and conclusions are discussed in Section 5.

2. Experimental Work

The present work was motivated by our recent experimental finding that near perfect single crystals could be obtained in a multi-component Fe-base alloy when solidified in an external magnetic field [6]. Fe-28Ni-17Co-11.5Al-2.5Ta-0.05B alloy (hereafter referred to as FeNiCoAl alloy) buttons were arc melted and drop cast, and the compositionally homogenous arc melted material was sectioned and loaded into a crucible made of a thermodynamically stable material. The final castings were approximately 2.5 inches tall with an outer diameter of 1 inch. Thermomagnetic solidification was carried out under a 19 Tesla magnetic field in an argon/helium mixed atmosphere using a radio frequency electromagnetic heating insert and at cooling rates of 30°K/min and 400°K/min. Additional sample was produced at 30°K/min with no applied field. Figure 1 shows optical micrographs of the dendritic structure obtained for the different samples.

Fig. 1. Dendrite morphology in the FeNiCoAl alloy solidified in an external magnetic field under different solidification conditions

It can be seen that the dendrites show significant alignment in the presence of the 19T magnetic field both under slow and fast cooling rates, while they are misaligned in the absence of the magnetic field. There is clear indication of near-single crystal formation under the action of the external magnetic field, although a better-aligned single crystal was obtained at 30°K/min than at 400°K/min where the material consisted of a few large grains. The second phase distribution at the interdendritic regions in Fig. 1 has been identified as a body-centered cubic (BCC) phase that forms in the final stages of solidification. Elemental mapping showed that the BCC phase has a slight enrichment of Al.

Figure 2 shows the $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ FCC- pole figures obtained from three different locations for the sample cooled at 30°K/min in the presence of 19T field (Fig. 1a). It is clear that there is very little difference in crystal orientation between these locations indicating the presence of a near single crystal alloy.

Figure 2. FC pole figures of sample shown in Fig 1b taken from three different locations indicated schematically across the cross-section of the approximately 1 inch diameter sample.

Figure 3. Orientation imaging of dendrites in a furnace cooled sample of FeNiCoAl alloy with an external magnetic field of 20T showing the coexistence of the FCC phase (left) and the BCC phase (right).

Closer examination of the dendrite orientations were carried out for the sample cooled at 400°K/min in the presence of a 19T external field. The results indicate the presence of a mixture of BCC and face-centered cubic (FCC) phases within the primary dendrites in the as-solidified microstructure. The orientation images of the typical BCC-FCC mixtures obtained is shown in Fig. 3. Typical pole figures for the BCC and FCC phase distributions shown in Fig. 3 are shown in Fig. 4. From the pole figures, it is clear that the orientation scatter within the FCC phase is much smaller than the BCC phase. The scatter within the BCC phase is due to the different variants of the BCC phase that precipitated from the parent FCC phase that probably formed first during solidification. The pole figures appear to indicate the following Nishiyama-Wassermann orientation relationship between the BCC and FCC phases [7].

Figure 4. Pole figures corresponding to the FCC (left) and BCC (right) phase distributions shown in Fig. 3.

3. Modeling

3.1 Thermodynamic Calculations

The solidification path for FeNiCoAl alloy was obtained using the commercial thermodynamics database Thermocalc™. Both the nickel alloy database TTNI8 and the iron alloy database TTFE61 were used to simulate the solidification path of the alloy using the Scheil model. Figure 4 shows the coexistence of phases in the initial stages of solidification.

Figure 5. Solidification path for Fe-28Ni-17Co-11.5Al-2.5Ta-0.05B alloy using the Scheil model

Figure 5 shows that the FCC phase begins form around 1530°K and the BCC phase also forms upon cooling through approximately 10°K. Both phases continue to grow in the liquid during cooling. However, based on the EBSD results shown in Section 2, it appears that the FCC phase formed prior to the BCC phase and the BCC phase precipitated later from the FCC phase.

However, the above calculations do not rule out the possibility of nucleating the BCC phase first from the liquid. Such a mechanism has been known to exist in Fe-Ni alloys due to the lower interfacial energy between the BCC phase and the liquid [8-10]. Thoma and Perepezko [10] have discussed different solidification pathways in highly undercooled Fe-Ni alloys. One of the possible solidification paths is Liquid→BCC→FCC→BCC (martensite). Here, the BCC nucleates and grows from the liquid, which then transforms to FCC phase and finally BCC precipitates as martensite laths. Since kinetic undercooling of the order of 100-150°K is required to nucleate BCC from the liquid, a high cooling rate is imposed that promotes martensite formation instead of BCC from the FCC phase. However, the thermodynamic stability of the BCC phase is significantly higher in FeNiCoAl. Figure 5 shows that undercooling of just 10°K is required to nucleate the BCC phase. Therefore, it is kinetically possible at lower cooling rates to form the BCC phase first, when could then grow in the liquid to some size and subsequently transform to FCC.

