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A new challenge: grain boundary engineering for advanced materials by magnetic field application

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Abstract This paper gives an overview of ‘‘Grain boundary engineering (GBE) for advanced materials by magnetic field application'' based on recent experimental work performed on different kinds of structural and functional materials. It is shown that magnetic field application has a great potential and unique advantage as ‘‘non-contact processing'' for microstructure control, irreplaceable by any other existing processing methods. The control of grain growth and texture by magnetic fields has been found to be generally applicable to many metallic materials, irrespective of whether they are ferromagnetic or not. Grain growth which is controlled by grain boundary migration was found to be strongly affected by magnetic field application. Recent attempts at the grain boundary engineering by magnetic field application through phase transformation have revealed that magnetic phase transformation can provide us a new approach to grain boundary engineering for iron alloys and steels, as well as a new nanocrystalline material produced by magnetic crystallization from the amorphous state. The possibility of engineering applications of enhanced densification using magnetic sintering and magnetic rejuvenation has been discussed for iron powder compacts and deformation-damaged iron alloys, respectively.

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Introduction

It is our great pleasure to present an overview paper of ‘‘grain boundary engineering for advanced materials by magnetic field application'', at the Brandon symposium in honor of Prof. David Brandon who was one of the pioneers of grain boundary research and has been leading this field since the time of 1960's. We have greatly benefited from his work and are now collecting the fruits of the scientific activities of many pioneers who were deeply involved in this field. According to the discipline of ‘‘Materials Science and Engineering'', the control of the microstructure by well-designed processing under optimum condition is a key issue of design and development of high performance engineering materials. In particular, the control of the grain boundary microstructure is essential in the development of high performance polycrystalline structural or functional materials, because structure-dependent grain boundary properties are known to control almost all bulk properties of polycrystalline materials. Extensive studies have been made on the grain boundary structure and properties in metals, semiconductors, and more recently ceramics, from the 1960's up to now [1–8]. It is well known that grain boundary properties strongly depend on the character and structure of the grain boundary. High-energy boundaries show higher activities, while low-energy boundaries have inactive boundary properties. The basic idea of grain boundary engineering came from the question of how to utilize structure-dependent activity of grain boundary properties in design and development of high performance in polycrystalline materials [9]. In the last two decades, it has been well established that the grain boundary microstructure can be effectively controlled by using newly introduced microstructural factors, i.e., the grain boundary character distribution (GBCD) and the grain boundary connectivity [10–12]. Thus a new concept of design and development of high performance materials'' called ''Grain boundary design and control'' or ''Grain Boundary Engineering, GBE'' started in the 1980's [9] and has been extensively attempted in the development of high performance structural and functional materials [13–16].

Now we need to find the most effective and optimum way of processing to produce a desirable grain boundary microstructure, in order to confer desirable bulk properties and high performance to a given material. There is a strong demand for the development of a new processing technique to produce a desirable and optimum grain boundary microstructure in polycrystalline materials. There have been various processing routes currently applied to engineering materials such as thermomechanical processing, unidirectional and rapid solidification, sintering, deposition and so on. These processing routes are, more or less, based on the application of external fields [17, 18]. In this paper we will take and discuss the case of magnetic field application which has been drawing increasing attention from researchers, in connection with the grain boundary engineering of metallic materials [19, 20].

Instrumental requirements for GBE by magnetic field application

Until recently, the literature on the effect of a magnetic field on grain boundary properties has been very scarce, although Mullins reported the effect of a magnetic field on grain boundary migration in bismuth bicrystals and polycrystals in 1956 [21]. Since grain boundary properties depend so strongly on the type and structure of the grain boundary, we need to quantitatively study the effect of a magnetic field on grain boundary-related phenomena, in connection with grain boundary type and structure by using samples with characterized grain boundaries. Fortunately, in the last decade, experimental tools needed for ''the grain boundary engineering by magnetic field application'' became available. These are SEM-EBSD/Orientation Imaging Microscope (OIM) for crystal orientation determination and grain boundary characterization, and a liquid helium-free superconducting high field magnet which is now commercially available and has become accessible even by university laboratories [18–20]. SEM-EBSD/OIM is now extensively used for grain orientation analysis and grain boundary characterization in polycrystalline materials. The inventors and others have already explained this tool and its applications in detail [22–24]. The advent of this situation has opened a new area of grain boundary engineering by magnetic field application, as will be discussed in this paper.

Figure 1 shows a helium-free superconducting high field magnet which has been used by the authors at Tohoku University. The maximum field strength is 7T at 1,773 K in vacuum or argon gas. One of the important features of this type of magnetic field heating system is that the specimen can be inserted and placed at a specific heating position within a few minutes after the test temperature and magnetic field strength have reached the programmed conditions and stabilized. Thus test temperature and magnetic field strength can be precisely controlled. This enables us to study the effect of a magnetic field on grain boundary-related phenomena like grain growth, at very early stages after a short annealing time. We have also used conventional DC and AC coil-winding magnets which can generate a magnetic field up to 1.5T tested at lower temperatures below 1,273 K.

Effects of magnetic fields on grain boundary-related phenomena

The control of grain growth, grain size distribution and texture evolution

Grain growth is an important grain boundary-related and collective phenomenon resulting from the migration and combination of a large number of grain boundaries, finally leading to the evolution of a specific grain structure and grain boundary microstructure in a polycrystal. It depends on the material, the initial microstructure, processing route, annealing condition, the type of external field and so on. Grain growth always plays important roles in the evolution of microstructure during material processing, as is well known for ordinary annealing, thermomechanical processing, solidification, sintering, and vapour deposition.

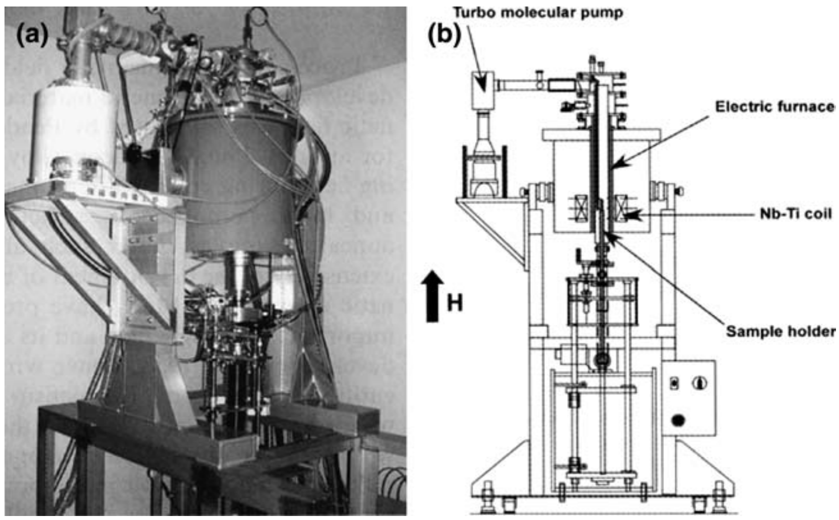


Fig. 1 Overall view (**a**) and schematic illustration (**b**) of as liquid He-free superconducting high magnet field heating system used by the authors at Tohoku University. The maximum field is 7T and the maximum heating temperature 1,773 K

