EFFECT OF IRON ON STRUCTURAL CHANGE OF GRAFOIL

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Introduction

We have investigated electronic properties of kish graphite (KG) specimens with low values of residual resistivity ratio ($RRR = \rho_{300K}/\rho_{4.2K}$), and anomalous positive behaviors were observed in Hall coefficient R_H and basal plane thermoelectric power for those of $RRR<10$[1,2]. These peculiar behaviors are possibly related to very slight amount of iron impurities in these KG specimens with low RRR values. We examined the effect of iron impurities on R_H and transverse magnetoresistance $\Delta\rho/\rho_0$ by doping high quality KG of $RRR=24$ and 48 with a slight amount of iron at high temperature, and found that iron atoms in graphite create hole carriers [3]. On the other hand, iron is known to be catalyst on carbonization and graphitization. Therefore, it is very interesting to investigate the changes of electronic properties and structure of graphite materials having relatively low crystal perfection by doping them with iron. However, no investigation has been made regarding the effect of iron on structure and electronic properties of such graphite materials by doping at high temperature. In the present study, we intend to examine the effect of iron on structure and electronic properties (R_H and $\Delta\rho/\rho_0$) of grafoil by introducing iron at high temperature. Grafoil is commercially available, and polycrystalline graphite with relatively defective structure.

Experimental

Grafoil with 120 μm thick produced by UCAR Carbon Company was cut into bridge shaped specimens with 15mm long and 3mm width. Grafoil is deformed by immersing it into liquid nitrogen of 77 K, and accurate data of electronic properties can not be obtained. Therefore, a heat treatment was made at 3000℃ for 30 min in a flow of pure argon. The grafoil specimens heat-treated were stable after cyclic measurements at 77K. Measurements of $\Delta\rho/\rho_0$ and R_H in fields up to 1T at 77K and RRR were carried out by a dc method for five grafoil specimens heated at 3000 ℃ (specimens A – E). XRD measurements were made for these specimens, and interlayer spacing d_{002} was determined from 006 line. The ratio $I_{min}/I_{K\alpha 1}$ of the minimum between $K_{\alpha 1}$ and $K_{\alpha 2}$ to peak intensity of $K_{\alpha 1}$ in 006 diffraction was obtained as a measure of crystallinity. After the measurements, each specimen and a pure iron foil were sandwiched between artificial graphite plates and embedded in a crucible, and heated to 2600℃ for 30 min, and then heated at 2800℃ for 30 min in a flow of pure argon. The boiling point of iron is 2754℃ in atmospheric pressure. After the heat treatment, the specimens were boiled in HCl for 3 hrs. For five iron doped grafoil specimens thus obtained (A-Fe - E-Fe), the XRD and electronic measurements were also carried out in the same condition as for the specimens A - E. For the specimen E-Fe, the $\Delta\rho/\rho_0$ measurement was extended at 1.4K in fields up to 9.5 T.

Results and discussion

Values of d_{002}, the ratio $I_{min}/I_{K\alpha 1}$ and RRR are listed in Table 1 for the specimens A - E and A-Fe - E-Fe in comparison with those of HOPG and grafoil. Even after the heat treatment at 3000℃, the crystallinity of grafoil does not improved well: d_{002}=0.3356nm and $RRR<1$ for the specimens A - E. $\Delta\rho/\rho_0$ in a field of 1T at 77K is almost the same for A – E, and shows small value about 17%. On the other hand, after the heat treatment with iron at 2800℃, the d_{002} value becomes 0.3354 nm as the same as that of HOPG. The separation of $K_{\alpha 1}$ and $K_{\alpha 2}$ of 006 diffraction is clear for the specimens A-Fe - E-Fe, though the values of $I_{min}/I_{K\alpha 1}$ are still higher than that of HOPG. The RRR values exceed 1 for A- and B-Fe, and 2 for C-, D- and E-Fe, indicating metallic temperature dependence of electrical resistivity. The field dependence of $\Delta\rho/\rho_0$ at 77K for the specimens A-Fe - E-Fe is shown in Fig. 1. $\Delta\rho/\rho_0$ increased enormously after the heat treatment with iron, up to about 500% in a field of 1T for C-, D- and E-Fe. These results show that the crystallinity of grafoil is improved extremely by the heat treatment with iron, though the degrees of crystallinity of A-Fe – E-Fe are different each other. For the best specimen E-Fe, a marked Shubnikov-de Haas oscillation was observed in the field dependence of $\Delta\rho/\rho_0$ at 1.4K.

Figure 2 shows R_H plotted as a function of magnetic fields up to 1T at 77K for the specimens heated at 3000℃ A – E and iron doped specimens A-Fe – E-Fe. The specimens A – E exhibit negative R_H, while the specimens A-Fe – E-Fe exhibit positive R_H. The results mean that iron impurities introduced to the graphite lattice, and create excess hole carriers in grafoil. The results are very similar to those for the high quality KG specimens heat-treated with iron at high temperature[3]. However, in the case of KG with high quality, $\Delta\rho/\rho_0$ decreased after the heat treatment with iron because of the introduced iron impurities in KG. The effect of iron on structural change of graphite materials depends on the original crystallinity, highly crystallized or defective.

