TOPICAL REVIEW

Structural control of Fe-based alloys through diffusional solid/solid phase transformations in a high magnetic field

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Abstract
A magnetic field has a remarkable influence on solid/solid phase transformations and it can be used to control the structure and function of materials during phase transformations. The effects of magnetic fields on diffusional solid/solid phase transformations, mainly from austenite to ferrite, in Fe-based alloys are reviewed. The effects of magnetic fields on the transformation temperature and phase diagram are explained thermodynamically, and the transformation behavior and transformed structures in magnetic fields are discussed.

Keywords: ferrite, pearlite, bainite, martensite, magnetic field, transformation temperature, transformation behavior, transformed structure, alignment

1. Introduction
Magnetic fields have been used in various types of research including measuring physical properties, electromagnetic processing [1], etc. Since helium-free superconducting magnets have been developed, new types of experiment such as heat treatments, deformation and material processing in high magnetic fields have become possible. Now it is very simple to induce high magnetic fields of 12 T (T is a unit of magnetic flux density, and 1 T = 10^4 gauss) in a room-temperature bore with a diameter as large as 10 cm. The effects of magnetic fields on solid/solid phase transformation behaviors and microstructures have been intensively studied and the number of papers in this area has increased markedly in the last several years. Most of the results in this area have been published in several special issues [2–10].

In some solid/solid phase transformations, not only the difference in magnetic moment but also the magneto-crystalline anisotropy, shape magnetic anisotropy, induced magnetic anisotropy and the magnetostriction affect the nucleation and growth rates, transformation kinetics, variants and microstructure of product phases. Thus, it is expected that phase transformations are affected by magnetic fields, and that magnetic fields are effective tools for the structural and functional control of materials. It is also expected that new properties may be developed in materials by applying magnetic fields during phase transformations. Iron-based alloys and steels are promising candidates for structural control by magnetic fields because they undergo many solid/solid phase transformations, such as recovery, recrystallization, precipitation, ordering, spinodal decomposition, ferrite, pearlite, martensitic and bainitic transformations and crystallization, which are potentially affected by magnetic fields due to the above mentioned reasons.

Kakeshita et al [11–13] have published review papers on martensitic transformation. Watanabe et al [14, 15] wrote review papers on grain boundary engineering by magnetic field application and Enomoto [16] published a review paper on the enhancement of phenomena in metals by applying magnetic fields. Several review papers have also been published by the author [17–19]. Recent studies on the effects of a magnetic field on diffusional solid/solid phase transformations
transformations, mainly from austenite to ferrite, in Fe-based alloys are reviewed in this paper. In most of these studies, the specimen is fixed in the center of a magnetic field; thus, the magnetic force acting on the specimen can be neglected.

2. Thermodynamic analysis of magnetic field effects

It is very important to thermodynamically evaluate the energy supplied by a magnetic field. Since the additional driving force for phase transformation is supplied by a magnetic field, it is expected that the transformation temperature, phase diagram, transformation kinetics and transformed structure are affected by the magnetic field. Peters and Miodownik [20] calculated the Fe–Co phase diagram in a magnetic field of 2 T, and measured the transformation temperatures for austenite (γ) to ferrite (α) and its reverse transformations. They observed a shift in both α → α + γ and γ → α + γ transformations to higher temperatures under magnetic fields. Choi and our group calculated the Fe–C phase diagram in magnetic fields using Weiss molecular field theory [21]. It was expected that (i) A1 and A3 temperatures, (ii) eutectoid carbon composition and (iii) carbon content in α would increase with increasing applied magnetic field. As a result, the α + γ two phase region is shifted to a higher temperature range. Later, some papers were published on the effects of magnetic fields on the Fe–C phase diagram [22–24]. Enomoto and co-workers calculated the paraequilibrium and orthoequilibrium γ/α phase boundary of Fe–C alloy using Weiss theory and predicted that the A3 temperature is increased by applying magnetic fields even above the Curie temperature [22, 23]. Measuring the transformation temperatures in magnetic fields is a straightforward method of ascertaining the validity of the calculated phase diagram in magnetic fields. Transformation temperatures for γ → α and its reverse transformations in magnetic fields of up to 30 T have been measured for pure iron and Fe–Co alloys [25]. The specimens were austenitized and cooled under various magnetic fields from 0 to 30 T and the temperature at which the recalescence due to the transformation was observed was determined as the transformation start temperature. Figure 1 shows the effect of the magnetic field on the transformation temperature for ferrite transformation of Fe–25Co. Here the transformation temperature means the average temperature for γ → α and α → γ transformations. The transformation temperature linearly increases with increasing magnetic field, and the increase is 48.4 °C for an applied magnetic field of 30 T. Transformation temperatures for pearlite, bainite and lath martensite have also been measured in magnetic fields [26–28]. For all of these transformations, the transformation temperature increases with increasing applied magnetic field. The transformation temperature for pure iron is significantly higher than the Curie temperature of ferrite but the effects of magnetic fields were nevertheless recognized. Kakeshita and co-workers measured the transformation temperature for γ → α and α → γ transformations in pure iron and Fe–Co alloys and discussed the experimental results on the basis of the Clausius–Clapeyron equation [29, 30]. The reason for this increase in transformation temperature is given in the next paragraph.

