Experimental Confirmation of Grain Boundary Magnetism in Fe–Si and Fe–Sn Alloys by TEM-EELS

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We measured the local magnetic moments at grain boundaries in Fe–Si and Fe–Sn alloys by electron energy loss spectroscopy with a transmission electron microscope and evaluated the relation between the grain boundary magnetism and grain boundary segregation in Fe–Si and Fe–Sn alloys. We found that the local magnetic moments at the random boundaries in these alloys were remarkably reduced in comparison with those in pure Fe, whereas there was no considerable change at the Σ5 grain boundary and low-angle boundary. The variation of the local magnetic moments at impurity-segregated grain boundaries was explained by the competition between magnetovolume effect and hybridizations of electrons. It was found that the grain boundary character remarkably affects this hybridization. The decrease in the magnetic moments at random grain boundaries was more pronounced in the Fe–Sn alloy than in the Fe–Si alloy.

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Keywords: grain boundary segregation, local magnetic moments, transmission electron microscopy/electron energy loss spectroscopy

1. Introduction

Microstructures often affect the magnetic properties of polycrystalline materials.¹,² In particular, extensive studies have been conducted on the influences of grain boundaries on magnetic properties.³–⁷ Within the last two decades, computational calculations by many researchers have indicated anomalous magnetism at grain boundaries.⁸–¹⁵ They calculated magnetic moments at the grain boundaries in Fe and Ni and found an increase in the local magnetic moments at grain boundaries. This enhancement of local magnetic moments at grain boundaries has been attributed to the magnetovolume effect.¹¹,¹³ However, limited reliable experimental data on such moments has been obtained, because the measurement of local magnetic moments around grain boundaries with conventional techniques is not straightforward. Fitzsimmons et al. determined experimentally the local magnetic moments at grain boundaries in a Ni bicrystal with a 19.7° twist boundary around the [001] axis by means of neutron diffraction.¹⁶ They confirmed the magnetic moment enhancement around the grain boundary. However, the measured magnetic moment and magnetically changed width were considerably large compared with those predicted by ab initio calculations. Recently, we measured the local magnetic moments at well-characterized grain boundaries in pure Fe and Ni by using a new method based on electron energy loss spectroscopy (EELS) equipped with a transmission electron microscope (TEM)¹⁷ and confirmed the local magnetic moment enhancement at grain boundaries.¹⁸,¹⁹ The observed enhancement was in good agreement with that obtained by ab initio calculations. In addition, we also found that this local magnetic moment enhancement at grain boundaries strongly depends on the grain boundary character for the first time.

Grain boundary segregation of solute atoms and/or impurities in alloys often affects many grain boundary-related phenomena.²⁰–²⁵ Szklarz and Wayman²⁷ found that the ferromagnetic transition significantly affects grain boundary segregation of impurities. The magnetic transition to ferromagnetic state induced an extra segregation of Sn to grain boundaries in a Co–50 at% Ni alloy.²⁸ In addition, Ozawa and Ishida made an interesting work in which they paid attention to grain boundary magnetism as a possible origin of brittleness due to Sn segregation to grain boundaries in Fe.²⁹ From the results of the Mössbauer measurements, they showed that Sn-segregation-induced embrittlement of Fe would be due to absence in internal magnetic field of Fe atoms next to Sn in the grain boundary because of a special state with respect to Fe atoms’ d-levels. Furthermore, theoretical calculations of the local magnetic moments at grain boundary in Fe with segregated impurity atoms have made by Čák et al.¹³ They studied the local magnetic moments of (310) Σ5 coincidence site lattice (CSL) boundary with segregated impurity atoms of Si or Sn in Fe and found that the local magnetic moments of Fe atoms at the grain boundary were reduced in Si and almost unchanged for Sn.¹³ In addition, Všíanská et al. conducted ab initio calculation of the local magnetic moment at sp-impurity-decorated (210) Σ5 boundary in Ni and found that it was steeply decreased at the boundary and called it “magnetically dead layer”.¹⁴ However, experimental study on the local magnetic moments at the impurity-segregated grain boundaries has not been performed.

Main motivation of this study therefore is to investigate an effect of grain boundary segregation on the local magnetic moments at grain boundaries in Fe–Si and Fe–Sn alloys experimentally by means of TEM-EELS method. Because Si and Sn are well known as the elements that strongly segregate to grain boundaries in iron. Watanabe et al. studied...
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Table 1 Chemical compositions (at%) of Fe–6Si and Fe–0.8Sn alloys.

