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論文内容要旨

Since the bulk properties such as mechanical and functional properties of polycrystalline materials are strongly affected by microstructure, the control and optimization of the microstructure are essential to obtain desirable properties and to develop high performance polycrystalline materials. The application of external fields such as stress, electric and magnetic fields have been noticed as a useful technique of controlling microstructure of structural and functional materials. However a magnetic field has never been applied to industrial technologies in the materials processing due to the difficulty of generating strong magnetic field enough to affect microstructural evolution of materials. For this reason, there were only a few reports of the observation of microstructural changes under a magnetic field during annealing, which were motivated not by industrial application, but by the academic interests. Then strategies for controlling microstructures and properties of materials by the application of a magnetic field have been suggested particularly since the helium-free superconducting magnet was developed in 1990's. Nowadays, the application of a strong magnetic field enough to affect the microstructural evolution of materials can be obtained without difficulty; the generators which can apply more than 10 T magnetic field are available. Although there have been reported many interesting metallurgical phenomena under a magnetic field, most of those mechanisms of magnetic field effects have not yet been revealed. The application based on the fundamental research infrastructure is essential to extensively apply magnetic processing to the technologies for materials development. Therefore, to conduct the systematic studies of EPM, the fundamental studies are required to clarify the elemental processes for microstructural development under a magnetic field.

The aim of current work is to obtain comprehensive knowledge of the mechanism of magnetic field effects on microstructural evolution in iron-based materials in order to conduct the structural and functional controls by the application of strong magnetic fields. The effects of strong magnetic fields on fundamental metallurgical phenomena (diffusion, grain nucleation and grain growth) were investigated to obtain comprehensive knowledge of the mechanism of the effects of magnetic field on microstructural evolution in iron-based materials. In addition, the fundamental physical properties of grain boundaries of iron closely concerning with the grain nucleation and growth were also investigated. The following results and conclusions were obtained in each chapter.

In chapter 2, some experiments were conducted to investigate the effect of a magnetic field on the carbon diffusion and its solid solubility in pure iron. Measurements of carbon diffusion in iron under a magnetic field and the field gradient were conducted with the explosive welded diffusion couples of pure iron (99.9 %) and eutectoid steel (Fe-0.87mass%C). The carbon diffusivities in pure iron were evaluated from the penetration profiles of carbon into iron measured by secondary ionization mass spectroscopy (SIMS) under non-magnetic and a magnetic field conditions using the solution of the Fick's 2nd law. Fig. 1 shows the Arrhenius plots of diffusion coefficients of carbon in α- and γ-iron without and with a 6 T magnetic field and a 45 T/m field gradient. The diffusivity of carbon in both α- and γ-iron decreased in a 6 T magnetic field by approximately 70 % and 40 %, respectively. The decrease in diffusivity is more significant in α-Fe than that in γ-Fe. The activation energy of carbon diffusion was less dependent on a magnetic field. The diffusion coefficients at 1150K was found to be lower than the values which was expected from the extrapolating the temperature dependence of diffusivity for without and with a 6 T magnetic field. This would indicate that the carbon penetration into α-Fe may have caused α-Fe to transform into γ-Fe, in which the carbon diffusivity is lower than that in α-Fe in the vicinity of the interface. The logarithm of carbon diffusion coefficient in α-Fe is a linear function of a magnetic field strength. This suggests that the activation entropy of diffusion decreases with increase in magnetic field. Consequently, the diffusivity of carbon in iron would decrease in a magnetic field. The decrease in activation entropy would be due to the magnetostriction of α-Fe. A "negative" magnetic field gradient can enhance the carbon diffusion in α-iron by approximately 115 %. The magnetic free energy gradient in α-Fe would give rise to increase in the flux of carbon atoms. The solid solubility limit of carbon increased by twice when a 6 T magnetic field was applied at the ferromagnetic temperature ranging from 950 K to 1000 K. The solid solubility limit of carbon will shift to higher concentration under a static magnetic field, as the free energy curve of ferrite phase will be lowered. In addition, the solid solubility limit of carbon increased with the increase in magnetic field strength and has a maximum value at 4 T magnetic field.