References

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Table 1. Values of d_{002}, $I_{min}/I_{K\alpha 1}$ and *RRR* for HOPG, grafoil and iron doped grafoil specimens.

Sample	d_{002} (nm)	$I_{min}/I_{K\alpha 1}$	*RRR*
HOPG	0.3354	0.107	6.37
grafoil	0.3357	-------	0.48
A ~ E	0.3356	0.53~0.61	0.50~0.56
A-Fe	0.3354	0.305	1.03
B-Fe	0.3354	0.254	1.47
C-Fe	0.3354	0.182	2.13
D-Fe	0.3354	0.193	2.21
E-Fe	0.3354	0.206	2.05

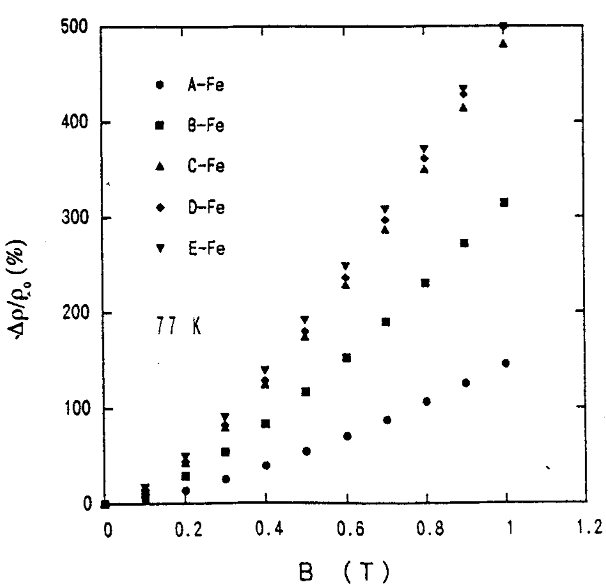

Fig. 1. $\Delta\rho/\rho_0$ as a function of magnetic field at 77K for the specimens of A-, B-, C-, D- and E-Fe.

Acknowledgment

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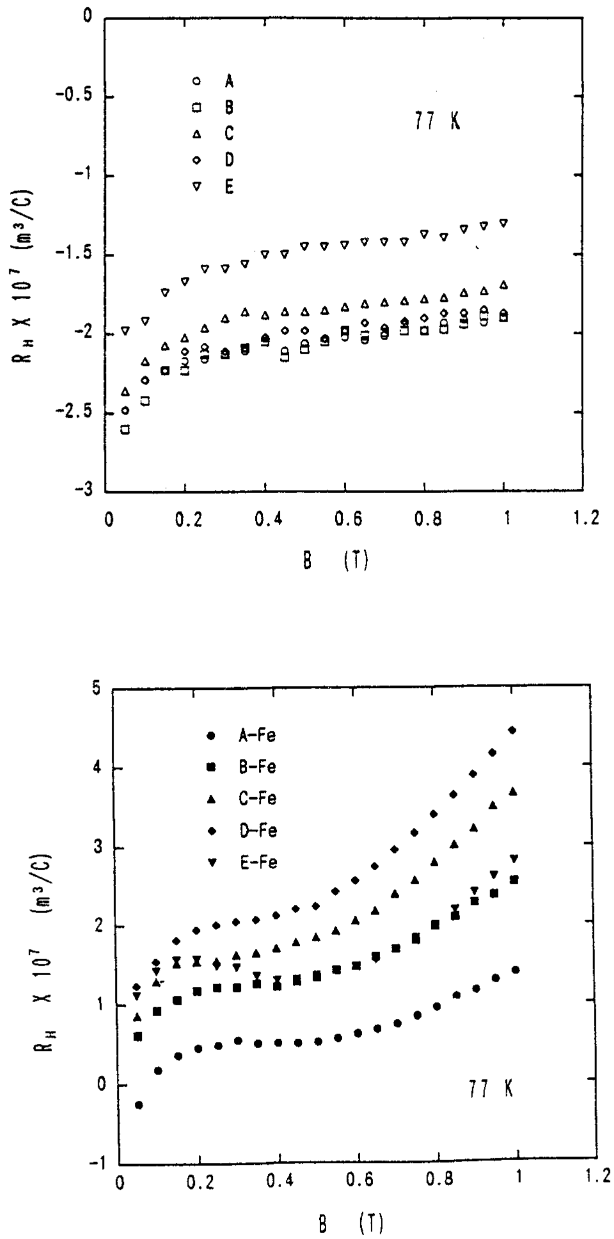

Fig. 2. R_H plotted as a function of magnetic field up to 1T at 77K for specimens of A – E and A-Fe – E-Fe.