The FCC phase could then transform partially to BCC instead of martensite because of the lower cooling rate. The operation of such a sequence obviously cannot be detected by the analysis of the final microstructure. However, it could promote alignment in the presence of the magnetic field because of the higher susceptibility of the BCC phase, as explained later.

3.2 First Principles

The exchange energy parameters for BCC and FCC iron as the function of the interatomic distance of neighboring atoms calculated using first principles calculations [11] is shown in Fig. 6.

Figure 6. Spin exchange energy between pairs of atoms for FCC and BCC iron as a function of the distance between the two atoms of the pair calculated for all pairs in a 128 atoms periodic model. Atoms are displaced from their average lattice positions according to the instantaneous positions at one step within a first principles molecular dynamics simulation of Fe at 900K [11].

The lattice parameter for BCC iron in the temperature range of 1480-1523°K based on [12] ranges from 0.290nm A to 0.2907nm and the corresponding first-nearest neighbor distances are 0.2515 nm and 0.2518 nm, respectively. The second-nearest neighbor distance is equal to the lattice parameter. It is clear from Fig. 6 that for BCC $J(r)$ is significant for the first and second-nearest neighbors. The lattice parameter of FCC iron is 0.3571 nm, and it increases to 0.3608 nm at 1480°K and 0.3609 nm at 1523°K. The corresponding first-nearest neighbor distance for FCC is roughly 0.255 nm at both temperatures. For FCC structure, the second-nearest neighbor distance is equal to the lattice parameter at temperature. The value of $J(r)$ from Fig. 6, and hence the exchange energy contribution are close to zero for the

FCC. While E_{ex} is dependent on whether the underlying structure is BCC or FCC, E_{ext} is independent of the crystal structure. E_{an} is typically very small compared to kT at the temperatures of interest both for BCC and FCC. E_{dip} can also be assumed to be roughly the same for FCC and BCC iron at these temperatures because the atomic volumes differ by only 1% and nearest neighbor distances differ only by 2% [13]. In the current Monte Carlo simulations the Fe atoms are assumed to be in BCC positions because of the requirement for the calculation of exchange energy. According to our arguments above, we can approximate the qualitative behavior of FCC at the selected temperatures by assuming BCC positions with vanishing exchange energy contributions.

3.3 Monte Carlo Simulations

As stated in Section 1, the current simulations are part of an ongoing investigation of microstructure evolution in the presence of magnetic fields in complex multicomponent alloys that include first principles calculations of the effect of different alloying elements on E_{exch} and E_{an} . Therefore, in the current simulations, we only consider pure iron without the alloying elements. In the current MC simulation approach, the total magnetic energy of the system is represented as the sum of the energy contributions arising from Eqns. 1 through. 4. The Metropolis algorithm [14] was used for the acceptance probability, p , is defined as

$$\begin{aligned} p &= 1.0 & \Delta E \leq 0.0 \\ p &= e^{\frac{-\Delta E}{kT}} & \Delta E > 0.0 \end{aligned} \quad [7]$$

where ΔE is the change in the energy due to an attempted MC move. The two MC moves considered are as follows: (1) a random rotation of the magnetic moment of a single atom keeping the orientation of the particle constant and (2) a rotation of the particle through a small angle keeping the moment directions the same with respect to the global coordinate system. The sizes of the elongated particles used in the study ranged from $7 \times 7 \times 49$ lattice constants to $15 \times 15 \times 105$ lattice constants with the atoms situated in the BCC crystal structure. In the case of move (1) Monte Carlo time is incremented after one flip attempt for all the atoms in the domain. In the case of (2) it is incremented for every rotation attempt of the particle. The simulations were used to calculate (1) the average magnetic moment of the solid at temperature, (2) the scaling of the dipole-dipole interaction energy with magnetization for an elongated particle with a specific aspect ratio, and (3) to demonstrate the aligning of the elongated particles in an external magnetic field.

