Strengthening of Carbon Fibers by Imposition of a High Magnetic Field in a Carbonization Process *1

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Carbon fibers produced from PAN (polyacrylonitrile) as a precursor are generally subjected to the three heat treatment processes of stabilization and carbonization followed by graphitization. Stabilized fibers and high-temperature heat-treated fibers were carbonized in a high magnetic field imposed parallel to the fiber axis under a temperature of 1773 K and a tension of 8 N per 12000 pieces of fibers. The carbon fibers produced from the stabilized fibers in a magnetic field of 5 T showed higher tensile strength than those done in no magnetic field, and the high-temperature heat-treated fibers processed in the magnetic field resulted in reverse. It is found that the fibers processed in the magnetic field have a larger crystallite size than those treated in no magnetic field. The mechanism of increase in the crystallite size due to the imposition of a high magnetic field has been discussed on the basis of an intermolecular cross-linking reaction model, in which the radical pair theory is modified by taking account of magnetic field.

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1. Introduction

Carbon fibers as reinforcements in composite materials had mainly been developed in 1970's from strong requirements of both performance and safety aspects in the aerospace industry¹⁾ and have been used from 1980's in a wide variety of industries such as construction, sports, medicine and so on. Now they are considered as one of the indispensable materials supporting crucial industries in future.

Even though the tensile strength and elastic modulus of PAN (Polyacrylonitrile)-based carbon fibers produced from polyacrylonitrile as a precursor can be increased to comparatively high values by stretching them in a heat treatment process, they are still confined within several percent of their theoretically expected values. This large discrepancy from theoretical values attributes to the lack of a low-dimensional regular structure in a graphite crystal plane.²⁾

Recently, high magnetic fields have become available rather easily due to the development of superconducting magnet technologies, so that a new materials processing is developing in which the effects of a high magnetic field is available in even nonmagnetic materials.³⁻⁶⁾ A number of researches have started to carry out studies on materials processing from the view point of a high magnetic field, which is mainly applied on materials of a liquid state.^{7,8)} However, the application of a high magnetic field to the processing of carbon fibers, in which many internal chemical reactions take place in the solid state, has been hardly studied yet.

Carbon fibers produced from PAN (polyacrylonitrile) as a precursor are generally subjected to the three heat treatment processes of stabilization and carbonization followed by

graphitization. Furthermore the carbonization process is divided into two stages with different chemical reactions which take place in different heat treatment temperatures.⁹⁾ The first stage is in the temperature between 573 K and 873 K and the second stage following the first stage is in the temperature between 873 K and 1973 K.

The authors improved the strength of PAN-based carbon fibers by applying a magnetic field in the carbonization process of carbon fibers and reported that the imposition of a magnetic field provides an increase in the regularity of graphite structure and tensile strength of carbon fibers.^{10,11)}

In this study, the effects of a high magnetic field have been studied in the first and second stages of the carbonization process. By using of a Raman spectroscopy, the structure change of carbon fibers was examined. The mechanism of the structure change due to the imposition of the magnetic field has been proposed on the basis of an intermolecular cross-linking reaction model, in which the radical pair theory is modified by taking account of a high magnetic field.

2. Experimental

A schematic view of the experimental apparatus and the setting configuration of fibers in it are shown in Fig. 1. The fibers were so installed as to be rolled from a lower robin to an upper one and a tension of 8 N was applied on a fiber tow of 12000 pieces by using a motor winding them to the upper part and a brake set in the lower part. The atmosphere was controlled by flowing Ar gas (purity of 99.9999%) from the upper part to the lower one in a reaction tube, the heat treatment temperature was kept at 1773 K, and a magnetic field of 0 or 5 T was imposed. Two-type fibers were prepared to evaluate the influence of magnetic field in the two stages of the carbonization process. One is A type fibers which have

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Fig. 1 Schematic view of experimental apparatus and fibers setting configuration in carbonization process.