Now let us begin with early work on the effect of a magnetic field on grain boundary-related phenomena such as recrystallization and grain growth. It was already found that magnetic annealing could retard recrystallization and grain growth during annealing of deformed ferromagnetic iron and iron-cobalt alloy [25, 26]. Of particular interest is that magnetic annealing can suppress abnormal grain growth and produce a more homogeneous grain structure with a narrower grain size distribution, as observed for the magnetic annealing of rapidly solidified iron-50at% cobalt ribbon [18]. By ordinary annealing without a magnetic field, a broad grain size distribution was observed due to occurrence of abnormal grain growth, while magnetic annealing under a magnetic field of 1.5T at 1,073 K (below the Curie temperature T_c = 1,253 K) produced a narrower grain size distribution without abnormal grain growth, as shown respectively by Fig. 2(a), (b). The DC magnetic field was applied in the direction perpendicular to the ribbon surface. It was also found that in the case of ribbon-shaped sample, the direction of the magnetic field can produce different effects on grain growth: when a magnetic field was applied in the direction normal to the ribbon surface, retardation of grain growth took place, but an enhancement in grain growth occurred when the field was applied along the direction of ribbon surface. These findings suggest the possibility of controlling grain growth, particularly abnormal grain growth. This is very important for nanocrystalline materials, which often show abnormal grain growth during processing or subsequent heat treatment; this leads to the degradation of the unique properties of nanocrystalline materials. Quite recently we have found that magnetic annealing can produce a different type of sharp texture from that produced by ordinary non-magnetic annealing of iron-6.5mass% Si alloy ribbon produced by rapid solidification. By ordinary annealing at at 1,373 K, a {100} type sharp texture was produced [27], while

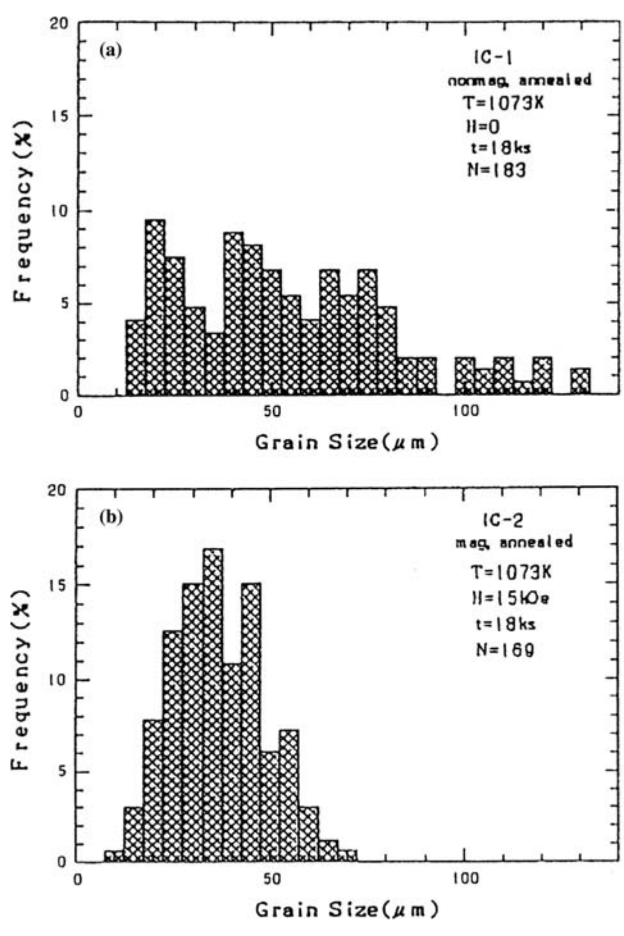


Fig. 2 A grain size distributions for Fe-50%at%Co alloy rapidly solidified and annealed at 1,073 K for 18 ks without (**a**) and with (**b**) a magnetic field of 1.5T

magnetic annealing under a DC magnetic field of 6T produced a {110} type sharp texture [28]. This finding clearly shows that the application of a magnetic field is very effective and useful for the selective control of texture and also the grain boundary character distribution (GBCD), since there is a close relationship between the type and sharpness of texture and GBCD [29, 30]. It is very interesting to reveal the reason why the application of a magnetic field can suppress abnormal grain growth. One of the possible reasons can be understood from our recent study on the effect of a magnetic field on grain boundary segregation in an iron-tin alloy [31, 32]. It was found that the application of a magnetic field up to 6T can suppress tin segregation at high-energy random boundaries, which are well known as preferential sites for segregation. Since grain boundary segregation strongly affects and retards the migration of grain boundary [33] and the amount of grain boundary segregation depends on grain boundary structure and boundary energy [34, 35], it is reasonable to consider that the suppression of grain boundary segregation by magnetic field application can reduce the difference in the structure-dependent migration velocity and make existing grain boundaries migrate similarly without occurrence of anisotropic rapid migration, resulting in the evolution of a more homogeneous grain structure, as discussed below.

The effects of a magnetic field on grain boundary migration, grain growth and texture evolution in nonferrous materials have been extensively studied by Molodov and his coworkers using bismuth [36] and zinc [37] bicrystals and polycrystalline zinc, zinc alloys [38], and titanium [39]. It was found that the direction of grain boundary migration could be controlled by manipulating the direction of the applied magnetic field in bismuth bicrystals [36]. Important findings on the effect of grain boundary dynamics have been discussed in detail in recent paper [40]. The observed effects of a magnetic field on grain boundary migration, grain growth and texture evolution are mostly interpreted with reference to the anisotropy and difference of magnetic susceptibility of individual grains and phases [40, 71].

The control of abnormal grain growth in nanocrystalline materials

Nanocrystalline materials often show severe microstructural heterogeneity due to the occurrence of rapid abnormal grain growth during processing. Such heterogeneity drastically degrades the special properties and performance of nanocrystalline materials. There is a strong demand for the control of abnormal grain growth and the evolution of homogeneous and equilibrium microstructures with higher thermal stability. For this purpose, the effect of a magnetic field on grain growth and grain boundary microstructure was investigated for nanocrystalline nickel and nickel-iron alloy sheets produced by electrodeposition [11, 41–43]. In this section, we look at some important features of the effect of a magnetic field on grain growth, particularly to show how effectively magnetic field application can control abnormal grain growth in the nanocrystalline materials studied. Furthermore, we also demonstrate our recent observations on the different effects of DC and AC magnetic fields on grain growth in nanocrystalline nickel [42]. The initial grain size of as-electrodeposited nanocrystalline nickel sample with thickness of 300 μm was about 30 nm.

