Enhanced Phenomena in Metals with Electric and Magnetic Fields: II Magnetic Fields
Masato Enomoto

Department of Materials Science, Ibaraki University, Hitachi 316-8511, Japan

Magnetic field effects were first noticed in texture formation in ferrous alloys more than half a century ago, when the available field intensity was an order of or less than one Tesla. With increasing availability of very intense magnetic fields of an order of ten Tesla, the potential of magnetic field as an additional controllable external parameter for microstructure control is widely recognized, not only in ferromagnetic, but also in non-ferromagnetic metals and alloys. As a companion paper to Part I on electric field effects the influence of magnetic fields on microstructure, morphology and kinetics of transformations in solid metallic materials are reviewed in Part II.

(Received January 17, 2005; Accepted March 7, 2005; Published June 15, 2005)

Keywords: recrystallization, grain growth, texture, boundary mobility, spinodal decomposition, martensitic transformation, precipitation, ferrite transformation, pearlite, microstructure control

1. Introduction

Recently, the use of a magnetic field for microstructure control in metallic materials has attracted considerable attention. According to the literature studies of magnetic field effects were made first on recrystallization and texture formation around 1950. This is probably because the effects could be observed at weaker fields, e.g. less than producing saturation magnetization. Then, the effects on spinodal decomposition were studied with a field of similar intensity. Magnetic field effects on martensitic transformation were studied using both pulsating and static fields. For the former a very strong field was readily available and so, it was used to study the effects on athermal martensitic transformation which proceeds extremely rapidly. On the other hand, a static field was needed to study isothermal martensitic transformation and it was first attempted in a field of 2T[3] in early 1970’s.

Much stronger static fields are needed to study precipitation and phase transformation of which the chemical driving force is large compared to the energy of interaction with external fields, that is, magnetization multiplied by field intensity. For these studies an experimental setup is needed that allows for a heat treatment in a static field for a substantial amount of time. Owing to the increasing availability of strong magnetic fields a larger number of precipitations and transformations are being studied. Under this circumstance developments so far made in this area are reviewed. Whilst magnetic fields are known to be a highly prospective means of controlling solidification microstructure, it is not included in this article.

2. Magnetic Field Effects on Recrystallization, Grain Growth and Texture

Smoluchowski and Turner[3,4] were probably the first to study the texture formation during magnetic annealing. They observed an increase in the (110) texture in the rolling direction of an Fe–35Co sheet by annealing in a magnetic field, probably strong enough to produce the saturation magnetization. Bhandary and Cullity[5] studied the texture of swaged iron wire by annealing the specimen in weak fields less than one hundredth of Tesla in the expectation that the difference in magnetostrictive strains between different crystal orientations is larger for not fully magnetized crystals. Indeed, they observed not only (110) fiber texture, but also a substantial amount of (111) and (112) components.

Two decades later, Martikainen and Lindroos[6] studied the influence of magnetic field on the texture formation in an iron sheet whose thickness dimension is so large that the surface effects are expected to be minimal. With the applied field of 1.5T they observed the preferential nucleation of grains whose (100) axes, the direction of easy magnetization of iron, were parallel to the field. Watanabe et al.[7] reported that the proportion of low-angle grain boundaries increased in an Fe–9Co alloy annealed in a field of 0.2 and 0.5T parallel to the rolling direction. Masahashi et al.[8] studied the development of preferred orientation in a cold rolled Fe–Si sheet using a strong field (10T) in which the magnetization was likely saturated in all crystallographic directions. The observed increase in the (100) texture component was ascribed to the magnetostriction. Recently, Bacaltchuk et al.[9] reported that magnetic annealing in a field of 13T increased the {110}[001] Goss texture even above the Curie temperature.

Martikainen and Lindroos[6] noted another important effect of magnetic field, that is, the retardation of recrystallization. They considered three reasons. The first is the decrease in grain boundary mobility by magnetic ordering. The second is that the domain walls act as a barrier to grain boundary migration and the third, the change in the structure of grain boundaries due to the magnetic field. The retardation of recrystallization and grain growth was also observed in much stronger fields by other authors.[7,8,10] Xu et al.[10] demonstrated that a magnetic field of 10T markedly decelerated the grain growth of a hot rolled and fully recrystallized Fe–Si alloy, as shown in Fig. 1.