The effects of magnetic fields on the martensitic transformation start temperature Ms have been measured and analyzed thermodynamically by Sadovskii [31], Satyanarayan [32] and Kakeshita et al [11]. Kakeshita et al used pulsed magnetic fields to show that Ms is increased with magnetic field strength. They calculated the increase in Ms as a function of magnetic field strength using thermodynamics and obtained a good agreement with experimental data. The principle used in the calculation is shown in figure 2 [33], which is a schematic illustration of Gibbs free energy, G, as a function of temperature, T. The subscripts p, m and H denote parent phase, product phase (martensite in this case) and applied magnetic field, respectively. To stands for the temperature at which the parent and product phases have the same free energy in the absence of an applied field. Martensitic transformation starts at Ms, which is below To, and the driving force for martensitic transformation is ∆G. If a magnetic field is applied, the free energy of the ferromagnetic product phase is decreased as shown by the dotted line in figure 2. The free energy of the
parent phase is also reduced but is neglected because the parent phase is paramagnetic and the decrease is very small. Ono et al. [34] determined the susceptibility of γ and α in pure iron and Fe–C alloys by measuring the magnetization force acting on a sample and they showed that the susceptibility of γ is much smaller than that of α. The temperature at which parent and product phases have the same energy shifts to $T_{e}$ in a magnetic field. $M_s$ is also increased to $M_e$ in a magnetic field at which the same driving force for martensitic transformation without a magnetic field can be obtained. For diffusional transformation, the same principle can be applied, and it is expected that the diffusional transformation temperature is increased by applying a magnetic field.

The additional energy supplied by a magnetic field is magnetostatic energy, which is the interaction energy between the magnetic field and the magnetic moment of the phase, and is expressed as $M_dH$, where $M$ stands for the magnetic moment of the product phase. To clarify the effects of magnetic fields on phase transformations, thermodynamic evaluation of the magnetostatic energy is very important, but such an analysis for transformations at high temperatures has rarely been carried out due to the lack of the data for the magnetic moment at high temperatures in a high magnetic field. The value of $M_dH$ was evaluated by Weiss molecular field theory [21]. Weiss [21] speculated that spins are aligned by a molecular field in ferromagnetic materials and that the field is proportional to the magnetic moment of the material. This theory is effective for clarifying the origin of ferromagnetism but the short-range ordering of spins is not considered. However, the temperature dependence of the magnetic moment and susceptibility can be estimated using this theory. Figure 3 shows the magnetic moment of pure iron as a function of temperature. The ordinate shows the magnetization normalized by the magnetic moment at 0 K, the solid line denotes the magnetic moment in the absence of a magnetic field and the dashed line denotes that at 10 T. It is clearly shown that the magnetization is nonzero above the Curie temperature. Therefore, the effects of magnetic fields, such as acceleration of the ferrite transformation, and the elongation and alignment of ferrite grains, are observed even above the Curie temperature [22, 35].