Firstly let us look at those micrographs which clearly show the effect of a magnetic field on grain growth during annealing in nanocrystalline pure nickel at 693 K (above the Curie temperature T_c = 627 K) under a DC magnetic field of 15KOe (1.5T). Figures 3 and 4 show microstructural changes as a function of annealing time for ordinary annealing without magnetic field and for magnetic annealing, respectively. As clearly seen in Fig. 3(a), grain growth took place heterogeneously from the early stage of annealing and a specific grain grew very rapidly at later stage of annealing after 10 h (Fig. 3(c), (d)). Recently it was found that grain growth in electrodeposited nanocrystalline nickel showed a rapid initial stage of abnormal grain growth followed by slower, more uniform growth

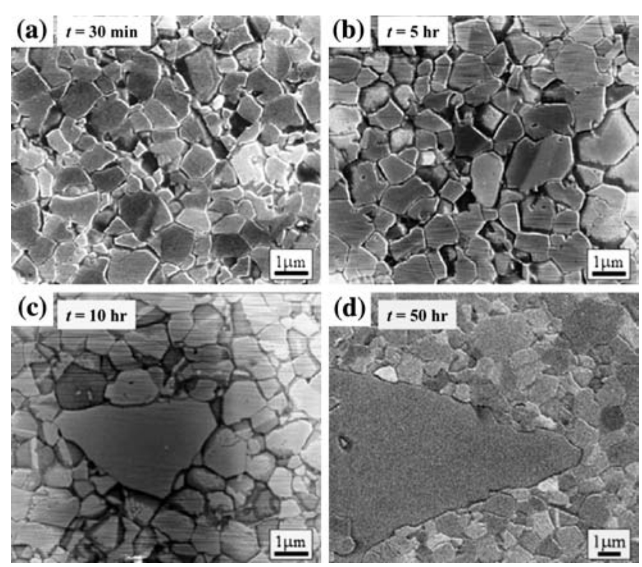


Fig. 3 SEM micrographs showing the heterogeneity of grain structure and abnormal grain growth in electrodeposited nanocrystalline nickel annealed without a magnetic field at 693 K for different annealing times [43]

stage [44]. More recently Hibbard et al. revealed that the origin of abnormal grain growth occurring at late stage of annealing of electrodeposited nanocrystalline nickel could be ascribed to the presence of a wetting sulfur-rich second phase at the abnormal growth interface [45]. Accordingly, the observed abnormal grain growth is understood to be caused by the formation of sulfur-rich second phase probably enhanced by grain boundary segregation of sulfur leading to a high mobility of the wetting planar interface associated with abnormally growing grain. On the other hand, we found that magnetic annealing could enhance grain growth at very early stages of annealing and produce more homogeneous grain structure by totally suppressing the abnormal grain growth until rapid grain growth started after long annealing times, (around 10 h at 693 K under DC magnetic field of 1.5T), as seen in Fig. 4. Please note the scale given at right bottom corner in Fig. 4(d). We see the evolution of homogeneous grain structure with grain size almost one order of magnitude larger. Moreover, it is worth noting that the effect of a magnetic field on grain growth could be observed even at 697 K, which is in the paramagnetic temperature range above the Curie temperature ($T_c = 627$ K). The difference in grain growth characteristics between ordinary annealing and magnetic annealing is clearly shown in Fig. 5. The crossover of the two curves for grain size versus annealing time occurs at a very early stage of annealing, due to an enhancement of grain growth by the magnetic field followed by a slower grain growth rate than for ordinary annealing. It is important to reveal the reason why magnetic field application can suppress abnormal grain growth and form a homogeneous grain structure even after rapid grain growth at late stage of annealing. In fact, as mentioned below, it was found that the grain boundary segregation of tin at high energy random boundaries which are known to be preferential sites for segregation, was suppressed by magnetic annealing in iron-0.8at% tin alloy [31, 32]. This finding is consistent with the mentioned observation of the suppression of abnormal grain growth by a magnetic field in nanocrystalline nickel. If we assume that magnetic field application could suppress the grain boundary segregation of sulfur and the formation of sulfur-rich second phase was difficult, abnormal grain growth caused by rapid migration of the wetting interface mentioned above could not occur. Thus we can easily understand the reason for the control of abnormal grain growth by magnetic field application in electrodeposited nanocrystalline nickel.

Now it is interesting to study whether DC and AC magnetic fields can differently affect grain growth in nanocrystalline nickel. We investigated the effect of the mode of a magnetic field, i.e., DC and AC magnetic field. The details of this work were recently published elsewhere [42]. At present, the maximum field strength of AC magnetic field generated by using a coil-winding conventional type magnet is much lower (around 0.5T) than that (6–10T) generated by a DC superconducting high field magnet. However, this kind of basic study may provide us some useful information to reveal the effect of magnetic field application on grain growth and grain boundary-related phenomena occurring in polycrystalline materials. Figure 6(a) and (b) show the results of our recent study of magnetic annealing,

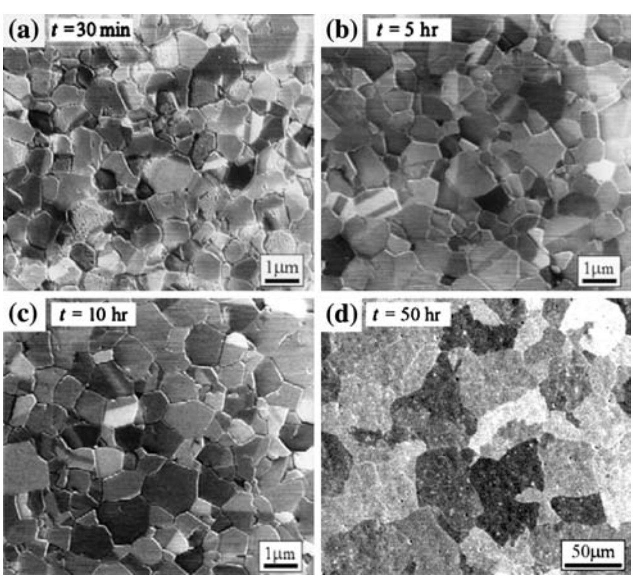


Fig. 4 SEM micrographs showing homogeneous microstructure without abnormal grain growth in electrodeposited nanocrystalline nickel annealed in a magnetic field of 6T at 693 K for different annealing times [43]

