ABSTRACT. The microstructural modification and property improvement of steels through the introduction of a magnetic field, especially a high magnetic field, to their solid phase transformation has aroused much attention in recent years. The effect of the magnetic field on martensitic transformation, bainitic transformation and ferritic transformation of steels has been the main topic of this domain. It has been found that the magnetic field can increase the martensitic and bainitic transformation start temperatures and accelerate the transformation. The application of a high magnetic field to the proeutectoid transformation in steels started relatively late, as there existed technical difficulty in obtaining high temperature and high magnetic field at the same time. Now more attention has been shifted to the diffusional transformations of steels under high magnetic fields. The author’s group has been active in this topic and conducted both theoretical and experimental researches in this domain. The main achievements in revealing the thermodynamic and kinetic effects of high magnetic fields on austenite decomposition and thus its positive application to practical heat treatment procedures are overviewed. In addition, the microstructural modification behaviors during martensitic decomposition by the magnetic field and the possible property improvement to a high strength low-alloyed steel are also summarized.

KEYWORDS: electromagnetic processing of materials (EPM); heat treatment; magnetization; martensitic transformation; bainitic transformation; ferritic transformation; precipitation.

INTRODUCTION

More and more demands have been placed on the property improvement of materials and innovation of manufacturing processes, especially the conventional materials like steels and conventional processing approaches. To meet these requirements, new ideas and novel techniques are needed. Introducing an external field such as electric field, magnetic field and etc. to conventional heat treatments of conventional materials has aroused much attention in hope of realizing microstructural modifications and thus property improvement. Magnetic field, especially high magnetic field, as clean, powerful and non-contacting energy, has received much attention in materials research area, as it can act on atomic behaviors, affect such as atom arrangement, matching and migration and hence exert powerful influence on microstructures and properties of materials.

Now the researches have mainly been addressed on martensitic, bainitic and ferritic transformation in steels under a magnetic field, as under different phase conditions, the phases show different magnetic
properties that can be made use to control the transformation and thus modify the microstructure. The main achievements will be summarized in the present work.

1. Martensitic transformation under magnetic fields

For ferrous alloys with phase transformations, the final strengthening results from the transformation from austenite to martensite. The amount of martensite obtained from the transformation directly affects the strengthening effect. As austenite is paramagnetic and martensite is ferromagnetic, the introduction of the applied magnetic field will certainly promote the transformation and thus enhance the effect of strengthening. Therefore, applying magnetic field to heat treatment started from quenching process in the late 50s and the 60s last century [1-8].

Like temperature or pressure, the magnetic field is one of the important thermodynamic parameters that are used to change the internal energies of materials. In the case of transformation from austenite to martensite, the Gibbs free energy of martensite would be greatly lowered as it has higher magnetization compared with that of austenite. The latter is paramagnetic and its Gibbs free energy does not change much with the applied magnetic field. Therefore the ferromagnetic martensite becomes much more stable in the field. As shown in Fig. 1, since magnetic field lowers the Gibbs free energy of martensite $G_\alpha$ to $G_\alpha^M$ and that of austenite changes only a little from $G_\gamma$ to $G_\gamma^M$, the equilibrium temperature of the two phases $T_0$ is thus be elevated to $T_0^M$ and then the $M_s$ will go up in the same direction. As the driving force of the transformation is determined by the Gibbs free energy difference between the two phases, the transformation can be greatly enhanced by the application of the magnetic field.

![Figure 1](image_url)

**Figure 1** Variation of Gibbs free energy of austenite and martensite versus temperature in the case without and with magnetic field, $\alpha$ – martensite; $\gamma$ – austenite; $M$ – magnetic field

Most early researches on field effects dealt with this issue. The representative investigations were conducted by the research group of Sadovksy et al. [1-4]. They carried out a series of researches on the effect of magnetic field on martensitic starting temperature, the amount of martensite obtained and microstructure morphologies appearing during martensitic transformation in some ferroalloys. It was found that the magnetic field can obviously increase the transformation temperature and promote
transformation amount. As the magnetic field can accelerate the transformation and enhance the amount of martensite obtained, the related properties are increased. Bernshteyn et al. [5] applied a magnetic field of 4000 Oersted to the martensitic transformation in some iron-nickel-carbon steels and found the transformation was greatly accelerated which resulted in an increase of yield point of the steel by 10-15%. Although the magnetic field applied can greatly affect the transformation starting temperature and transformation speed, no morphology change of the martensite was spotted.