3. Isothermal $\gamma \rightarrow \alpha$ transformation behavior and structure of Fe–Mn–C–Nb alloy

When specimens are heat treated, a larger driving force is provided when a magnetic field is applied because magnetostatic energy is supplied by a magnetic field. Therefore, diffusional transformations are accelerated by applying magnetic fields. The acceleration of ferrite and pearlite transformations is considered to be due to three factors: (i) increase in the nucleation rate, (ii) increase in the growth rate and (iii) decrease in the austenite grain size [17, 18, 36, 37]. The numbers of ferrite grains and pearlite nodules were counted and their maximum radii were measured. In the case of the ferrite transformation, Fe–1.5Mn–0.1C–0.05Nb was austenitized and isothermally transformed at various temperatures between 650 and 720 °C for various periods of time then cooled to room temperature. The number of ferrite grains and the volume fraction of ferrite and austenite grain size were measured and the nucleation rate was calculated. It was found that the nucleation rate is a few times larger in a magnetic field of 10 T than that without a magnetic field. The growth rate was decreased to 70% of that without a magnetic field in the lower temperature range and was increased by 40% in the higher-temperature range. In the case of the pearlite transformation for Fe–13Mn–1C, the nucleation and growth rates at 600 °C were measured. The nucleation rate was increased to two or three times larger than that without a magnetic field, but the growth rate of pearlite formed at grain boundaries increased by only 22% and that formed inside austenite grains decreased by 5%. It was found that the nucleation rate was increased but the effect of the magnetic field on the growth rate was much smaller than that on the nucleation rate. The austenite grain size is decreased in a magnetic field, for example, it decreases by 12 μm in the case of Fe–1.5Mn–0.1C–0.05Nb austenitized at 1150 °C for 15 min. Thus, the main reason for the acceleration of transformations is considered to be the increase in nucleation rate. The bainitic transformation is also accelerated by magnetic fields. Isothermal bainitic transformation behavior with and without a magnetic field was observed for Fe–3.6Ni–1.5Cr–0.5C alloy [28]. The specimens were austenitized at 1150 °C for 15 min and then isothermally transformed at 360 °C for 5 min. The transformation behavior was accelerated using a magnetic field of 10 T, and the volume fraction of bainite increased from 0.08 to 0.97 by applying 10 T when measured on an area of $5 \times 10^3 \mu m^2$. The acceleration of the isothermal bainitic transformation was also confirmed in Fe–0.52C–0.24Si–0.84Mn–1.76Ni–1.27Cr–0.35Mo–0.13V alloy [38].

4. Effects of a magnetic field on $\gamma \rightarrow \alpha$ transformed structure during continuous cooling in Fe–C alloy

The elongated and aligned structure is a unique feature of the transformed structure in magnetic fields, but such a structure
has not been observed for the isothermal $\gamma \rightarrow \alpha$ transformation in an Fe–Mn–C–Nb alloy. The effects of a magnetic field on the $\gamma \rightarrow \alpha$ transformation behavior and structure during continuous cooling in Fe–C alloy are discussed in this section. It was reported that ferrite grains are elongated and aligned along the direction of the applied magnetic field during continuous cooling [39]. Figure 4 shows optical micrographs illustrating the effects of a magnetic field on the transformed structure. An Fe–0.4C alloy was austenitized at 950 °C for 15 min and cooled at a rate of 0.5 °C min$^{-1}$ (a) without a magnetic field and (b) with a magnetic field of 10 T. The equiaxed ferrite grains are distributed homogeneously in (a), but in (b) the ferrite grains are elongated and aligned, which means that most of them are distributed head to tail and are connected with each other along the direction of the applied magnetic field. A method for the quantitative characterization of the degree of structural elongation has been developed by our group [40] and it was found that the degree of structural elongation formed by cooling increases monotonically with increasing magnetic field. The degree of elongation is also increased with decreasing austenite grain size and cooling rate [18, 41]. The effects of magnetic field strength, cooling rate and austenite grain size on the transformed structure in a magnetic field were observed for Fe–Mn–C–X (X = Nb, V, Ti) alloys, but no elongation or alignment of ferrite grains has been observed so far. The effects of a magnetic field of 10 T on the transformed structure have also been examined for an Fe–3.6Ni–1.5Cr–0.5C alloy [28]. An isothermally transformed structure at 360 and 490 °C was observed, but no elongation or alignment of bainite was observed. Bainitic laths with various directions of the long axis were observed inside austenite grains, and no significant difference was found between the transformed structures with and without a magnetic field except for the fraction transformed. Structural alignment was also reported by Shimotomai and Maruta [42] and Shimotomai et al [43] and they concluded that a combination of prior rolling and transformation in an external field is essential for yielding a two-phase microstructure with elongated ferrite grains, but an elongated structure was obtained without any deformation, as discussed in our paper [39].

5. Effects of a magnetic field on transformed structure for $\gamma \rightarrow \alpha$ isothermal transformation in Fe–C alloy

To clarify the mechanism of the elongation and alignment of ferrite grains, the following were investigated: (i) whether ferrite grains are elongated and aligned by an isothermal transformation, (ii) whether ferrite grains are elongated and aligned above the Curie temperature of $\alpha$, (iii) whether the elongated structure is formed in the nucleation stage or the growth stage, and (iv) the dependence of the degree of elongation on the transformation temperature.