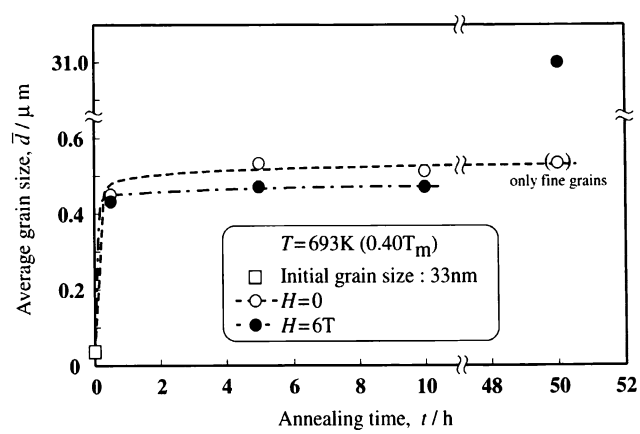


Fig. 5 Average grain size as a function of annealing time for electrodeposited nanocrystalline nickel, annealed at 693 K without and with a magnetic field of 6T [43]

particularly on the effect of DC and AC magnetic field on grain growth in electrodeposited nanocrystalline nickel, the same as was used in the previous work [41, 43]. We carried out magnetic annealing at 693 K (in the paramagnetic temperature region) under DC or AC magnetic field as indicated. Different effects of the magnetic field were observed between DC and AC field, particularly on the onset of rapid grain growth at late stage. In the case of DC magnetic field annealing, rapid grain growth took place after the same time as for non-magnetic annealing, and then the homogeneous grain structure mentioned before was observed. The average grain size after DC magnetic annealing was larger than the average grain size after ordinary annealing without magnetic field, in the late abnormal grain growth range. This indicates that the application of a magnetic field can enhance grain growth, but differently at the very early stage and the late rapid grain growth stage of annealing. It should be noted that there still remained many small grains which could not grow even at the late rapid grain growth stage of ordinary annealing. Thus the evolution of a very heterogeneous microstructure and the mixture of coarse grains and fine grains was observed. On the other hand, as seen in Fig. 6(b), the onset of the late rapid grain growth occurred earlier when an AC magnetic field was applied. It is interesting to clarify the reason for the different effects of DC and AC magnetic field on the onset of the late rapid grain growth stage. Why does AC magnetic field facilitate the late rapid grain growth stage? Although we need a further study to clarify this point, we are considering whether it is possible for grain boundaries to increase their migration mobility under AC magnetic field, particularly for random grain boundaries which have higher electrical resistivity than low-energy special boundaries, because the magneto-electrical energy supplied is expected to increase the local temperature at grain boundary resulting in an increase of the boundary mobility.

The control of grain boundary segregation and brittleness

The grain boundary segregation of solute or impurity atoms is well known to affect many grain boundary-related phenomena and mechanical properties, such as grain growth, phase transformation, and intergranular corrosion and fracture in metallic materials. Recently the recycling of used materials like steels, aluminium and copper has been in increasing demand from the view point of maximum usage of limited resources. However there is a serious unsolved problem of the degradation of mechanical properties and performance of materials due to enrichment in detrimental elements and the resultant effects of grain boundary segregation on material properties after repeated recycling. For example, tin and sulfur tend to become concentrated in steels by recycling many times. To solve this problem, we have recently attempted to develop a new process to control grain boundary segregation by magnetic annealing [31, 32]. Here we briefly introduce important findings.

We studied the effect of magnetic annealing on Sn segregation to iron grain boundaries in iron-0.8at% tin alloy. FEG-TEM/EDS analysis was made to quantitatively examine Sn segregation to characterized grain boundaries. Prior to TEM/EDS analysis, orientation imaging microscopy (OIM) was applied to determine the grain boundary character using TMS specimens, because the grain boundary segregation is well known to depend on the grain boundary character and structure [34, 35]. As shown in Fig. 7, the level of Sn segregation at high-energy random boundaries is 1.5 times higher than the Sn concentration in the grain interior. However Sn segregation vanished under influence a magnetic field of 3T during annealing at 973 K for 6 h. It was also confirmed by subsequent mechanical tests that the control of Sn segregation by this processing could solve segregation-induced embrittlement and

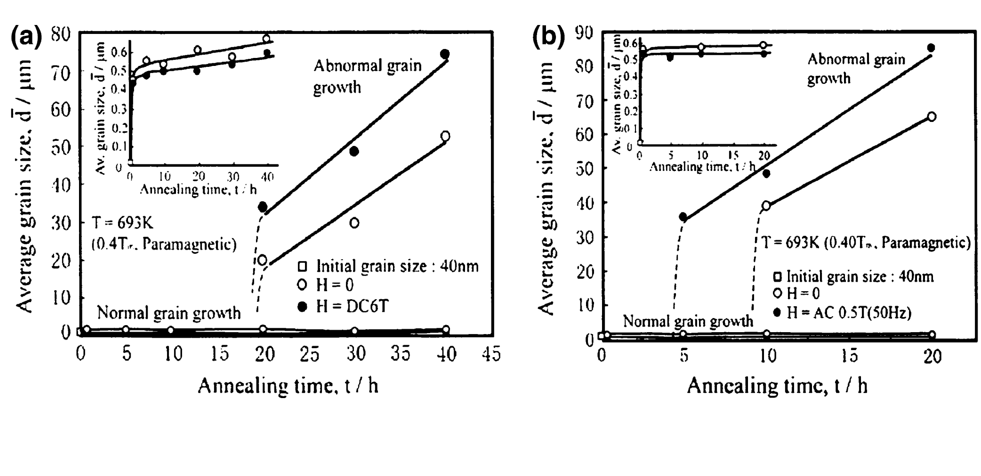


Fig. 6 Grain growth characteristics for electrodeposited nanocrystalline nickel: (**a**) during non-magnetic annealing and DC magnetic annealing at $H = 6T$, $T = 693$ K in the paramagnetic temperature region, (**b**) during non-magnetic and AC magnetic annealing at $H = 0.5T$ (50 Hz), $T = 693$ K in the paramagnetic region [42]

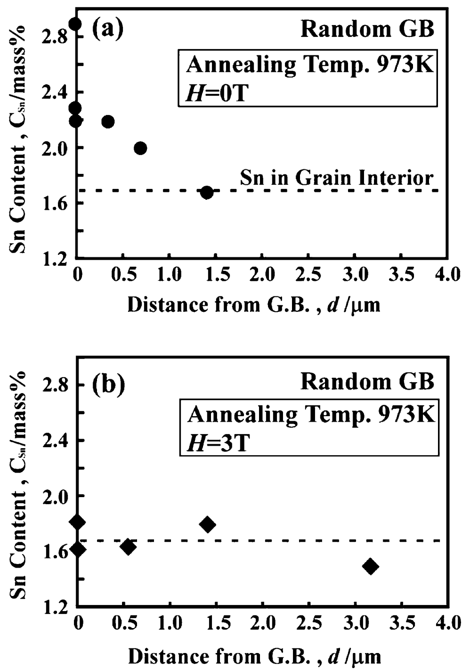


Fig. 7 Effect of magnetic annealing on the segregation of tin (Sn) to random boundaries in αFe-0.8 mol% Sn alloy annealed at 973 K: (**a**) ordinary annealing without a magnetic field, (**b**) magnetic annealing in DC magnetic field of 3T [31]

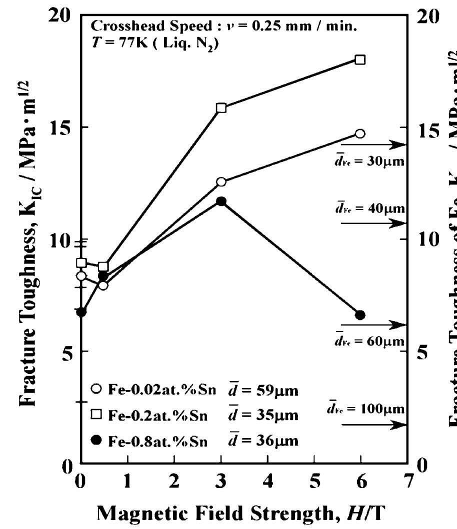


Fig. 8 Fracture toughness as a function of strength of magnetic field for magnetic annealing of αFe-0.8 mol% Sn alloy specimens. For comparison, the fracture toughness values for pure iron with different grain sizes are indicated by the arrows along the vertical axis on the right hand side [32]

improve the fracture toughness of an iron-tin alloy which contained even such high concentration of tin as 0.8at% [32]. The fracture toughness was found to increase with increasing magnetic field strength up to 6T, depending the grain size. The alloy specimens with smaller grain size showed greater improvement of fracture toughness, as shown in Fig. 8.