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Al</th>
<th>Mn</th>
<th>P</th>
<th>Ti</th>
<th>S</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-6Si</td>
<td>5.67</td>
<td>0.90</td>
<td>0.20</td>
<td>0.03</td>
<td>0.0023</td>
<td>0.0017</td>
<td>0.0039</td>
</tr>
</tbody>
</table>

<table>
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<tr>
<th></th>
<th>Sn</th>
<th>C</th>
<th>N</th>
<th>P</th>
<th>S</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-0.8Sn</td>
<td>0.80</td>
<td>0.09</td>
<td>0.008</td>
<td>0.040</td>
<td>0.005</td>
<td>0.001</td>
</tr>
</tbody>
</table>

the grain boundary segregation in Fe–1.08 at% Sn alloy, and they found strong misorientation dependence of grain boundary segregation of Sn by Auger spectroscopy. On the basis of these results, they proposed a grain boundary segregation diagram to predict the structure-dependent grain boundary segregation. Later, Lejček and Hofmann also analyzed interfacial segregation from a thermodynamic viewpoint and they found the relation between the segregation enthalpy, ΔH, and the solid solubility, and more precisely described grain boundary segregation diagram for Si, P and C in α-Fe. In present study, although we did not perform any direct measurements for the segregation of Si and Sn to grain boundaries in Fe–Si and Fe–Sn alloys, these alloys are considered to have a strong tendency of the grain boundary segregation.

2. Experimental Procedure

The materials used in this study were an Fe–6 at% Si alloy (Fe–6Si) and Fe–0.8 at% Sn alloy (Fe–0.8Sn), which both were fully annealed at 973 K and then air-cooled to room temperature. The chemical compositions of these alloys are listed in Table 1. Although the actual compositions at the grain boundary were not measured experimentally, the listed in Table 1. Although the actual compositions at the grain boundary were not measured experimentally, the concentrations of Si and Sn atoms at the random boundaries, X_{GB} for bulk concentration X_{Bulk} were estimated to be 10.0 (89.9) at% and 85.2 (99.9) at% at the annealed temperature of 973 K (room temperature), respectively, based on the Langmuir-McLean equation known as

\[ \frac{X_{GB}}{1 - X_{GB}} = \frac{X_{Bulk}}{1 - X_{Bulk}} \exp\left(\frac{-(\Delta H - T \Delta S)}{RT}\right) \] (1)

with the segregation enthalpy, ΔH, and entropy, ΔS given by Lejček et al.

For the TEM-EELS analysis, the annealed specimens were thinned by a focused ion beam (FIB, Quanta 200 3D, FEI Co.) at an acceleration voltage of 30 kV. The TEM-EELS measurements were performed with FEI TECNAI 20F microscope equipped with a Gatan Imaging Filter at an acceleration voltage of 200 kV. The conditions used for EELS measurements were an energy dispersion of 0.1 eV/channel, an electron probe size of less than 1 nm, and a convergence angle of 15 mrad. To evaluate the white line ratio on the EELS profile, the background intensity was eliminated by using a method suggested by Pearson et al., and the ratio was calculated based on the areas under each peak. The white line ratio, R, was evaluated with following process shown in Fig. 1(a). A tangent was drawn from the background region beyond L2 edge and extrapolated to the perpendicular line at the peak position of L2 edge. The perpendicular line at the L3 edge was also drawn and both perpendicular lines were connected to each other by the parallel line. The height of perpendicular line at L3 was defined to be twice of that at L2. And then, the area enclosed by dashed line was determined as the intensity of the edge. The white line ratio, R, was evaluated as the ratio of the intensity of L2 and L3 edges. As the white line ratio, R, could depend on the thickness of area measured, we studied the variation of the white line ratio with the thickness. Specimen thickness of each region, t, is easily measured by EELS spectra in low loss region including zero loss peak. The specimen thickness is related to a ratio of the intensity of zero loss peak, I_0, and total intensity, I_t, of spectra as following equation,

\[ \frac{t}{A} = \ln\left(\frac{I_t}{I_0}\right) \] (2)

where A is a total mean free path for all inelastic scattering, we took EELS spectrum for low loss region in every measuring region of white line ratio, the specimen thickness with above method was estimated by the software (Digital Micrograph, Gatan Inc.). Based on this estimation, we confirmed the dependence of the white line ratio, R, on the specimen thickness, t (nm), is very low, expressed as

\[ R = -0.0004t + 3.30 \] (3)