Figure 5 shows optical micrographs of specimens isothermally transformed at 785 °C for (a) 10 min and (b) 240 min with a magnetic field of 10 T. It was found that during the transformation, most of the ferrite grains (white regions) precipitate at austenite grain boundaries and triple junctions. At the initial stage (a), $\alpha$ grains are equiaxed and distributed randomly at austenite grain boundaries. With increasing holding time, the amount of transformed ferrite increases and some ferrite grains start to elongate along the magnetic field, that is, ferrite grains grow preferentially along the magnetic field. After 240 min holding (b), most of the ferrite grains are elongated and some of them are distributed head to tail and are connected with each other along the direction of the applied magnetic field. It is clearly shown that ferrite grains become elongated and aligned during an isothermal transformation above the Curie temperature of ferrite. The degree of structural elongation can be evaluated by counting the number of intersections between test lines and $\alpha/\gamma$ phase boundaries [40]. The degree of elongation $\omega$ is calculated from the following equation [44]:

$$
\omega = \frac{(N_\perp - N_\parallel)}{(N_\perp + 0.571N_\parallel)},
$$

in which $N_\perp$ and $N_\parallel$ are the number of intersections when test lines are vertical and parallel to the direction of the magnetic field, respectively. Figure 6 shows the degree of elongation as a function of isothermal holding time [35].
Figure 5. Optical micrographs showing the effects of a magnetic field of 10 T on isothermal $\gamma \rightarrow \alpha$ transformation at 785 $^\circ$C in Fe–0.4C for (a) 10 min and (b) 240 min.

During the transformation, the degree of elongation increases monotonically. At the initial stage, grains are not elongated. Then, the degree of elongation rapidly increases. Finally, the degree of elongation becomes almost saturated. The elongated and aligned structure is mostly formed during grain growth rather than nucleation. The degree of elongation $\omega$ at different temperatures is shown in Figure 7. The degree of elongation increases with decreasing temperature and reaches a peak at $T_c$ and then decreases gradually. It can be seen from this figure that a magnetic field has greatest effect on the elongation of ferrite at approximately $T_c$. It was shown that the degree of elongation of ferrite grains is determined by the competition between the demagnetization effect and the chemical driving force, and their combined effects result in $\omega$ reaching a peak value at approximately $T_c$ [35].

The reason for the elongation of ferrite grains is not well understood. It is speculated that $\alpha$ grains elongated along the direction of the magnetic field reduce the demagnetization field in ferrite grains and therefore decrease the free energy of the system [39]. Shimotomai et al [43] explained the alignment in terms of the dipole interaction effect and calculated the shape of the aligned ferrite grains from the magnetostatic and interfacial energies. As discussed above, ferrite grains are elongated as a result of preferential growth along the magnetic field. However, it is very difficult to explain the microscopic mechanism of elongation because the growth rate depends on several factors, such as the $\gamma/\alpha$ phase boundary energy, the chemical driving force for the ferrite transformation, the demagnetization effect and the diffusion of carbon. The effects of a magnetic field on carbon diffusivity have been reported by Nakamichi et al [45] and Ohtsuka and Hao [46] and they both found that carbon diffusivity is retarded by a magnetic field, but they did not find any anisotropy of diffusivity. Koyama and Onodera [47] have modeled the structural change and carbon distribution for the lath martensite to austenite transformation in a magnetic field using the phase-field method. They found that the carbon distribution is affected by a magnetic field and results in the formation of an elongated structure. Beaugnon et al [48] considered that the local magnetic force causes the elongation of particles. Near a ferromagnetic particle, the local magnetic field is distorted with a maximum value at the vertical poles.

Figure 6. Degree of elongation of ferrite grains as a function of isothermal holding time at 785 $^\circ$C in a magnetic field of 10 T in Fe–0.4C.

Figure 7. Degree of elongation of ferrite grains as a function of isothermal transformation temperature for 30 min in a magnetic field of 10 T in Fe–0.4C.
(along the external field direction) and a minimum value at the equatorial plane. Strong local magnetic gradients exert forces on the diffusing solute atoms in the surrounding matrix. These two models predict the anisotropy of diffusivity in a magnetic field, but they have not yet been verified experimentally. Ohtsuka et al [49] examined the crystal orientation of elongated ferrite grains by electron backscatter diffraction, but found that it was random and no preferential texture was observed. Zhang et al [50] investigated the effects of a magnetic field on texture formation in ferrite in a plain medium-carbon steel and found a decrease in the frequency of low-angle misorientation and an increase in low $\Sigma$ coincidence boundaries.