A magnetic field is known to have an influence on texture formation not only in ferromagnetic materials, but also in non-ferromagnetic (i.e. paramagnetic and diamagnetic) materials, as first pointed out by Mullins nearly half a century ago, using polycrystalline Bi.[11] Bi is well known to have a relatively large anisotropic magnetic susceptibility. In a
magnetic field grain boundaries in such materials experience a force (or pressure) given by,

$$ p = \frac{\mu_0 H^2}{2} (\chi_1 - \chi_2) $$

(1)

where $\chi_1$ and $\chi_2$ are the susceptibility of the two grains forming the boundary, $H$ is the field strength, and $\mu_0$ is the magnetic constant (the permeability of vacuum). This equation provides an opportunity for measurement of grain boundary mobility. Indeed, the mobility of grain boundaries in Bi\textsuperscript{12,13} and Zn\textsuperscript{14} bicrystals, both being hexagonal and diamagnetic, was measured applying a field of 10–20 T. It was found that the grain boundary mobility varied not only with the misorientation of the two grains, but also with the boundary inclination, and that the mobility depended on the direction of the motion when the boundary was not a symmetric tilt boundary.

The texture development in magnetic fields was also studied in Ti\textsuperscript{15} and zinc alloys\textsuperscript{16}. Whilst the (0002) pole density is usually symmetric in cold rolled Ti, magnetic annealing in a field of 19 T produced asymmetric texture peaks when the sample was tilted by ±30° to the field direction around the rolling direction. This is probably because the c-axes of grains responsible for the peaks were aligned at different angles to the magnetic field direction and selective grain growth occurred.\textsuperscript{14}

3. Spinodal Decomposition

The influence of magnetic fields on spinodal decomposition was studied soon after the new mechanism of alloy decomposition was proposed. In the presence of magnetic field the limit of instability for infinitesimal composition fluctuation is expressed as,\textsuperscript{17}

$$ \frac{\partial^2 f}{\partial c^2} + 2\eta Y + \pi \left( \frac{\partial M}{\partial c} \right)^2 = 0 $$

(2)

where $f$ is the free energy of the solution, $\eta = d\ln a/dc$ (a is the lattice parameter), $Y$ is the elastic constant, $M$ is the magnetization and $c$ is the solute concentration. Since the 3rd term in the left hand side is positive the wave number of composition waves parallel to the field always becomes smaller than that of perpendicular waves. Thus, the microstructure consists of uniformly spaced rods elongated in the direction of the applied field, as was observed in AlNiCo alloy.\textsuperscript{17,18} It is noted that magnetic aging is effective at temperatures near the Curie temperature at which $\delta M/\delta c$ becomes infinite.

4. Martensitic Transformation

In early 1960’s it became known that magnetic fields promote martensitic transformation in ferrous alloys. The increase in $M_s$ temperature was reported for the athermal type.\textsuperscript{19–21} It was also found that a magnetic field accelerates the isothermal martensitic transformation.\textsuperscript{22,23} These were accounted for initially by the interaction energy of the induced magnetization with the applied field. Subsequently, Kakeshita et al.\textsuperscript{24} and Menshikov\textsuperscript{25} conducted a more sophisticated analysis of the transformation temperature and proposed the following equation,

$$ \Delta G(M_s) = \Delta G(M'_s) = -\Delta M \cdot H - \frac{1}{2} \chi_{hf} H^2 + \varepsilon B \frac{\partial M}{\partial H} \cdot H. $$

(3)

Here, the left hand side is the difference in Gibbs free energy between the parent and martensite phases ($M'_s$ is the $M_s$ temperature in a magnetic field), $\Delta M$ is the difference in the spontaneous magnetization, $H$ is the intensity of the applied field, $\chi_{hf}$ is the high field susceptibility, $\varepsilon$ is the volume change attending the transformation, $B$ is the bulk modulus and $\omega$ is the forced volume magnetostriction (the 3rd term is thus the strain energy produced by the volume change due to magnetostriction). Kakeshita et al. demonstrated that incorporating all these terms the shift of $M_s$ temperature due to external magnetic fields are explained very well in Fe–Ni\textsuperscript{24} and Fe–Pt alloys\textsuperscript{26}. They also showed in an Fe–Ni–Mn alloy that with increasing field intensity the isothermal martensitic transformation exhibits athermal nature in a field stronger that a critical value\textsuperscript{27,28} This lends support to their view that both athermal and isothermal martensitic transformation can be treated in a unified manner.