Magnetic crystallization from the amorphous state

The control of microstructure by solid/solid phase transformation is extensively applied to ordinary processing routes to produce high-performance polycrystalline materials, particularly iron-base alloys and steels. However the density and distribution of potential nuclei for a new phase may be restricted when the solid/solid phase transformation starts from the initially crystalline state, as expected for the case of γ/α or α/γ transformation during thermomechanical processing of steels. The initial microstructure may affect the resultant microstructure after the phase transformation; as some heredity of the initial microstructure can often be recognized. In this context, we can expect that the nucleation of crystallites from the amorphous state would be less restrictive, and a more random orientation distribution and a homogeneous grain structure may occur during crystallization. However if we apply an external magnetic field to the material during crystallization from the amorphous state, we expect the evolution of a different kind of microstructure, which is never produced by conventional processing based on solid/solid phase transformation, and which depends on the direction and the strength of applied magnetic field. This was the motivation of our study on magnetic crystallization of amorphous $Fe_{78}Si_9B_{13}$. The detail of this work was just recently published elsewhere [46].

The material used was an $Fe_{78}Si_9B_{13}$ which had been prepared by vacuum melting and then rapidly solidified into amorphous ribbons in 18–20 μm in thickness, by single-roller melt spinning at a roller speed of 31.4 m/s in vacuum. The Curie temperature of the amorphous phase (T_c^{AM}), and the crystalline phase (T_c^{X}), and the crystallization temperature (T_x) are 680 K, 940 K and 800 K, respectively. Magnetic crystallization was carried out at temperatures ranging from 653 K to 853 K for 1.8 ks in a vacuum in a magnetic field of up to 6T using a specially designed superconducting magnetic field heating system. A magnetic field was applied in the direction either parallel or perpendicular to the ribbon surface. Analyses of texture and microstructure were made with an X-ray diffractometer and a FEG-SEM/OIM system. A significant influence of the magnetic field on the nature of crystallization was observed at 853 K (between $T_c^{AM} = 680$ K and $T_c^{X} = 940$ K), while there were no pronounced differences in XRD profiles for specimens crystallized at other temperatures, irrespective of whether a magnetic field was applied. Figure 9 shows XRD profiles for specimens crystallized at 853 K in magnetic fields of different strengths. For comparison, an XRD profile for the amorphous precursor is shown at the bottom of the figure. It is evident that a magnetic field of 6T in a direction parallel to the ribbon surface intensified the {110} peak associated with the α-Fe (Si) phase. This finding suggests the evolution of {110} texture by application of the 6T magnetic field. Figure 10 shows a set of OIM micrographs for $Fe_{78}Si_9B_{13}$ crystallized at 853 K for 1.8 ks without a magnetic field or under the 6T magnetic field in different field directions. It was found that a very sharp {110} texture was developed only by the application of a magnetic field in the direction parallel to the ribbon surface, as seen in Fig. 10(b). It should also be noted that the shape of {110} oriented grains appears almost rectangular and has ragged interphase boundaries with the amorphous matrix. The evolution of a sharp {110} texture by magnetic field application in the direction parallel to the ribbon surface can easily be explained by the mangetocrystalline anisotropy of bcc iron. Furthermore, Fig. 11 shows the grain size distributions of the specimens crystallized at 853 K (a) ordinary crystallization without a magnetic field and (b) magnetic crystallization under a 6T magnetic field parallel to the ribbon surface. The distribution for the ordinarily crystallized specimen is log-normal, as is often observed in the case of normal grain growth. On the other hand, there are two peaks in the grain size distribution for the magnetically crystallized specimen. As is evident from Fig. 11 (b), the peak in the grain size distribution at larger grain size is almost entirely composed of {110} grains. This finding may suggest that randomly oriented nuclei form from an amorphous precursor and then {110} nuclei preferentially grow in a 6T magnetic field at 873 K, as we expected initially.

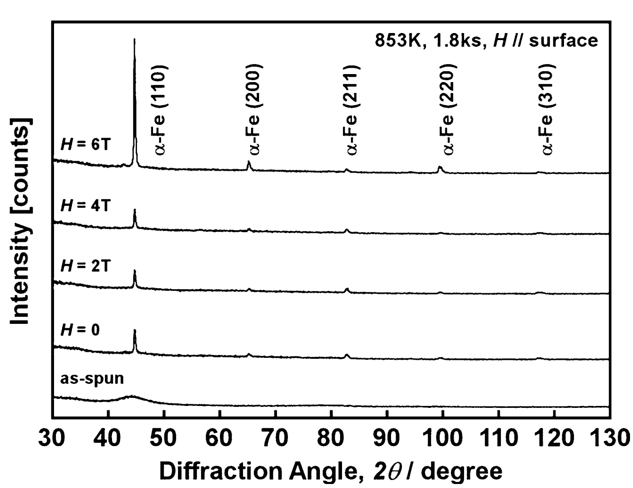


Fig. 9 X-ray diffraction patterns of $Fe_{78}Si_9B_{13}$ ribbons crystallized at 853 K for 1.8 ks in DC magnetic fields of different field strengths and of an as-spun amorphous ribbon [46]

Grain boundary engineering (GBE) based on magnetic phase transformation

Most solid-solid phase transformations associated with materials processing are diffusion-controlled processes, except for the martensitic transformation which occurs by a diffusionless process at rapid cooling rate and low temperatures. It is interesting to study whether the application of a magnetic field can affect the diffusion of component element atoms involved in phase transformations. In particular, the effect of a magnetic field on the diffusion of carbon is of primary interest and importance, in order to study the effect of magnetic field application on microstructure evolution in iron-based alloys and steels. We have recently investigated the effect of a magnetic field and field gradient on the diffusion of carbon and titanium in γ-iron [47], because significant effects of a magnetic field on γ/α or α/γ phase transformation and the evolution of unique microstructure have been observed in iron-base alloys and steels [48–60]. Here we will briefly introduce several important findings and discuss the applicability of those findings to grain boundary engineering using magnetic field application for iron-based alloys and steels, referring to important previous work reported by our group [48–52] and others [53–60]. The most recent review on magnetic field effects for different types of phase transformation in iron alloys and other materials was given by Enomoto [61].