Fig. 2 heat-treated conditions of the A and B types fibers.

been subjected in the stabilization process and the other is B type fibers, which are made from the A type fibers by heat-treating between 673 and 773 K so as to reduce the structural defects. Thus, a high magnetic field was imposed on the A type fibers in the first and second stages of the carbonization process and on the B type fibers in only the second stage. Figure 2 shows heat-treatment conditions for the A and B types fibers. Broken lines show the heat-treated conditions previously given for each type fibers and solid lines show the heat-treating and magnetic conditions in this study.

Fifty pieces of fibers were randomly selected as tensile test specimens in each type fibers. Each test specimen with a gauge length of 6 mm was pasted on a slotted paper tab as shown in Fig. 3. After being gripped to a tensile testing equipment, the paper tab was burnt off by an electric resistance cutter. The specimens were extended at a constant rate of 0.29 mm/min until being fractured and the fracture load was measured by use of a load cell with a 1 N capacity.

In order to obtain a Raman spectrum, a carbon fiber was

Fig. 3 Setting configuration of testing tab for a single-fiber filament tensile test.

mounted on a glass slide and its axis was so positioned on a table as to be parallel to the polarization direction of an incident beam. The laser power was approximately 1.5 mW with a wavelength of 514.5 nm and the exposure time required for spectrum acquisition was 5 s.

3. Results and Discussion

Figures 4 and 5 show an example of Raman spectra and the intensity ratio $R (= I_{1355}/I_{1580} \text{ and } I_D/I_G)$, respectively. In general, the G-line near 1580 cm^{-1} appears due to the vibration of a graphite cell in high graphitization materials such as HOPG (Highly oriented pyrolytic graphite) and carbon fibers,^{12–15} and the D-line seen near 1355 cm^{-1} indicates a slightly graphitized state that is going to disappear in higher graphitization temperatures.^{13–20} The D'-line appeared near 1620 cm^{-1} , which is detected as a shoulder of the G-line, is attributed to a small crystallite size and structural disorder.^{16–19}

In order to simulate the distribution of the Raman spectrum, the original data were analyzed to give three different curves. Figure 4 shows the effect of the magnetic field on the intensity of the D'-line. The intensity of the D'-line of the carbon fibers processed under a magnetic field of 5 T is suppressed in comparison with the one processed without a magnetic field in both cases of A and B types fibers. The intensity ratio R , which is defined as the ratio of the area under the D-line curve to the area under the G-line curve, was used for the structural analysis of carbon.²¹ In Fig. 5 the intensity ratio R of the fibers processed under the magnetic field is smaller than that of the fibers processed without a magnetic field. This may imply that the imposition of the magnetic field contributes to the reduction of structural defects.

The average tensile strength of fibers obtained in the carbonization process of A and B types fibers is shown in Fig. 6. In the case of the A type fibers, the strength of fibers processed under the magnetic field of 5 T is 4320 MPa, while that of the fibers processed without a magnetic field is 3990 MPa. On the other hand, in the case of the B type fibers, the strength of the fibers produced under a magnetic field of 5 T is 3330 MPa and that without a magnetic field is 4110 MPa.

Fig. 4 First-order Raman spectra for the A and B types fibers. A: Stabilized fibers B: Heat treated fibers in 673–773 K after stabilization.

Fig. 5 $R (= I_D/I_G)$ intensity ratio of Raman spectra of the A and B types fibers. A: Stabilized fibers B: Heat treated fibers in 673–773 K after stabilization.

Fig. 7 Crystallite size L_a of the A and B types fibers. A: Stabilized fibers B: Heat treated fibers in 673–773 K after stabilization.

Fig. 6 Average tensile strength of the A and B types fibers. A: Stabilized fibers B: Heat treated fibers in 673–773 K after stabilization.

Comparing the tensile strengths of A and B types fibers processed without a magnetic field, the B type fibers is stronger than the A type fibers by 120 MPa. That is, the higher strength in the B type fibers seems to be attributed to the heat treatment at 673–773 K during the first carbonization stage. The tensile strength of the A type fibers processed under the magnetic field of 5 T is higher by about 210 MPa than that of the B type fibers treated without a magnetic field. This indicates that the imposition of the magnetic field in the A type fibers produced

from stabilized fibers play a role to reduce the structural defects of carbon fibers compared to the B type fibers. That is, the imposition of a magnetic field during the first carbonization stage is more favorable to reduce defects in fibers.