Magnetic fields are used for controlling martensitic transformation in various alloys. They observed the so-called magnetoelastic behavior in an Fe–Ni–Co–Ti alloy, that is, martensite is formed above $A_f$ (temperature at which the martensite to austenite reverse transformation is completed) and upon demagnetization the martensitic phase disappears.\textsuperscript{29} A Heusler compound Ni\textsubscript{2}MnGa has a large uniaxial magnetostructural anisotropy\textsuperscript{30} and the mobility of twin boundaries are so high that one can control the formation of a specific variant of martensite by applying a magnetic field (Fig. 2).\textsuperscript{31} The alloy has a fast response to the change of the field intensity compared to conventional thermally controlled shape memory alloys and thus this compound is regarded as one of the most prospective alloys for actuator material.\textsuperscript{32–34} Koyama\textsuperscript{35,36} studied the formation of $\alpha'$ Fe\textsubscript{6}Ni\textsubscript{3} from Fe–N austenite in an attempt to fabricate a bulk single crystal of $\alpha'$ Fe\textsubscript{6}Ni\textsubscript{3}. They observed that $\gamma$ to $\alpha'$ martensitic transformation occurred isothermally at liquid helium temperature, which was above $M_s$ in a field of less than 40 T.
5. Precipitation and Ordering Transformation in Iron Alloys

The influence of magnetic fields on the phase stability, precipitation and ordering reaction were noted in iron alloys from earlier times. Peters and Miodownik\(^{37}\) reported that the temperature of \(\gamma\) (fcc) to \(\alpha\) (bcc) transformation in Fe–Co alloys, close to 1000°C, was increased by several degrees in a magnetic field of 1.9 T (the transformation was probably massive because of the very narrow \((\alpha + \gamma)\) two phase field). The same group reported a remarkable increase in hardness of an Fe–20Cr alloy when it was aged at temperatures lower than 575°C in a field of 14 T.\(^{38}\) Since the precipitation of non-magnetic \(\sigma\)-phase could be delayed, they ascribed the observed hardening to the acceleration of phase separation due to the magnetization induced by the external field.

Plate-like \(\alpha''\)-Fe\(_{16}\)N\(_2\) particles have a large transformation strain in the direction normal to the broad face. Thus, under a stress they are formed with preferred orientation, \(i.e.,\) the broad face being parallel to one of the \(\{100\}\) planes of the bcc iron. A similar orientation of the particles is expected to occur under an external magnetic field because of a strong magnetocrystalline anisotropy of \(\alpha''\)-Fe\(_{16}\)N\(_2\) phase. This was indeed observed by Sauthoff and Pitsch.\(^{39}\) Both the matrix and precipitate phases are ferromagnetic at the aging temperature. Thus, the orientation is considered to be due to the magnetic interaction between the magnetic domain of the matrix and magnetization of the precipitates.

It is reported that the formation of ordered domains in FePd alloys is influenced by external stresses and magnetic fields.\(^{40,41}\) The ordered FePd phase has a large uniaxial magnetocrystalline anisotropy. In a magnetic field a specific variant of ordered FePd phase (L1\(_0\) structure) is nucleated preferentially with its \(c\)-axis parallel to the field direction. According to Tanaka et al.\(^{41}\) a crystal almost composed of mono-variant ordered domain was obtained from disordered single crystal of Fe–49.8%Pd alloy when the alloy was aged in a field of 10 T at temperatures at which the ordering occurred by nucleation and growth. Though not in a ferrous alloy, it is reported that the morphology of ferromagnetic Co particles precipitated in a fcc Cu–Co alloy was influenced by an external magnetic field. The particles were elongated in the field direction to minimize the magnetostatic energy of the particles.\(^{42,43}\)

6. Proeutectoid Ferrite Transformation in Fe–C and Fe–C–X Alloys

The influence of magnetic fields on proeutectoid ferrite transformation, if any, has a special meaning because the transformation affects profoundly the final microstructure of steels. The ferrite transformation occurs in a wide temperature range depending on the steel composition, and thus, thermodynamic analyses of magnetic field effects were conducted both below and above the Curie temperature. Choi et al.\(^{44}\) evaluated the driving force for the transformation in a magnetic field using the magnetic susceptibility data. As shown in Fig. 3, the \(Ae_1\) and \(Ae_3\) temperatures were increased by 1–2° per Tesla for the field strength of \(H \leq 20\) T. Similar results were obtained from calculations by means of Weiss molecular field theory.\(^{35,46}\) These calculations have shown that bcc iron is more stable than fcc iron at all temperatures in a field of \(H \geq 70\) T. The same analysis was conducted in Fe–C–X alloys, where X is a substitutional alloying element, taking into account the influence of alloying element on the magnetic moment and Curie temperature of \(\alpha\) iron, and para- and ortho-equilibrium \(\alpha/\gamma\) phase boundaries\(^{47}\) were calculated.\(^{46}\)