Effects of magnetic field and field gradient on diffusion of carbon in γ-iron

In order to study the effect of a magnetic field on diffusion of carbon in iron, we used a decarburization technique which could provide us useful and reliable information on the carbon diffusion caused by the reaction of carbon with titanium, using the explosively joined specimens of hypoeutectoid steel (0.09mass%C) and commercially pure titanium sheets. Decarburization annealing was carried out at temperatures ranging from 873 to 1,323 K under a magnetic field of up to 6T or under magnetic field gradients from 30 to 45T/m in a vacuum. A magnetic field gradient was applied by placing the specimen at a distance from a uniform

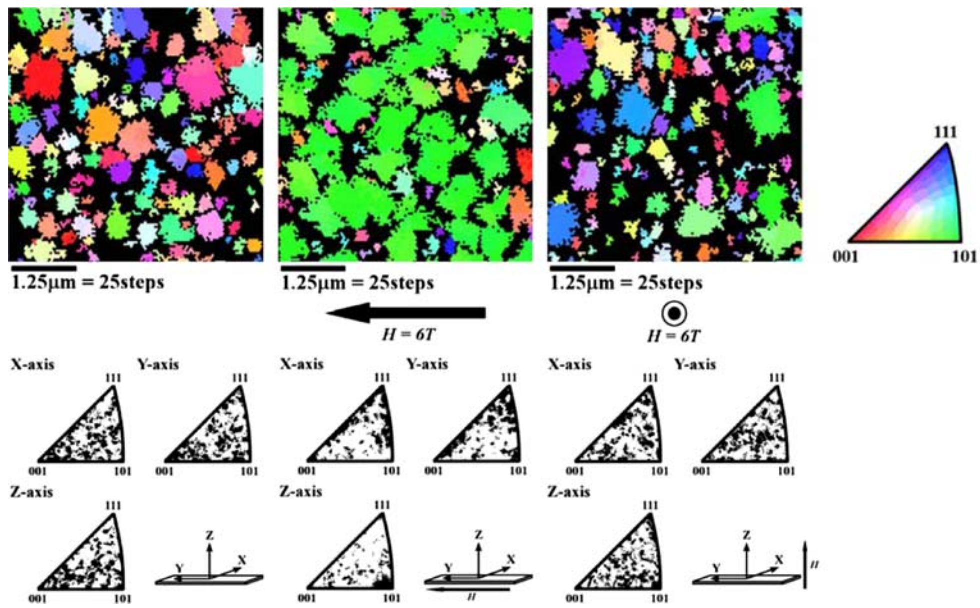


Fig. 10 Orientation imaging microscopy images for $Fe_{78}Si_9B_{13}$ ribbons crystallized at 853 K for 1.8 ks (**a**) without magnetic field, (**b**) with a magnetic field of 6T applied parallel to ribbon surface, (**c**) with a magnetic field of 6T applied normal to the ribbon surface [46]

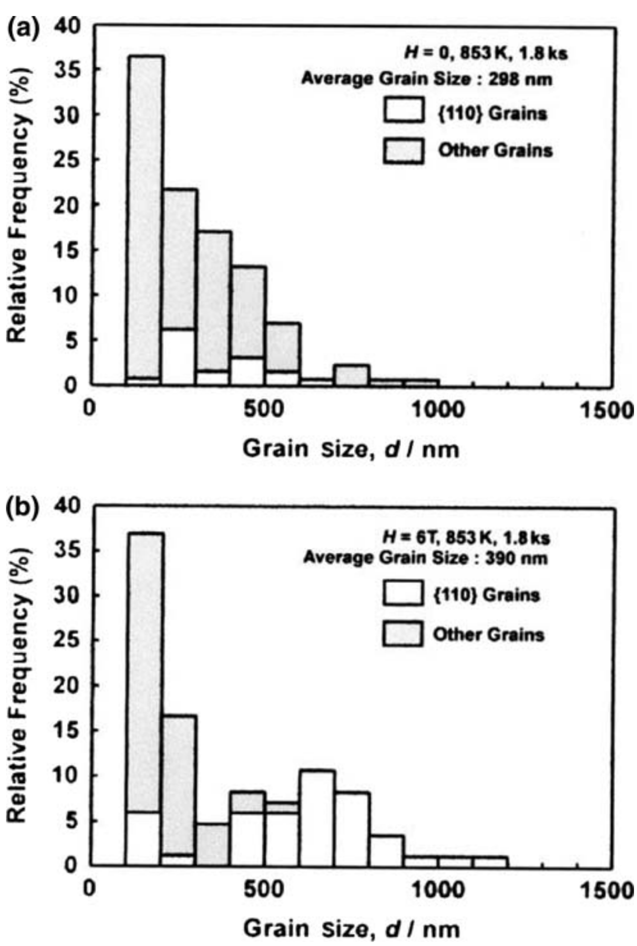


Fig. 11 Grain size distributions for $Fe_{78}Si_9B_{13}$ ribbons differently crystallized at 853 K for 1.8 ks (**a**) without and (**b**) with a 6T magnetic field applied parallel to the ribbon surface [46]

magnetic field region. The detail of this work can be obtained elsewhere [47].

Figure 12 shows the temperature dependence of the diffusion coefficient of carbon in γ-iron in a magnetic field of 6T and in a magnetic field gradient of 45T/m, with the non-magnetic case for comparison. The effect

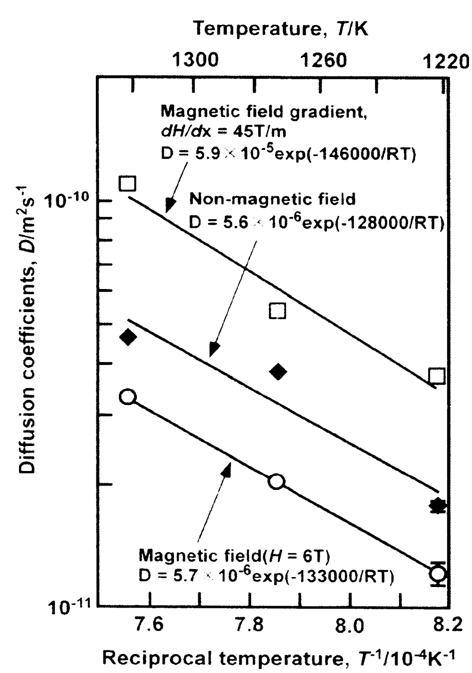


Fig. 12 Temperature dependence of diffusion coefficients of carbon in γ iron under a 45 T/m magnetic field gradient and under a uniform magnetic field of 6T [47]. For comparison, data obtained by non-magnetic diffusion annealing are given