As there was no powerful superconducting magnet, the intensity of magnetic field obtained was limited and hence further investigations were restricted. Until 1980s with the progress in high field generating technique, study on this aspect started to go deeper and wider. Japanese researchers, Kakeshita et al. [9-18] carried out a relatively thorough researches on effects of composition [11], grain boundary, crystallographic orientation [13], Invar character [12], thermal elastic nature [10] and magnetism of austenite [17] on magnetic field induced martensitic transformation under much higher magnetic field. Many useful results were obtained on influence of magnetic field on $M_s$ temperature, the amount of martensite obtained, morphology and TTT diagram of the transformation. Their study further confirmed that the magnetic field can greatly increase the $M_s$, increase the transformation amount, shift the nose of the TTT curve to the lower temperature and shorter time area.

2. Bainitic transformation under magnetic fields

There were also some reports on bainitic transformation of steels under magnetic field. Grishin studied the effect of a magnetic field on austenitic decomposition of different structural steels in bainitic transformation zone [19]. According to the hardness test, he obtained the information about transformation progress with the isothermal time and found that the magnetic field promotes the bainitic transformation and enhances the dispersion degree of carbide precipitates. Later Fokina and co-workers introduced magnetic fields to the bainitic transformation of several structural steels [20]. They found that the magnetic field applied shortens the incubation time and enhances the transformation amount. Similar phenomena were also found in bearing steels. Ren and co-workers applied an impulse magnetic field to the isothermal quenching of a 9SiCr steel [21]. They found that the magnetic field can shorten the incubation time, accelerate the bainitic transformation and reduce the amount of retained austenite. After magnetic quenching, the microstructure becomes fine and the hardness of the material is increased as seen in Fig. 2 and 3. The possible reasons for the effect of the impulse magnetic field could be summarized as [21]: (1) magnetic field increases the transformation driving force and thus enhances the transformation; (2) the magnetostrictive effect under the impulse magnetic field causes the interspacing between Fe atoms to change periodically that enhances diffusion of carbon atoms and decreases their diffusion activation energy and thus promotes the transformation; (3) the magnetic field lowers the internal energy of the ferromagnetic phase and thus decreases nucleation barrier and increases the nucleation rate. In this way, the magnetic field shows positive influence on improving the mechanical properties of the conventional materials.
3. Ferritic and pearlitic transformation under magnetic fields

With further progress in cryocooling technique and manufacture of superconducting magnet, installation of high temperature heat treatment equipment inside superconducting magnet has been available. Therefore, researches on high temperature phase transformations under high magnetic field of more than 10 Tesla are possible. Since 1990s, high magnetic field has been introduced into various solid-state phase transformations, such as transformation from austenite to ferrite and its reverse [22-24], and other diffusional transformations. Many valuable microstructure phenomena and their evolution under magnetic field have been revealed. Now more attention has been paid to the diffusional phase transformation in steels under magnetic fields, especially under high magnetic fields.