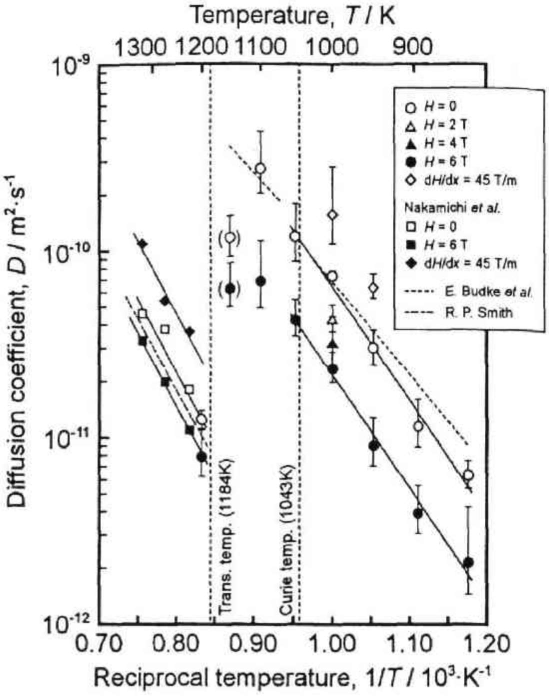

Fig. 1 Arrhenius plots of carbon diffusion coefficients in pure iron under static magnetic fields of 2 – 6 T and a magnetic field gradient of 45 T/m.

In chapter 3, the physical and mathematical models were constructed to clarify the mechanism of the effect of a static magnetic field and a field gradient on the carbon diffusion in pure iron. These analyses were compared with experimental results obtained in chapter 2 and the effects of a magnetic field and a magnetic field gradient on the carbon diffusivity in iron were discussed. At first, the effect of a static magnetic field on carbon diffusion was discussed from a viewpoint of site occupancy of carbon atoms in bcc iron using dual occupancy model. The carbon atoms occupy the octahedral and tetrahedral sites in bcc iron in this model. From the experimental results in chapter 2, the fraction of the octahedral site occupancies was expected to increase under a magnetic field due to the change of entropy. The carbon diffusivity calculated on the basis of dual occupancy model was in good agreement with the experimental results under non-magnetic conditions. Whereas the carbon diffusivity calculated on the basis of assumption that all carbon atoms located at the octahedral sites was in good agreement with the experimental results under a 6 T magnetic field. The difference between the entropy of carbon atoms in tetrahedral and octahedral sites decreases by the application of a magnetic field due to the magnetostriction of ferromagnetic α-iron and its effect on site occupancy, so that the carbon diffusion would be retarded. The next, the effect of a magnetic field gradient on carbon diffusion was analyzed on the basis of the Fick's law with potential gradient. Numerically, it was proven that the increase in carbon diffusion by the application of a negative magnetic field gradient was caused by the increase in flux of carbon atoms induced by the magnetic potential gradient. The diffusion coefficient was found to increase monotonically with the increase in strength of magnetic field gradient. In addition, the diffusion coefficient could be described as the quadratic function of a magnetic field gradient.

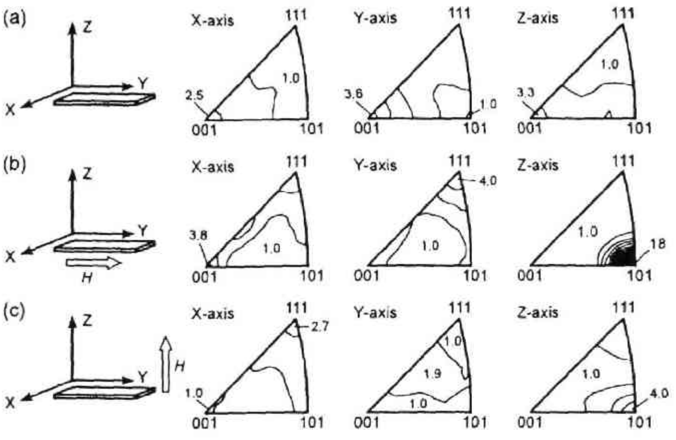

Fig.2 Inverse pole figures for $Fe_{78}Si_9B_{13}$ ribbons crystallized at 853 K for 1.8 ks (a) without magnetic field, (b) with a 6T magnetic field applied parallel and (c) perpendicular to the ribbon surface.