of a magnetic field on the diffusion of carbon in γ-iron is quite different depending on whether the specimen was kept in a uniform magnetic field or a magnetic field gradient; retardation of the diffusion of carbon was observed in a uniform magnetic field, while an acceleration of carbon diffusion was observed in a magnetic gradient. Moreover, the diffusion coefficient of carbon was found to increase by about four times with increasing magnetic field gradient (HdH/dx) in the range of the field gradients from the value in a uniform magnetic field, i.e., no magnetic field gradient, as shown in Fig. 13. In contrast to the effect of a magnetic field on the diffusion of carbon, which is an interstitial process, magnetic field had no significant influence on the titanium diffusion, which occurs by the vacancy mechanism in γ-iron. The difference in the observed effects of a magnetic field on the diffusion of carbon and titanium could be explained in connection with the difference of diffusion mechanism and particularly, the stiffening of the lattice due to magnetic ordering for carbon diffusion; this effect explains even above the Curie temperature. It has already been pointed out that the carbon diffusion, by interstitial mechanism, responds more strongly to the stiffening of lattice due to magnetic ordering than does the vacancy mediated self-diffusion in iron [62]. Thus we have successfully demonstrated that the application of a magnetic field can significantly affect carbon diffusion which always plays an important role in γ/α or α/γ phase transformation in iron-carbon alloys and steels. Diffusion- and interface-control of reactions in γ/α or α/γ phase transformation has been a key issue in microstructural evolution and control in iron-base alloys and steels for many years [63–66].

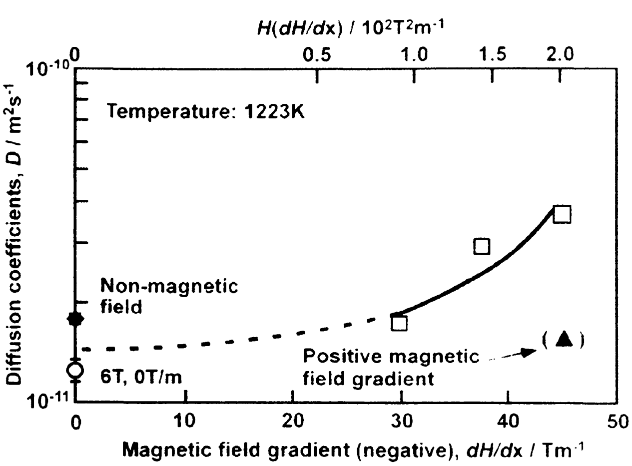
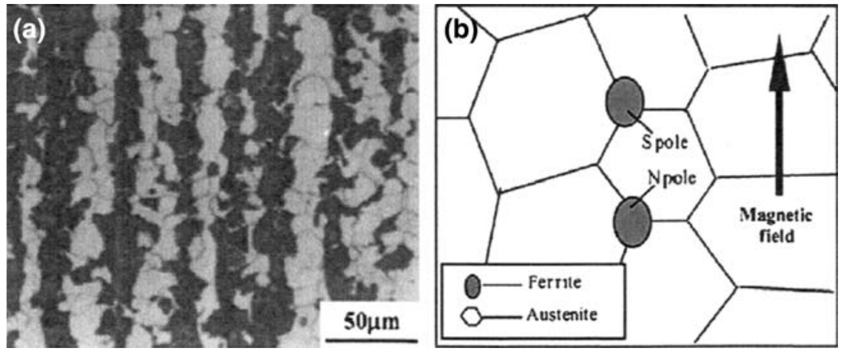


Fig. 13 Diffusivity of carbon in γ iron at 1223 K as a function of strength of magnetic field applied during diffusion annealing [47]

Magnetic phase transformation in iron alloys and steels

In this section we look at recent observations of microstructural evolution in γ/α or α/γ phase transformation performed under a magnetic field in iron alloys and steels. In the last 5 years, many scientists and engineers who have been involved in studies of microstructural processing in steels have been paying increasing attention to the evolution of a unique pearlite microstructure in γ/α phase transformation under a magnetic field in iron alloys and steels. This interest may be due to recent development in our research field, notably the accessibility to a liquid helium-free high field magnets. Since the time when Choi et al. first reported the effects of a strong magnetic field on the phase stability of plain carbon steels [53], showing an increase of the eutectoid carbon content, critical temperatures (Ae_1 and Ae_3), and carbon solubility in ferrite phase, and the evolution of elongated ferrite phase in the direction parallel to the magnetic field direction, this area has been attracting a particular attention from researchers. In Fig. 14(a), which shows the microstrucure observed after heating at 1,153 K and then cooling at a constant rate of 10 °C/min with a magnetic field of 14T [50], the bright area corresponds to the ferrite phase and dark area pearlite colonies. This unique elongated ferrite/pearlite microstructure controlled by the direction of the magnetic field has never been produced by ordinary γ/α phase transformation without a magnetic field. Zhang et al. have proposed a model of the evolution of the elongated ferrite phase as schematically shown in Fig. 14(b). They considered that the nucleation of ferrite to occur at triple junctions in the austenite matrix during cooling, and this has recently been confirmed by the present authors from in-situ observations [67]. When a high magnetic field is applied, ferrite grains and pearlite colonies tend to align due to the attraction between neighboring ferrite grains along the direction of a magnetic field. Hao et al. [55] found that the degree of elongation of the ferrite phase, ω, tends to increase with transformation temperature up to the Curie temperature, where it shows a peak, then decreases, as shown in Fig. 15. Now it is likely that the alignment and the volume fraction of the ferromagnetic ferrite phase can be controlled by manipulating the direction and the level of strength of the magnetic field. From the view point of grain boundary and interface engineering, recent studies of magnetic phase transformation in iron alloys and steels have brought about a new stage of interface engineering, suggesting the possibility of controlling the inclination of grain

Fig. 14 (**a**) Microstructure observed after heating at 1,153 K for 33 min and cooling at 10 °C/min with a magnetic field of 14T [50], (**b**) schematic illustration of nucleation of ferrite phase at austenite grain boundary triple junctions along the magnetic field direction [50]



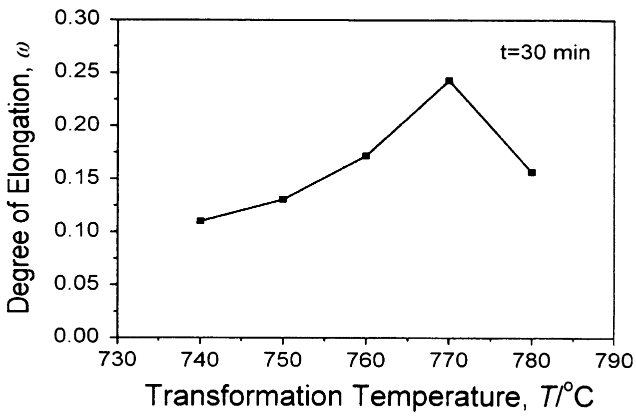


Fig. 15 Degree of elongation of transformed ferrite grains along the magnetic field direction as a function of transformation temperature in Fe-0.4mass%C alloy (after Hao, Ohtsuka and Wada [55])

boundaries and interphase boundaries in polycrystalline materials.