Experimental studies have revealed that transformations between austenite and ferrite in steels have shown many new microstructure characteristics. In late 1970s, Pustovoit and Yu [25] applied a field of 1.2 T during the austenite decomposition in high carbon steels and found that the amount of ferrite was increased. Palmai [26] found that a magnetic field of 0.45 T retarded the inverse transformation in a 0.6%C (wt%) steel. Peters and Miodownik [27] observed that the phase equilibrium boundary between
the austenite and ferrite of Fe-Co alloy was shifted to a higher temperature. Ghosh et al. [28] found that magnetic field can obviously accelerate the isothermal transformations from austenite to pearlite and bainite in high carbon high chromium AISI D3 steel. Recently, our group has conducted relatively thorough investigation on the kinetic and thermodynamic effects of high magnetic fields on austenite to ferrite and then pearlite transformation in a hot-rolled low-alloyed medium carbon steel (42CrMo) [29-31]. A 14-T magnetic field was introduced when the fully austenitized 42CrMo was cooled at 46°C/min [32]. Results show that without the field the microstructure is mainly composed of bainite; while with the field, the microstructure is still of ferrite and pearlite, as shown in Fig. 4. As the magnetization of the bcc phase in Fe-based alloys is higher than that of the paramagnetic fcc phase, its total Gibbs free energy under the applied magnetic field is considerably lowered. In this way, the transformation driving force is increased and thus the transformation time is reduced. Even at relatively fast cooling rate, the holding time at high temperatures is long enough to allow austenite to transform into ferrite and later pearlite. As a result, the microstructure obtained with the field is still ferritic and pearlitic. Hardness test shows that the hardness of the field treated specimen is HB192-210 just within the HB 160-230, the optimum hardness for machining. This result is quite positive, as the ferritic and pearlitic microstructure in medium carbon steels can be obtained through conventional full annealing during which furnace cooling (about 1°C/min) is required. The aim of the annealing is to adjust the hardness of the work pieces for subsequent machining and, in parallel, to improve the microstructure for final quenching and tempering. However, when the magnetic field is applied, the cooling rate to obtain the required ferritic and pearlitic microstructure can be greatly increased. Based on this result, a new annealing method - rapid annealing under a high magnetic field - was worked out [29]. The advantages of this technique are: (1) through increasing the cooling rate, the productivity can be considerably increased; (2) it avoids the formation of banded structure along hot rolling direction that occurs frequently during ferritic transformation when furnace cooling is applied, as seen in Fig. 5 [29].

![Figure 4](image-url)  
**Figure 4** Microstructure of specimen heat treated at 880°C for 33min and cooled at 46°C/min without (a) and with (b) a 14-T magnetic field, Field direction is vertical in the picture [32]
Then a respective 6, 10 and 14-T magnetic field was introduced when the fully austenitized 42CrMo was cooled at 10°C/min [32]. It was found that the magnetic field increased the amount of proeutectoid ferrite, as seen in Fig. 6. This is attributed to the influence of the magnetic field on phase equilibrium. As the magnetic field applied shifts the Ae3 line in the Fe-C diagram to high carbon content side, the amount of proeutectoid ferrite is increased [33].

4. Martensitic decomposition in a high magnetic field

To investigate the decomposition of martensite or tempering behaviors of steels in a high magnetic field is relatively recent and original. A 14-T magnetic field was applied to both high temperature [34] and low temperature tempering [35] of the hot rolled 42CrMo after it was water quenched. For high temperature tempering, it was found that the magnetic field showed spheroidization effect on the formation of cementite precipitates, as show in Fig. 7. Without the field, the cementite precipitates are in long strips and distributed along martensite plate and twin boundaries (Fig. 7 (a)); while when the field was applied, they are in spherical shape and distributed homogeneously (Fig. 7 (b)). This phenomenon is attributed to the change of the interfacial energy and magnetostrictive energy by the magnetic field [34]. As both ferrite and cementite can be magnetized to some extents, their Gibbs free energies are lowered by the magnetic field. As the interface between these two phases is highly disordered, its energy level remains unchanged. Consequently, the relative interfacial energy is increased as schematically illustrated in Fig. 8. So the shape of cementite that has minimum interface area is advantageous to minimize the final total interfacial energy. Therefore, the sphere or particle like cementite is most favorable. In addition, the magnetostriction of the cementite and ferrite are also different. In the case of the hard cementite growing within the soft ferrite matrix, the directional growth of cementite will cause large increase in strain energy [36] and is thus not favored. Under these two effects of the magnetic field, the particle like cementite that has minimum total interfacial area and minimum magnetostriction strain energy is most energetically favorable and consequently occurs in the magnetic field.
It was also found that the magnetic field has some effect on the recovery of the ferrite matrix. Fig 9 shows the OIM maps of the specimens tempered at 650°C without and with a 14-T magnetic field, respectively. In the pictures, the blue areas represent the ‘distortion-free’ regions and the rest parts in yellow are the ‘distorted’ ones. Further analysis show that the area percentages of the ‘distortion-free’ regions are 7.24% without and 5.42% with the 14-T field and the percentages in the number of the ‘distortion-free’ regions are 55.41% without and 51.64% with 14-T field [34]. This indicates that magnetic field has obvious effect of retardation on the formation and growth of the ‘distortion-free’ regions. As magnetic field may lower the mobility of the grain boundaries either by atomic diffusion
through magnetic ordering or by the obstructive effect of domain walls [37] and the formation and the growth of the ‘distortion-free’ regions need the atom diffusion and boundary migration, the recovery could be retarded by the application of the magnetic field. During this high temperature tempering process, the magnetic field shows strong positive effect on spheroidization of the precipitates, which will surely lead to the improvement of properties.