In chapter 4, the effect of a magnetic field on the crystallization from amorphous $Fe_{78}Si_9B_{13}$ and $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$ alloys has been studied with the aim of observing the nucleation and growth of α-Fe grains in the amorphous matrix under a magnetic field. Fig. 2 shows the inverse pole figures of the $Fe_{78}Si_9B_{13}$ crystallized at 853 K for 1.8 ks (a) without a magnetic field (b) with a 6 T magnetic field parallel and (c) perpendicular to the ribbon surface. The crystallization from an $Fe_{78}Si_9B_{13}$ amorphous alloy under a magnetic field of 6 T at 853 K causes a development of a {110} sharp texture when a magnetic field is applied in a direction parallel to the specimen surface. The <001> orientation, which corresponds to the easy magnetization direction in the {110} textured grain structure, lies randomly in the {110} ribbon surface. The {110} grains preferentially grow, and the fraction of crystallized volume is increased by the application of a magnetic field of 6 T in $Fe_{78}Si_9B_{13}$ alloy. A magnetic field of 6 T could decrease the crystallization rate at the temperature below the crystallization temperature and increase that at the temperature above the crystallization temperature. Furthermore, there would be threshold of magnetic field strength between 4 and 6 T where the magnetic field effects on the crystallization rate would appear. The crystallization of $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$ amorphous alloy under a magnetic field also enhanced a {110} texture formation of α-Fe(Si) grains. The preferential nucleation of {110} oriented grains due to a magnetic field would be predominantly responsible for the texture formation rather than the preferential grain growth. The application of a magnetic field increased the nanocrystallization kinetics, particularly the nucleation rate of the ferromagnetic α-Fe(Si) grains from the paramagnetic $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$ amorphous phase. The volume fraction of the nanocrystalline α-Fe(Si) phase was increased with the increase in magnetic-field strength. A primary role of the magnetic field may enhance the kinetics of nanocrystallization rather than modify the thermodynamics.

In chapter 5, the grain boundary energy in iron with the purity of 99.9mass% under a magnetic field was investigated with particular emphasis on the effect of temperature and grain boundary character. From ICP qualitative analyses, the 99.9% iron was found to include Si, Mn, Co and Cu as impurities. The grain boundary

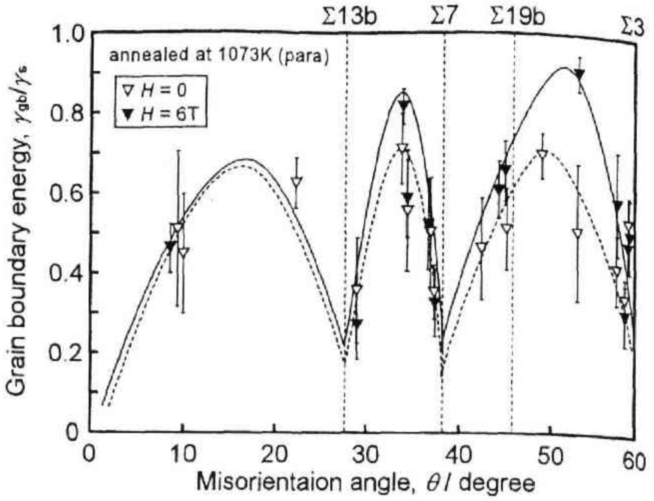

Fig. 3 Grain boundary energy vs misorientation angle around <111> rotation axis for 99.9 % iron under non-magnetic field and a 6 T magnetic field at 1073K.

energy was evaluated by the dihedral angle obtained from the cross-sectional profiles of grain boundary grooves measured by atomic force microscopy after determination of grain boundary character on the basis of the coincidence site lattice theory using FE-SEM/EBSD/OIM technique. Grain boundary energy in the iron increased with the increase in temperature under non magnetic conditions. On the other hand, the energy decreased with the increase in temperature under a 6 T magnetic field. This would be due to the retardation of grain boundary segregation of impurities by the application of a magnetic field. In addition, the energy discontinuously changed around the Curie temperature due to the difference between energetic contribution of the magnetic field to the Gibbs free energy in ferromagnetic state and that in paramagnetic state. The next, the effect of a magnetic field on the misorientation angle dependence of grain boundary energies was investigated. Fig. 3 shows the grain boundary energies at 1073K in the paramagnetic state under (a) non magnetic conditions and (b) a 6 T magnetic field. It was found that the energy cusps occurred at Σ3, Σ7 and Σ13 CSL boundaries, irrespective of whether a magnetic field being applied. In addition, random grain boundary energy increased and its misorientation dependence was enhanced under a magnetic field in the 99.9% Fe. This is also due to retardation of solute and impurities segregation to grain boundaries by a magnetic field.