Engineering applications of magnetic densification

Finally let us briefly mention our recent experimental work on densification under a magnetic field and discuss the engineering importance of magnetic densification for those materials, which have an initial state as a powder compact, or a damaged condition. We discuss some important features of the magnetic sintering of powder compacts and of magnetic rejuvenation of a polycrystalline material damaged intergranularly by plastic deformation at high temperature.

Magnetic sintering in iron powder compacts

Recently we studied the effect of a magnetic field on densification by sintering of carbonyl iron powder compacts in which the initial particle size was about 2 μm [68, 69]. When the iron powder compact was sintered in a DC magnetic field of 1.5T at 973 K (lower by 70 K than the Curie temperature; T_c = 1,043 K) of iron, a significant enhancement of densification was observed at early stages of sintering, as seen from Fig. 16. It is evident that the application of a magnetic field can shorten the sintering time necessary to reach a given level of densification, for example to 1/4 of the time required for 95% relative density in the non-magnetic case. It was also found that the final relative density reached by magnetic sintering at 973 K, increased with increasing magnetic field strength of up to 3T. Beyond this the sintering of pores which were at grain boundaries along the direction perpendicular to the magnetic field direction was suppressed and moreover intergranular cavitation was enhanced by the application of a magnetic field higher than 4T [19]. This finding suggests that some effects of magnetostriction and stress-directed diffusion may become involved in magnetic sintering at higher magnetic fields. We should remember that an increase of magnetic field strength cannot always meet our requirement for development of desirable microstructures and material properties. We still need further basic studies in order to reveal the effect of a magnetic field and to effectively utilize magnetic sintering.

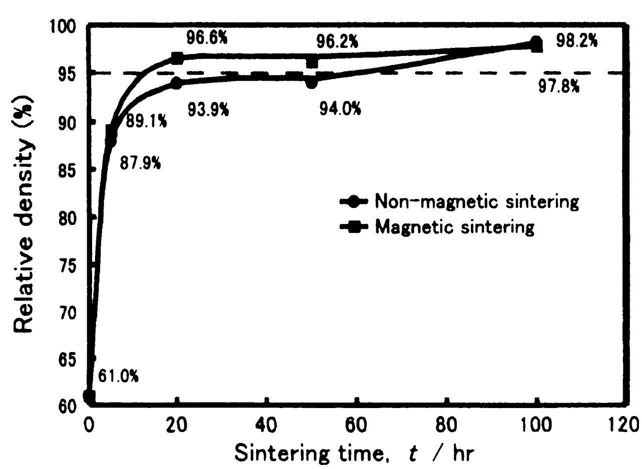


Fig. 16 Density change of carbonyl iron powder compacts sintered with and without a magnetic field of 1.5T at 973 K [18, 69]

Rejuvenation of damaged material

The other example of an engineering application of magnetic densification is taken from our recent work on magnetic rejuvenation in polycrystalline iron-2.9at% cobalt alloy which was intergranularly cavitated by high temperature deformation [70]. The motivation of this work was to find a new approach to the possible rejuvenation of damaged materials kept in severe service environments, for example high temperature materials for turbine blades and nuclear reactors at power stations. The detail of this work can be found in the paper mentioned above. The iron-cobalt alloy specimens were deformed at 1,023 K to different plastic strains (ϵ = 0.03,0.06,0.1) in order to introduce different levels of grain boundary cavitation, prior to a rejuvenation anneal in a magnetic field at 1033 K for different annealing times. Figure 17 shows the degree of rejuvenation (D.R.) which is given by the following equation,

$$\mathrm{D.R.}(\%) = (D_{\mathrm{mag}} - D_{\mathrm{p}})/(D_{\mathrm{o}} - D_{\mathrm{p}}) \times 100 \quad (1)$$

where D_{mag} is the density of the specimen deformed and subsequently magnetically annealed, D_{p} the density of the as-deformed specimen, and D_{o} the initial density of the annealed specimen before deformation. It was found that the degree of rejuvenation (D.R.) increases with increasing annealing time and tends to saturate for specimens deformed to the true strain 0.1 and subsequently annealed in a magnetic field of 3T or 6T. It is evident that the level of D.R. is higher for magnetic rejuvenation in 6T than for 3T. For the specimen which was ordinarily annealed without a magnetic field, D.R. tends to decrease at later stage of annealing, as shown by the bottom curve. Thus the effect of magnetic annealing on the rejuvenation of damaged material is more effective in higher magnetic fields, almost irrespective of the amount of plastic strain which may determine the density of cavities in deformed material.

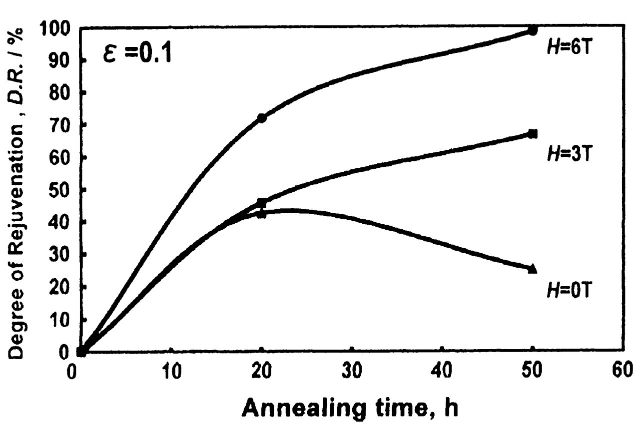


Fig. 17 Degree of rejuvenation (D.R.) as a function of annealing time for magnetic and non-magnetic annealing for deformation-damaged specimens of αFe-2.9at% Co alloy [70]

Open problems and future prospect

We have shown that grain boundary engineering by magnetic field application, although begun very recently, has a great potential for development of high performance or new advanced materials. This non-contacting processing was found to be applicable not only to ferromagnetic metals and alloys, but also to paramagnetic and nonmagnetic materials. However, currently available basic knowledge is limited to the application of DC high magnetic fields and is very scarce for AC magnetic fields. We need more fundamental knowledge on the effect of magnetic fields on grain boundary/interphase boundary-related phenomena which always play important roles in the formation and evolution of microstructures in polycrystalline single-and multiphase materials.

Summary

We have overviewed a new area of grain boundary engineering using magnetic field application which has been drawing increasing research interest, and been extensively investigated quite recently for iron alloys and steels, and also for non-ferrous materials. The application of a magnetic field was found to be powerful for controlling the evolution of microstructures produced by various processing routes based on grain growth and phase transformation. Abnormal grain growth in nanocrystalline materials can be effectively controlled by magnetic field application. Tin segregation to iron grain boundaries and segregation-induced brittleness were suppressed by magnetic annealing, which may solve the problem of the degradation of material properties by repeated recycling of used materials. The rejuvenation of intergranularly damaged material by magnetic annealing was confirmed by experiments. The great potential of grain boundary engineering by magnetic field application awaits future applications to the development of advanced materials.

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