These calculations also showed that the driving force of ferrite transformation is increased in magnetic fields and thus, the transformation is accelerated. Indeed, it is reported that the transformation kinetics are substantially increased in both isothermal\(^{48}\) and continuous cooling transformation.\(^{44,49}\) Furthermore, the kinetics are reported to be increased not only below the Curie temperature, but also above it.\(^{48}\) This can be attributed to the large magnetic susceptibility of paramagnetic bcc iron compared to that of austenite.

One of the remarkable features of \(\gamma \rightarrow \alpha\) and reverse \(\alpha \rightarrow \gamma\) transformations in magnetic fields is the formation of aligned microstructure. This was first noted by Shomotomai et al.\(^{50,51}\) in the reverse transformation in an Fe–0.1 mass%C alloy. As shown in Fig. 4, austenite grains formed upon heating were aligned along the direction of the applied field. Subsequently, Ohtsuka et al.\(^{52–54}\) reported the alignment of ferrite grains in the forward transformation in a field of 10 T. The alignment occurred more readily when the alloy was cooled slowly, which may indicate that the magnetic
interaction between the two ferrite grains played an essential role during the transformation at a small undercooling at which the chemical driving force for the transformation is small.

7. Pearlite Transformation

As seen in Fig. 3, the $\gamma/(\alpha + \gamma)$ phase boundary, i.e., $\gamma\gamma$ temperature, of Fe–C alloys is raised in a magnetic field. The Curie temperature of cementite ($\text{Fe}_3\text{C}$) is $210^\circ-215^\circ\text{C}$, and thus, the formation of cementite may be little influenced by external fields at temperatures at which pearlite transformation normally occurs. This leads to an increase in both the eutectoid composition and temperature. A few studies are available of pearlite transformation behavior in medium and high carbon steels during isothermal holding. Xu et al. showed an increase in the number of pearlite nodules in hypereutectoid steels in a field of 10 T. The implication of these findings as to the leading phase in the nucleation of pearlite has not been much discussed.

Russian researchers reported an increase in the microhardness of pearlite formed in a magnetic field of $1.2\text{T}$. Very recently, a similar increase in the hardness of pearlite was reported in an eutectoid alloy transformed in a strong field ($5$–$12\text{T}$). They both attributed the increase in strength to the increase in the carbon solubility in ferrite, whilst Shomotomai et al. considered the presence of a steep gradient of magnetic field to be essential in the hardening of pearlite nodules.

8. Summary

As seen above, magnetic fields are used for microstructure control in various alloys and compounds. In theoretical analyses the influence of magnetic fields on thermodynamic phase stability is understood fairly well. In contrast, the influences on kinetics, e.g., influence on diffusion and grain boundary mobility etc., are least understood. It is also noted that a number of studies are available of magnetic effects on mechanical properties, some of them having been done quite recently. It is likely that the advent of a superconducting magnet, small-sized and readily capable of producing a field stronger than 10 T in a large bore ($\sim 10\text{cm}$), facilitates not only our understanding of underlying mechanism, but also technological developments that would not be achieved by a field of conventional strength.

Acknowledgements

The support from Research Forum of Magnetic field effects on microstructure in steels, The Iron and Steel Institute of Japan, Tokyo, and the Ferrous Supermetal Consortium of The Japan Research and Development Center for Metals (JRCM), Tokyo, are gratefully acknowledged.

REFERENCES

2) $T = 10^4\text{Oe}$ or $7.97 \times 10^5\text{A/m}$.
30) K. Ulakko, J. K. Huang, V. V. Kokorin and R. C. O’Handley: Scr.
In Fe–C–X alloys diffusion of X is very sluggish compared to diffusion of carbon. Thus, it is necessary to analyze a pseudo-equilibrium in which only equilibrium with respect to carbon is achieved between ferrite and austenite without a change in the X composition. This is called paraequilibrium. On the other hand, ortho-equilibrium is an ordinary equilibrium in which equilibrium is achieved with respect to all component species. The term “ortho” is used to note the difference from paraequilibrium.