In chapter 6, the electron energy loss spectroscopy was applied to measure the local magnetic moment near grain boundaries in pure Fe and Fe-Sn alloy. The grain boundaries are characterized on the basis of the coincidence site lattice theory. To make standard curve for determination of the magnetic moment from EELS data, the measurement of EELS spectra was conducted in pure iron and titanium, which are well-known magnetic moment. The relationship between white-line ratio of EELS spectrum and the local magnetic moment was revealed using linearization method. The local magnetic moment at random grain boundary increased by 5 - 9 % in comparison with the moment at neighboring grains, whereas the moment at Σ3 grain boundary did not significantly change. The Σ3 grain boundary is known to be geometrically coherent boundary, whereas the random boundary is incoherent boundary. Therefore the local magnetic moment would increase with the increase in the free volume between the atoms at the grain boundary due to its geometrical disordered structure. The corrected local magnetic moment at the random grain boundary, which can be obtained by the subtraction of the EELS spectrum occurred from grains, increased by approximately 20 % in comparison with the moment at grains. This is in good agreement with the previous calculation result. The local magnetic moments at grain boundaries do not change in the Fe-0.8at%Sn alloy. This would be due to the relaxation of geometrical disordered structure at grain boundaries by the grain boundary segregation of tin atoms.

In chapter 7, this chapter gives concluding remarks of this study.

論文審査結果の要旨

材料の微細組織制御のツールとして強磁場の利用が注目され，様々な金属学的現象に及ぼす磁場効果が報告されている。これらの磁場効果の発現機構に関わる材料の基礎現象・基礎物性に対する理解は未だ不十分である。著者は，鉄系材料を用いて系統的な実験および数値解析を行うことにより，材料の組織制御に関わる金属学的な基礎現象および基礎物性を明らかにしている。本論文はこれらの成果についてまとめたものであり，全編７章からなる。

第１章は緒論であり，本研究の背景および目的と意義について述べている。

第２章では，純鉄および共析鋼の拡散対を用い，鉄中の炭素の拡散に及ぼす静磁場および勾配磁場の影響を実験的に調べ，静磁場中においては炭素の拡散が抑制され，負の勾配磁場中においては促進されることを明らかにしている。また，磁場作用下においては鉄中の炭素の固溶限が増加することを明らかにしている。本結果は，鉄系材料の組織制御，機械特性制御を行う上で重要な知見であり，工学的に有用な成果である。

第３章では，鉄中の炭素分布状態を基にして物理モデルを構築し，このモデルに基づいた炭素拡散数値解析を行っている。静磁場中の炭素拡散においては，鉄格子中の炭素原子の配置に注目し，その存在頻度と磁歪の観点より議論を行い，炭素の拡散の抑制メカニズムを明らかにしている。また，勾配磁場中の炭素の拡散においては，磁気的なポテンシャル勾配を駆動力とした炭素の拡散の促進効果を数値解析により定式化している。

第４章では，鉄系アモルファス合金を磁場中において結晶化することにより，結晶の核生成・成長過程に及ぼす磁場の影響を結晶方位に着目して観察している。その結果，磁場作用によって Fe-Si-B 合金においては{110}結晶粒が優先的に成長し，Fe-Si-B-Nb-Cu 合金においては{110}結晶粒の核生成が促進されることを明らかにしている。本結果は，磁場作用による材料開発を行う上で組織形成過程を理解する重要な成果である。

第５章では，純鉄を用いて粒界エネルギーに及ぼす磁場の影響を実験的に調べ，磁場によってエネルギーが上昇し，粒界性格依存性が顕著になることを明らかにしている。本結果は，粒界移動を伴う組織形成過程における磁場の役割を明らかにするもので，工学的に重要な成果である。

第６章では，純鉄および Fe-Sn 合金の粒界近傍における局所磁気モーメントを定量的に調べ，粒界の幾何学的構造の乱れによって，磁気モーメントが上昇する効果があることを見出している。本結果は，磁場作用下における材料の微視的な組織変化を議論する上で重要な知見である。

第７章は結論である。

以上要するに本論文は，強磁場作用下における鉄系材料の組織制御に関わる基礎現象（炭素の拡散，結晶核生成，結晶成長）および基礎物性（粒界エネルギー，粒界磁性）を実験・理論の両面より明らかにし，磁場を利用した材料開発を行う上で重要な知見を与えている。ここで得られた成果は，機械技術を支える鉄系材料の機能および構造特性の向上に有益なものであり，ナノメカニクスおよび機械工学の発展に寄与するところが少なくない。

よって，本論文は博士(工学)の学位論文として合格と認める。