Furthermore, since the specimens with almost uniform thickness were prepared by FIB in our study, we did not take into account differences in specimen thickness for evaluating the white line ratio. Pease et al. investigated the relationship between the magnetic moment, m, and white line ratio, R, and proposed the methodology of the linearization of R and m.

\[ R_{corr} = \frac{R}{m} \] (4)

Based on this concept, they empirically exhibited the linearizing R_{corr}, which was corrected with a consideration of experimentally evaluated R and d-electron occupancy in 3d and 4d transition metals, as a function of m. According to this method, we examined a relationship between m and R_{corr} using the elements whose magnetic moments were ready known in the previous study. The magnetic moment, m, can be given by,
Combining eqs. (4) and (5), the magnetic moments, $m$, is the corrected white line ratio defined as

$$m = \sqrt{\frac{(10 - N) \cdot (R_{corr} - 0.17)}{1.61}}$$  \hspace{1cm} (4)$$

where $n$ is a constant depending on the elements: e.g. 2 for Ti, 3 for V, 6 for Fe, 8 for Ni and 9 for Cr, respectively.17) Combining eqs. (4) and (5), the magnetic moments, $m$, can be expressed as a function of white line ratio, $R$.

$$m = \sqrt{\frac{(10 - N) \cdot (R - 0.63 + 0.015n^2)}{1.61}}$$  \hspace{1cm} (6)$$

The character of each grain boundary in the TEM samples was determined by electron backscatter diffraction (EBSD) with TSL’s orientation imaging microscopy software. We measured the local magnetic moments at individual grain boundaries with different grain boundary characters. Because the probe size in TEM-EELS analysis was approximately 1 nm in diameter, the EELS spectra obtained at a grain boundary included the contribution from both grain interior and grain boundary. If the absolute values local magnetic moments at the grain interior and the grain boundary are denoted $m_g$ and $m_{gb}$, respectively, the total magnetic moment obtained experimentally at the grain boundary, $m$, is presumed to be

$$m = \frac{S_0 - S_{gb}}{S_0} \cdot m_g + \frac{S_{gb}}{S_0} \cdot m_{gb}$$  \hspace{1cm} (7)$$

where $S_0$ is the area corresponding to the electron probe, and $S_{gb}$ is the area of the grain boundary within the electron probe (1 nm). In order to subtract the contribution from the grain interior, magnetically changed width in Fe–Sn and Fe–Si alloy was assumed to be 0.4 and 0.5 nm, respectively, from the results of the $ab$ initio calculations for $\Sigma 5$ grain boundaries.13) However, it should be noted that the local magnetic moments of Fe atoms vary with the atomic layer within the grain boundary region. Therefore, the magnetic moments experimentally obtained, $m_{gb}$, are actually the average value of magnetic moments in the grain boundary region rather than the value just at the grain boundary. In order to reveal the direction of magnetic moments in a nano scale, other techniques such as TEM holography should be used in combination with this TEM-EELS method, but that is beyond the aim of this work.

3. Results and Discussion

Figure 1(a) to (i) show typical Fe-L$_2$ and L$_3$ edges in the EELS spectrum taken from the grain interior ((a), (d) and (g)), $\Sigma 5$ grain boundary ((b), (e) and (h)), and random grain boundary ((c), (f) and (i)) in pure Fe ((a) to (c)), Fe–6 at% Si alloy ((d) to (f)) and Fe–0.8 at% Sn ((g) to (i)) alloy, respectively.
boundaries are considered to be composed of Fe atoms. This is probable reason why the strong Fe-L$_{2,3}$ peaks were obtained by EELS even from the grain boundaries in the Fe–Sn alloy. Comparing the spectra taken from the Fe–6Si and the Fe–0.8Sn alloys with those from pure Fe, some of L$_{2,3}$ peaks seem to be slightly shifted beyond the energy resolution of about 1.0 eV in EELS used; 1.3 eV in the grain interior of Fe–6Si, 1.6 eV and 1.7 eV at the Σ5 grain boundary in Fe–6Si and Fe–0.8Sn, 2.4 eV and −1.0 eV at the random boundary in Fe–6Si and Fe–0.8Sn, respectively. The origin of the chemical shift might come from an interaction between Fe and solute atoms, however the nature of this is still unclear, and we need more theoretical analysis such as ab initio calculations as well as the experimental work.