The lattice constant at temperature was obtained from the atomic volume of BCC iron calculated using molecular dynamics simulations [12]. J_{ij} values in units of eV were obtained from [15]

$$J_r = 0.5190575 - 0.367938r + 0.0865305r^2 - 0.0066755r^3 \quad [8]$$

where r is the distance between atoms. The simulations were performed at temperatures of 1523K and 1480 K that correspond to a liquid fraction of 0% and 30% respectively based on the thermodynamic calculations shown in Fig 5.

In the next two subsections we will describe two different MC simulation tasks involving calculation of magnetic moment for a fixed particle in a field and the calculation of a scaling law for the dipole-dipole interaction energy. These two calculations will be used to simulate the alignment of elongated particles in a magnetic field described in the third subsection.

3.3.1 Calculation of magnetic moment for fixed particle in a field

For these simulations, the particle orientation was fixed with the z-axis of the reference coordinate system and an external magnetic field was applied in the z-direction. The initial magnetic moment for each atom was assigned randomly. The simulations were used to calculate T_C for iron to ensure that there is no spurious contribution from the exchange energy term (Eqn. 2) above T_C . The simulations were then carried out at temperatures of 1523°K and 1480°K for applied fields of 0, 10, or 20 Tesla to obtain the time-averaged moments in the x, y and z directions as a function of MC time step.

3.2.2 Scaling of dipole-dipole interaction energy

It is clear from Eqn. 3 that the calculation of the dipole-dipole interaction energy for each atom in the simulation domain requires a summation over all the other atoms in the system. Therefore, as the system size increases it becomes very computationally expensive. Therefore, a scaling approach was developed in order to calculate this term efficiently for large particle sizes. As described in Section 1, the dipole-dipole interaction term contributes to the net energy change due to a change in the orientation of an elongated particle with respect to the external field. This also requires that the particle have a net magnetic moment that points in a certain direction relative to the field. The initial configuration involved assigning magnetic moments to the individual atoms such that there is net magnetic moment for the particle. The net magnetic moment was varied from 0.02 to 0.5. In order to obtain a specific value for the net moment as a result of an applied field in the z-direction, a fraction of the sites was assigned a moment vector of magnitude 1.0 parallel to the z-direction while the remaining atoms were assigned a moment of 0.0. In reality, the net magnetic moment averaged over the whole particles has a small non-zero z component, while the sum of the x and y components tend to average to zero. However, the simplified assignment of the moments helps in reducing the scatter in the trend for the scaling of the dipole-dipole interaction energy. Initially the particle is oriented such that its long axis is parallel to the global z direction. The difference in the interaction energy was calculated before and after a 90° rotation of the particle about the x-axis while the magnetic moments were held constant with respect to the global frame. The change in the interaction energy was calculated for

different particle sizes ranging from $7 \times 7 \times 49$ to $15 \times 15 \times 105$ lattice constants, keeping the particle aspect ratio fixed at 1:7. The choice of the aspect ratio is rather arbitrary; it is intended to capture the shape of a dendrite long arm during solidification. For each particle size, the simulations were repeated using different random seeds used for generating the coordinates of the atoms that were assigned a non-zero moment. For particles with a small net magnetic moment, averaging over as many as 10,000 seeds were required in order to get a statistically significant result for the interaction energy. The interaction energy as a function of particle size was fitted using a polynomial.

3.2.3 Particle alignment in the magnetic field

The initial configuration for these simulations involved the assignment of atomic moments using a procedure similar to the one outlined in section 3.2.2. The particle size for these simulations was $7 \times 7 \times 49$ lattice constants. The choice of the particle size is based on a compromise between good statistics and the simulation time required to converge to a stable configuration. The MC move involved a random rotation of the particle while keeping the magnetic moments of atoms the same. The change in energy comes from the dipole-dipole interaction term which is calculated by scaling the value for the $7 \times 7 \times 49$ for larger sizes based on the scaling polynomial fit obtained 3.2.2. In these simulations, it is assumed that the particles can freely rotate in the liquid and the resistance offered to particle rotation due to viscous forces is neglected.

4. Results

Figure 7 shows the development of the z-component of the magnetic moment at 1523°K and 1480°K due to the presence of the external magnetic field. At zero field, the time averaged magnetic moments in all three directions tend to be zero as expected since the thermal free energy is much higher than the exchange interaction energy. However, for external fields of 10T and 20T, the time averaged z-component is non-zero. In the presence of a 10T field, the time averaged z moment is roughly 0.0098 for both 1480°K and 1523°K . However, for the 20T field, the time averaged z-moment increases from 0.026 at 1523°K to 0.031 at 1480°K . When the crystal structure is FCC and the exchange energy is zero, the net magnetic moment generated at 1523°K for an applied field of 20T is only 0.0074. It is the presence of a small residual magnetic moment that is responsible for particle alignment, provided the particle is elongated and is large enough to support in a significant change in the dipole-dipole interaction energy compared to the thermal energy. The significant reduction in the exchange energy leads to much lower susceptibility for FCC iron and therefore a significantly reduced magnetic moment in the presence of the magnetic field. In other words, to rotate an FCC particle requires a larger rotating field or that the particle be bigger than in the case of a BCC particle of the same aspect ratio.