6. Other transformations in a magnetic field

Other than the $\gamma \to \alpha$ transformation, many transformations in a high magnetic field have been reported. Xu et al [51, 52] showed that recovery is accelerated but that recrystallization and grain growth are retarded by a magnetic field in Fe-based alloys. Tong et al [53] claimed that a magnetic field enhances grain growth in nanostructured pure iron and produces a uniform nanocrystalline grain structure. Tanaka et al [54] found that a monovariant structure of the L1$_0$ ordered phase is formed in FePd by heat treatment in a magnetic field, and Kakeshita and Fukuda [29] obtained a single variant of an L1$_0$-type ordered phase in CoPt by ordering heat treatment in a magnetic field. Ichitsubo et al [55] formed a triangular lattice of nanoparticles in FePt thin film by annealing under an external magnetic field. Fujii et al [56] studied the effects of a magnetic field on the crystallization of amorphous Fe$_{78}$Si$_{10}$B$_{12}$ alloy and observed the development of sharp texture in nanocrystalline materials. Yasuda et al [57] proposed a coarsening model that includes interfacial energy and magnetic anisotropy energy and calculated the kinetics of grain alignment during coarsening in a magnetic field. Chiba et al [58] reported that a Co–Ni-based superalloy aged in a magnetic field exhibits higher strain-age hardening. Ohtsuka et al [59] investigated the transformed structure in a reverse transformation from lath martensite to austenite in a magnetic field and observed an elongated and aligned structure. Watanabe et al [60] spot-welded stainless steel in a magnetic field and observed the structure of the heat-affected zone (HAZ) and found that the area of the HAZ increases with increasing magnetic field. Koyama and Onodera modeled various types of transformation behavior in a magnetic field using the phase-field model and simulated the structural change for Fe–Cr–Co alloy [61] and Ni$_2$MnGa [62]. Jamilillo et al [63] observed the formation of extremely fine perlite in a magnetic field of 30 T in a novel bainitic steel. Zhang et al [64] reported that a magnetic field prevents the directional growth of cementite and makes particle-like cementite when quenched steel is tempered in a magnetic field. Thus, it has been shown that many types of transformation are affected by a magnetic field. Among these transformations, diffusion is very important in diffusional transformations, but there have been very few studies on the effects of a magnetic field on diffusion. Youdelis et al [65] reported that a magnetic field of 3 T suppressed the diffusivity of Cu in Al perpendicular to the direction of the field by about 25%. Now ever, Nakajima et al [66] did not find any effect of a magnetic field on the diffusion of Ni in Ti. The effects of a magnetic field on diffusion should be clarified in detail in the future.

So far the effects of a magnetic field on phase transformations have been discussed, and in these cases the specimen was fixed in the center of a magnetic field. When the specimen is in a gradient magnetic field, both a magnetic field and a magnetic force are applied to the specimen simultaneously and some interesting phenomena can be observed. Shimotomai [67] showed that the hardness of pearlite in steel increases when it is transformed in a magnetic field gradient. Nakamichi et al [45] reported that the diffusion of carbon in $\gamma$ is enhanced in a magnetic field gradient when carbon atoms move in the direction with a higher magnetic field and retarded when an opposite magnetic field gradient is applied. Ono et al [34] determined the susceptibility of $\gamma$ and $\alpha$ by measuring the magnetic force in a gradient magnetic field and obtained a time-temperature-transformation (TTT) diagram for Fe–C alloys in a magnetic field. Rivoirard et al [68] also observed the isothermal $\gamma \to \alpha$ transformation behavior by measuring the susceptibility. In the above-mentioned transformations, the product phase was mostly ferromagnetic, but even for nonmagnetic materials, the effects of a magnetic field can be observed when their magnetic anisotropy is sufficiently large. Sheikh-Ali et al observed a magnetically induced texture in zinc alloy [69] and measured the mobility of the interface of Zn bicrystal in a magnetic field [70]. Molodov and Sheikh-Ali [71] studied the effects of a magnetic field on texture in titanium.

7. Conclusions

Many papers presenting new findings on the effects of magnetic fields on solid/solid phase transformations have been published recently. Some of the effects are explained theoretically but there are still many subjects to be clarified. First of all, information on magnetic properties at high temperatures and high magnetic fields is required, so that the effects of a magnetic field can be analyzed and its magnetic energy can be evaluated. On the basis of this knowledge, it is important to know the type of structure, and as a result, the physical properties that can be obtained in a magnetic field for the structural and functional control of materials through phase transformations in a high magnetic field.

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