The white line ratios were evaluated as 3.46, 3.44 and 3.38 for pure Fe, Fe–6Si and Fe–0.8Sn alloy, respectively. For showing the reliability of the TEM-EELS method, we estimated in the beginning the local magnetic moments of Fe atoms in the grain interior, $m_g$, and obtained the values of 2.16 $\mu_B$ for pure Fe, 2.14 $\mu_B$ for Fe–6Si and 2.11 $\mu_B$ for Fe–0.8Sn alloy. These values evaluated by TEM-EELS method show similar tendency to the saturated magnetic moments for several materials whose magnetic moments are already known, the local magnetic moments of the grain interior were measured to be 2.2 $\mu_B$ for Fe, 2.14 $\mu_B$ for Fe–6Si and 2.11 $\mu_B$ for Fe–0.8Sn alloy. The values of the local magnetic moments measured by TEM-EELS method show similar tendency to the saturated magnetic moments evaluated by a vibrating sample magnetometer (VSM) for pure Fe (2.2 $\mu_B$) and the Fe–0.8Sn alloy (2.0 $\mu_B$) and by a nuclear magnetic resonance (NMR) for the Fe–6Si alloy (2.0 $\mu_B$). The local magnetic moments of Fe–6Si and Fe–0.8Sn alloys measured by TEM-EELS are approximately 5 to 7% higher than that by VSM and NMR and these differences are larger than that for pure Fe (2%). It may be due to an inhomogeneity of the solute atoms in iron, and as the accuracy of the magnetic moment measured by VSM and NMR may be essentially higher than that by TEM-EELS technique. However, to the authors’ knowledge, the TEM-EELS technique is the only technique to measure the local magnetic moments in the area with nanoscale. From our previous study, in which we measured the local magnetic moments for several materials whose magnetic moments are already known, the local magnetic moments of the grain interior were measured to be 2.2 $\mu_B$ of Fe,$^{18}$ 0.55 $\mu_B$ of Ni,$^{19}$ and 1.95 $\mu_B$ of FeC$^{37}$ respectively. Thus, the absolute value of the magnetic moment measured by the TEM/EELS technique is possible to include the experimental error within about 10%. It should be noted, however, that the reproducibility of experimentally obtained values was rather good for each specimen.

Figure 2 shows the local magnetic moments of Fe atoms at grain boundaries in the Fe–6Si alloy and in the pure Fe as a function of misorientation angle around the (110) rotation axis. For comparison, the data obtained at the Σ5 grain boundary with (100) rotation axis were also shown in Fig. 2. The solid and open marks represent the data for Fe–6Si and pure Fe, respectively. The local magnetic moments are found to be 2.18 $\mu_B$ for low-angle boundary ($\theta = 12.8^\circ$), 2.40 $\mu_B$ for Σ5 boundary and 2.25 $\mu_B$ (on an average) in Fe–6Si alloy. Those were enhanced by approximately 2%, 12% and 5% (2.14 $\mu_B$), respectively, in comparison with that in the grain interior of the Fe–6Si alloy. Comparing the misorientation-dependence of the local magnetic moments at grain boundaries in the Fe–6Si with that in the pure Fe, the local magnetic moments at random grain boundaries in the Fe–6Si are considerably lower than those in the pure Fe (2.61 $\mu_B$ on average). On the other hand, there is no significant difference between the magnetic moments at the Σ5 grain boundary around (100) rotation axis (2.40 $\mu_B$) in the Fe–6Si alloy and those in the pure Fe (2.42 $\mu_B$).

A grain boundary has five degrees of freedom (DOF); three for the misorientation between two adjoining grains and two for grain boundary plane orientation. In this study, grain boundary misorientation (gain boundary character) was only determined, so that the influence of the grain boundary plane orientation on the local magnetic moments was not taken into account. However, extensive experimental studies related to grain boundary properties show that the misorientation scheme is effective to explain the variation of grain boundary properties to large extent. In order to systematically investigate the effect of the grain boundary structure taking into account five DOF on the local grain boundary magnetic moments, orientation-controlled bicrystal experiments should be necessary.