Figure 9 OIM maps of specimens tempered at 650 for 1 h (a) without field and (b) with a 14-T magnetic field. The field direction is horizontal in the picture [34].

When the 14-T magnetic field was applied to the low temperature tempering process (200°C; 1h), the 14-T magnetic field showed strong effect on changing the precipitation sequence of the transition carbides [35]. The carbide precipitates obtained without and with the field is shown in Fig. 10. It is seen that with the field, the carbides are distributed more densely and with smaller sizes. The crystal structure of precipitates and their orientation relationship with matrix has been identified by electron diffraction of TEM. The carbide formed during non-magnetic tempering is of typical orthorhombic η-Fe2C and is correlated to tempered martensite α'' by (110)α''//(200)η and [1 1 3]α''//[0 2 0]η. However, the carbide precipitating in the magnetic field is referred to as the monoclinic χ-Fe5C2 with the orientation correlation by (01 1)α''//(02 1)χ and [1 3 3]α''//[5 3 6]χ. Normally, χ-Fe5C2 precipitates at higher temperature after η-Fe2C dissolves. Therefore, the magnetic field has an equivalent effect of promoting the tempering temperature. This results in the improvement in the impact toughness of the material. When treated with the magnetic field, the toughness is increased by 9% [35].
Figure 10 SEM secondary electron images of carbide precipitates (bright areas) within martensite in specimens tempered at 200°C for 60 min (a) without and (b) with a 14-T magnetic field (the magnetic field direction is vertical in the micrograph) [35].

η-Fe₂C, and χ-Fe₅C₂ are both ferromagnetic at 200°C, and from the thermodynamic point of view, the application of an external magnetic field can lower their Gibbs free energies and thus their formation sequence. Calculation shows that the magnetization of χ-Fe₅C₂ is lower than that of η-Fe₂C at 200°C, as displayed in Fig. 11 [35]. Therefore, its total Gibbs free energy may go lower than that of η-Fe₂C and then it precipitates before η-Fe₂C as schematically illustrated in Fig. 12.

Figure 11 Temperature variations of magnetization of Fe₂C, Fe₅C₂ and α-Fe [35].

Figure 12 Schematic diagram of Gibbs free energy vs. carbon concentration for α’ martensite, χ-Fe₅C₂ and η-Fe₂C at 200°C without (dash line) and with (solid line) a 14-T magnetic field [35].
Summary

The magnetic field has strong thermodynamic and kinetic effects on transformations between phases with different saturation magnetizations. When it is applied to a transformation from a low magnetization phase to a high magnetization phase, as in the case from austenite to martensite, bainite or ferrite, it enhances the transformation temperature, accelerates the transformation speed and increases the amount of the product phase. These effects could be applied to shorten the heat treatment time, increase productivity and thus innovate the conventional heat treatment processes.

For the effects of the magnetic field on martensitic decomposition, they are quite tempering temperature dependent. In the case of high temperature tempering, the magnetic field applied can effectively prevent the cementite from growing directionally along the martensite plate and twin boundaries through affecting the interfacial boundary energy and magnetostrictive energy. Moreover the magnetic field can obviously retard the recovery progress of the ferrite matrix through hindering grain boundary migration by magnetic ordering and domain walls. In the specific case of low temperature tempering, the magnetic field can change the precipitation sequence of transition carbides by changing their Gibbs free energies through magnetization and hence improve the impact toughness of the material. These effects could be useful in optimizing the microstructure and further the properties of the materials.

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