The crystallite size L_a , which is closely related to the intensity ratio R ,^{12–14, 17)} can be calculated by using the empirical equation, $L_a = 4.35/R$, (nm).^{22, 23)} The L_a is a parameter indicating the order of the graphitization. That is, the decrease of this value means the increase of the gap from the graphite structure and shows the increase of structural defects. Figure 7 shows the calculated crystallite size for A and B types fibers processed with and without a magnetic field. The values of L_a for fibers processed under the magnetic field of 5 T are higher than those processed without a magnetic field in both A and B types fibers. The relationship between the crystallite size L_a and the tensile strength of fibers is shown in Fig. 8. The tensile strength increases with increase of L_a in the A type fibers, but is inversely proportional to L_a in the B type fibers. As far as the A type fibers is concerned, the direct relationship between the tensile strength and L_a agrees with the result in a previous report,¹⁰⁾ but on the result obtained in the case of the B type fibers a further study is required.

Fig. 8 Relationship between crystallite size L_a and tensile strength.

Fig. 9 Schematic view on intermolecular cross-linking mechanism in carbonization process of stabilized carbon fibers.

Now, let us introduce a radical pair mechanism to explain the increase in the crystallite size L_a caused by the imposition of a magnetic field. An ideal intermolecular cross-linking reaction mechanism in a dehydration reaction in the carbonization process is proposed as shown in Fig. 9, in which (a) indicates the representative structure of stabilized fibers with ROH and R'H molecules. Due to heat treatment, they are converted into free radicals $\cdot R$ and $\cdot R'$ by passing through the homolysis as shown in (b), where dot “ $\cdot$ ” means an unpaired electron. The chains of free radicals are cross-linked by a collision process as shown in (c). When these free radicals come into collision at random, the ratio of generating singlet radical pairs to triplet radical pairs is 1:3.^{8,24)} Then, ISC (= intersystem crossing) takes place through an electron-nuclear hyperfine mechanism.²⁴⁾ In the case of no magnetic field, the ISC of triplet radical pairs takes precedence over escape through the loop (B) as shown in Fig. 10. This mechanism rapidly increases the ratio of the singlet radical pairs which quickly cause random recombination reactions and terminate polymerization. This mechanism leads to increase of defects in a graphite crystal plane and to reduce L_a . On the other hand, when a high magnetic field is imposed, the electron-nuclear hyperfine mechanism does not work so that the ISC in the loop (A) indicated in Fig. 10 is not shown in Fig. 11. The high magnetic field also causes the ISC in the loop (C) shown in Fig. 11 and increases the ratio of the triplet radicals in comparison with the case with no magnetic field.

Fig. 10 Intermolecular cross-linking mechanism in carbonization process of stabilized fibers under no magnetic field.

Fig. 11 Intermolecular cross-linking mechanism in carbonization process of stabilized fibers under the imposition of high magnetic field.

The triplet radical pairs are hardly recombined due to the difference of their spin-states so that they escape from the loop (B) and become free radicals as shown in Fig. 11, and the ratio of escaped radicals increases in comparison with that in the case with no magnetic field. That is, the application of a high magnetic field reduces the recombination reaction rate due to the decrease of the ratio of the singlet radicals to the triplet ones and plays a role of forming better regular graphite crystal planes due to propagating of polymerization. This mechanism implies that the imposition of a magnetic field is favorable for increasing of L_a and explains the experimental results given in Fig. 7.

4. Conclusion

The effects of the imposition of a high magnetic field in the first and second stages of the carbonization process of PAN-based carbon fibers have been studied. The tensile strength of carbon fibers processed under the imposition of a high magnetic field was examined and the reaction mechanism was studied through the Raman spectra. The following results have been obtained:

- (1) The crystallite size L_a increased by imposition of a high magnetic field. This mechanism has been explained by use of an intermolecular cross-linking reaction model in the radical pair theory, which has been developed to take account of a magnetic field.
- (2) The imposition of a high magnetic field increased the

tensile strength of carbon fibers in low heat-treating temperatures, but decreased that in high ones.

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