Figure 3 shows the local magnetic moments at grain boundaries in the Fe–0.8Sn alloy as a function of misorientation angle around (110) rotation axis. This figure also shows the local magnetic moments at grain boundaries in pure Fe for comparison. The values of the local magnetic moments are 2.14 $\mu_B$ for low-angle boundary ($\theta = 10^\circ$), 2.32 $\mu_B$ for Σ5 grain boundary and 2.17 $\mu_B$ (on average) for random grain boundaries. The enhancements of the local magnetic moments at low-angle, Σ5 and random grain boundaries in the Fe–0.8Sn were by approximately 2, 10 and 3%, respectively, in comparison with that in the grain interior of Fe–0.8Sn alloy (2.11 $\mu_B$).

In the theoretical calculations, Čák et al. proposed that the variation of the magnetic moments for Fe–Si and Fe–Sn alloys was determined by two competing effects. One is the volume expansion at the grain boundary increasing the magnetic moment and another is Fe–Si or Fe–Sn hybrid-
The local magnetic moments at grain boundaries in the Fe–0.8 at% Sn (solid) alloy and pure Fe (open) as a function of misorientation angle around the (110) rotation axis. For comparison, the local magnetic moment at Σ5 grain boundary around (100) rotation axis in the Fe–0.8 at% Sn alloy are also shown in the figure. The error bar is also shown and data points indicating no error bar are data points taken from single EELS measurement. The broken line in this figure indicates the saturated magnetic moment evaluated by a vibrating sample magnetometer (VSM) for the Fe–0.8 at% Sn alloy.

4. Conclusions

We experimentally determined the local magnetic moments at grain boundaries in the Fe–6Si alloy and in the Fe–0.8Sn alloy by the TEM-EELS method. We found that the local magnetic moments of Fe atoms at grain boundaries, particularly at random boundaries in these alloys are considerably lower than those in pure Fe, though there is no significant change in the magnetic moments at the Σ5 grain boundary in these alloys compared with that in pure Fe. These results suggested that the disfavoring effect of the hybridization of electronic states of Fe–Si or Fe–Sn on magnetism is more significant than that of a volume expansion enhancing magnetism at the Si or Sn segregated grain boundaries. In addition, on comparing the Fe–6Si and the Fe–0.8Sn alloy, the decrease in the magnetic moments of Fe atoms at random grain boundaries was less difference between those alloys, though occupancies of solute atoms at grain boundaries were estimated to be much higher in the Fe–0.8Sn alloy than in the Fe–6Si alloy, as mentioned in the experimental section, but the difference of the local magnetic moments at grain boundary between these alloys is not so large as expected from the difference of these occupancies. Therefore, the effect of hybridization of electronic states on local magnetic moments of Fe atoms is considered to be significant between Si and Fe atoms than between Sn and Fe atoms. These findings are good agreement with the results from the ab initio calculation by Čak et al.\textsuperscript{[3]}\)

In addition, oxygen is known to be one of important elements (impurities) affecting for the magnetism of Fe. We have already discussed the effect of the segregated oxygen on the grain boundary magnetic moments by ab initio calculation for the (310) Σ5 grain boundary in iron.\textsuperscript{[38]} The calculation for O segregated grain boundary showed an enhancement of the magnetic moments of Fe atoms by approximately 10% comparing to those in the O-free grain boundary. However, taking into account the total amount of O segregation at the grain boundary of 0.4 at%, the magnetic moments of Fe atoms were estimated to be 2.203 \(\mu_B\) on the basis of Stöger-Pollach’s study in which they examined effect of oxygen on the white line ratio.\textsuperscript{[39]} The value obtained is almost same as that in bulk, therefore, we concluded that the grain boundary magnetic moments is strongly affected by the structural factor rather than oxygen segregation.

Consequently, taking together with our previous findings that the local magnetic moments at the low-\(\Sigma\) boundaries such as \(\Sigma3\), \(\Sigma5\) and \(\Sigma9\) grain boundaries in pure Fe\textsuperscript{[18]} and Ni\textsuperscript{[19]} tended to decrease comparing to those in random grain boundaries, the variation of the local magnetic moments at solute (impurity) segregated grain boundaries with misorientation angle will be determined by competing between the anisotropy of grain boundary segregation that disfavors magnetism and that of the grain boundary local magnetic moments depending on their structure that favors magnetism, as schematically illustrated by Fig. 4.
on local magnetic moments of Fe atoms would be significant between Si and Fe atoms than between Sn and Fe atoms, which is in good agreement of the results obtained by ab initio calculation.

Acknowledgements

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