Fig 7. Time averaged magnetic moment in the x, y and z directions as a function of MC simulation time at selected temperatures and applied magnetic fields. The expectation value of M_z is non-zero in the presence of external field.

The change in the dipole-dipole interaction energy due to a fixed change in the orientation of an elongated particle with respect to an oriented magnetic field is

calculated for different particle sizes with the same aspect ratio. This quantity is normalized with respect to the smallest particle and plotted as a function of the particle size in Fig. 8. The particle size depicted in Fig. 8 is a number N , that represents a physical size of a particle whose dimensions are $(N+6) \times (N+6) \times 7(N+6)$ lattice parameters. The scaling behavior appears to be independent of the net magnetic moment except for very small moments where there is a deviation due to poor statistics. As mentioned in previously, at small moments the results had to be averaged over as many as 10,000 seeds for the random number generator that used to identify the atoms that are assigned non-zero z moments. The polynomial fit to the scaling behavior based on the mean curve shown in Fig. 8 is given by

$$\Delta E_{dip} = 0.5973 + 0.3477(size) + 0.05032(size^2) + 0.00362(size^3) \quad [8]$$

Fig. 8. Scaling of the dipole-dipole interaction energy with particle size and net magnetic moment of the particle.

The alignment of the elongated particle in the presence of the magnetic field is shown Fig. 9. When the particle size is small its orientation fluctuates with simulation time. One way to represent the fluctuations is to plot the maximum values of the x , y and z coordinates of the particle as a function of the simulation time. The $7 \times 7 \times 49$ particle was centered on the coordinate system with respect to which the rotations attempts were made. When the particle is completely aligned with the coordinate system, the maximum absolute value of the z coordinate should be 24.5 and the maximum value of the x and y coordinates should be roughly 5.0 ($3.5\sqrt{2}$). Any deviation from these values shows misalignment of the particle. Figure 9 shows the maximum value of x , y and z coordinates of the particle as a function of the simulation time at 1523°K and 1480°K in external fields of 10T or

20T with the net magnetic moments in the x, y and z directions shown in Fig. 7 as a function of the particle size. The simulations clearly showed that the spatial fluctuation of the particle with respect to the global z coordinate decreases significantly when the particle size increases from 100 to 1000 in all of the above cases. The results shown in Fig. 9 are for the most favorable conditions for alignment, $T=1480^{\circ}\text{K}$ and $H=20\text{T}$ and the least favorable conditions for alignment, $T=1523^{\circ}\text{K}$ and $H=10\text{T}$.

Fig. 9. Effect of particle size, temperature, and external field on particle alignment. Good alignment in the z-direction is achieved while the alignment in the x and y directions are poor under the conditions shown.

While the fluctuation with respect to the z-direction is significantly reduced when the size increases from 100 to 1000, fluctuations along the x and y directions are still quite significant. The simulations showed that the x and y fluctuations could be further reduced by increasing the particle size. The simulations were extended to particle sizes up to 10000. The results are shown in Fig. 10.

Fig. 10. Effect of increasing the particle size on alignment normal to the particle axis

For conditions most favorable to particle alignment, $T=1480^{\circ}\text{K}$ and $H=20\text{T}$, increasing the particle size to 5000 results in a significant reduction in orientation fluctuations in the x and y directions. However, for conditions least favorable to

alignment, $T=1523^{\circ}\text{K}$ and $H=10\text{T}$, achieving similar reduction in the x and y fluctuations requires a particle size of 10,000. A similar particle size is required for the FCC particle where the net magnetization at $T=1523^{\circ}\text{K}$ and $H=20$ is only 0.007, which is roughly 25% of the magnetization obtained for the BCC crystal.

5. Discussions

In elongated nanoparticles of BCC iron far above TC and in FCC iron elongated nanoparticles significant shape magnetic anisotropy can be induced in the presence of an external magnetic field provided the particle has a net magnetic moment, and external the field and the particle size are large enough. The objective of the simulations was to provide a better quantitative basis for Eqn. 5 so that the conditions under which the alignment of elongated nanoparticles can be achieved with external magnetic field, and to extend the findings to understand the formation of near-single crystal during solidification of the FeNiCoAl alloy in a magnetic field. First, the simulations are able to quantify the net magnetic moment in BCC and FCC iron nanoparticles at the temperatures of interest where solid and liquid phases co-exist during the solidification of FeNiCoAl alloy. The simulations are also able to establish a scaling law for the dipole-dipole interaction energy as a function of the particle size. The scaling law allows the calculation of E_{dip} for much larger particles and allows identification of particle sizes at which changes in E_{dip} become significant compared to the thermal energy.

A significant finding from the simulations is that the orientation fluctuations in the axial direction (z-direction) of the particle die down at a much smaller particle size than the fluctuations in the x and y directions of the particle. If the z-axis of the particle is aligned exactly with the global z-axis, then any rotation of the particle about the z-axis will not result in any energy change because E_{dip} should be independent of such a rotation. However, since the particle is not exactly aligned in the z-direction, rotation about its axis that does not significantly change the height in the z-direction but will cause small energy changes due to changes in the orientation of the x and y axes of the particle with respect to global x and y directions. The large fluctuation in the x and y directions is due this energy being much smaller than the thermal energy. As the particle size increases, due to the scaling of E_{dip} these energy changes also become larger and therefore they tend to rotate to an orientation that minimizes E_{dip} .

The calculations indicate that particle sizes of the order of 5000 and 10000 for the BCC and FCC phases, respectively, are required for achieving particle alignment under the experimental solidification conditions for the FeNiCoAl alloy. A size of 5000 corresponds to a particle dimension of $5006 \times 5006 \times 35042$ lattice parameters. Assuming a lattice parameter of 0.296 nm in the temperature range of $1480\text{-}1523^{\circ}\text{K}$, the particle size becomes $1462 \times 1462 \times 10232 \text{ nm}^3$. In the case of FCC the calculations are only approximate because the simulations did not consider the underlying differences in the atom positions but considered only the fact that

the exchange energy contribution was zero for the FCC particle. Based on the lattice parameter of BCC iron, the particle size of 10000 corresponds to an effective FCC particle size of $2892 \times 2892 \times 70084 \text{ nm}^3$. Since the simulations are for an iron particle, the effective size at which alignment occurs in a multicomponent dendrite could be much higher because of the potential reduction in the effective magnetic moment due to the addition of solutes that are non-ferromagnetic. The simulations indicate that the particles that can respond to the external field are much larger than the nuclei that form initially in the melt.

The simulations indicate that the particle does not exactly align with the global x, y , and z axes but is inclined. This deviation is significantly larger in the xy plane compared to the z direction. This is probably due to the finite aspect ratio of the particle. If the particle is extremely long and thin, the mean angle between the vector that connects any two atoms and the long-axis of the particle is smaller compared to a shorter and thicker particle. It is significant to note that the dendrites shown in Fig. 1 and the pole figures in Fig. 2 also show such a deviation.

The comparison between the simulations and the experiment are only qualitative because the simulations are carried out for pure iron and the experimental results are for a multicomponent alloy. However, the proposed simulation approach can be easily extended to multicomponent alloys if the magnetic properties of the alloy can be calculated using first-principles approaches. A key input to the multicomponent alloys is the effect of alloying additions on the effective exchange parameters for the BCC and FCC phases.

Summary and Conclusions: MC simulations of the response of elongated iron particles to external magnetic field have been simulated taking into account magnetic energy contributions due to external field, magneto-crystalline anisotropy, exchange energy and magnetic dipole-dipole interaction. MC simulations were used to calculate the net magnetic moment of the particles at temperatures and magnetic fields of interest. The simulations were also used to establish a scaling law for the dipole-dipole interaction that allowed the extension of the simulation to particle sizes of the order of a micrometer. It was shown that under such length scales it was possible to orient particles with an aspect ratio of 1:7 in an external magnetic field of 10-20T in a temperature range of 1480°K-1523°K that correspond to the early solidification conditions for a FeNiCoAl alloy that showed single crystal formation. The simulations show that the small amount of polarization of the magnetic moment in the direction of the external field is sufficient to provide the driving force for alignment through the dipole-dipole interaction energy provided the particles are large enough. The simulations help to quantify the relationship particle size, temperature and external field for alignment. Extension of the simulations to complex alloys requires atomistic input to the magnetic properties.

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