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Application of a High Magnetic Field in a Carbonization process of Pitch

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Mesophase spherules, which are a carbonaceous liquid crystal, are formed as the specific arrangement of the carbonaceous mesophases. The graphitized mesophase spherules are mainly expected as an electrode material for a high efficiency battery. In this study, a high magnetic field was imposed to control the structures of the mesophase spherules in their formation stage. The effect of the imposition of the high magnetic field in the carbonization process of pitch has been discussed in the two viewpoints of a crystal alignment and a radical pair mechanism in the magnetic field.

Key words: pitch, Mesophase, Carbonization, high magnetic field, electromagnetic processing of materials

1. INTRODUCTION

Carbon is an advanced material accompanied with many distinguished properties, which are independently seen in three typical materials of metal, ceramic and polymer, and has been utilized in a wide variety of industries such as constructions, sports, medicines and so on. Carbon materials have mainly been produced from organic materials by controlling parameters such as temperature, atmosphere, pressure, etc. Recently, a high magnetic field has become available in a rather easy way due to the development of superconducting magnet technologies, so that the studies using the high magnetic field have been carried out in several fields. Especially, it is reported that in the production processes of carbon fibers from PAN fibers as an organic precursor, the imposition of the magnetic field improves the mechanical properties of carbon fibers [1-4].

Mesophase spherules produced from pitch in a heat treatment process are used as a precursor of the mesocarbon microbeeds (MCMB), which has been used in a lithium ion secondary battery. Thus, it is necessary to control the structure of the mesophase spherules for the improvement of the properties of the MCMB. In this study, a high magnetic field was imposed on the carbonization process of pitch and the structure of the mesophase spherules and the propagation of the carbonization reaction were examined.

2. RESULTS AND DISCUSSION

Microstructures of the separated mesophase spherules are shown in Fig.1. In order to estimate the degree of the carbonization, diameters of the mesophase spherules were measured in pictures given in Fig.1. In the case with no magnetic field, the average diameter of the mesophase spherules is 0.5 μ m and does not change with increase of heat treatment time. On the other hand, in the case with the magnetic field of 10T, the average diameter of the mesophase spherules is increased from 0.5 μ m to 10 μ m. That is, the imposition of the high magnetic field increases the diameter in 20 times in comparison with that of no magnetic field. Also, when pitch was heat-treated during 18ks under 10T, which is shown in Fig. 1 (d), the spherules was changed to have a board structure. From this result, the carbonization reaction is found to be promoted by the imposition of a high magnetic field.

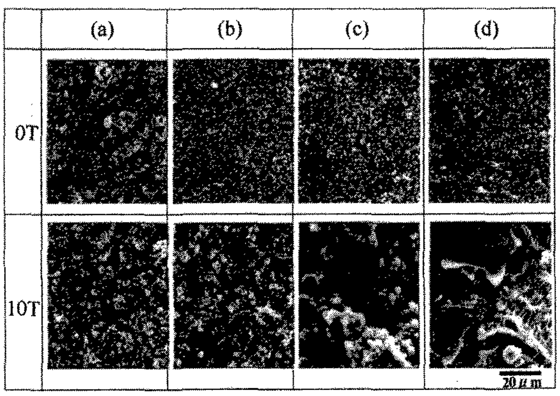

Fig.1 SEM micrographs of each sample
(a) treated to 638K in 0.05K/s, (b) kept for 3.6ks at 703K, (c) kept for 7.2ks at 703K, and (d) kept for 18ks at 703K.

FT-IR spectra for the heat-treated samples under different magnetic intensities are shown in Fig.2. Except the background spectrum of 2350cm^{-1} of CO_2, the spectra exhibit a tendency to decrease with increase of the magnetic field intensity. Especially, the peak of 750cm^{-1}, which indicates 4 hydrogen atoms adjacent to an aromatic carbon ring, remarkably decreases. Hence, it can be understood that the removal of low molecular components like hydrogen are accelerated by the imposition of a high magnetic field.

Now, let us introduce a radical pair mechanism in a magnetic field and a magnetic alignment theory based on the anisotropy of magnetic susceptibility in order to explain the increase of the diameter of mesophase spherules. In the initial stage of the heat treatment, the alignment cannot be expected because a molecular size of pitch is so low that the magnetization force, which is

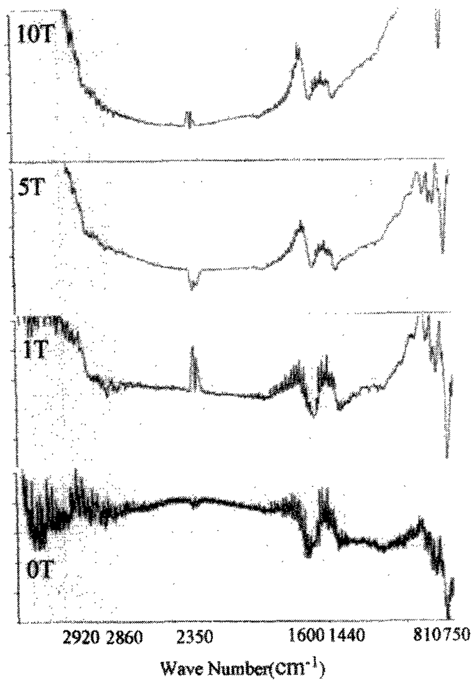

Fig.2 IR spectra of each sample heat-treated for 0.9ks at 638K in the different magnetic intensity.

in proportion to the molecular size, is weak.

The schematic view of the cross-linking mechanism in the carbonization process of pitch is shown in Fig.3. When free radicals take collision at random through the loop Ⓐ, the ratio generating of singlet radical pairs (S) to that of triplet radical pairs $T_m(T_+, T_0, T_-)$ should be 1 : 3[5]. In the case of no magnetic field, the singlet radical pairs are increased by an intersystem crossing(ISC) between S state and T_m state, which takes place through an electron-nuclear hyperfine mechanism. Therefore, the ISC of triplet radical pairs takes precedence over the escape through the loop Ⓑ as shown in Fig.3 so that the singlet radical pairs, which cause random recombination reactions and terminate the polymerization, are increased. That is, the forming and growing of the carbonaceous mesophase become difficult. On the other hand, when a high magnetic field is imposed, the ISC is suppressed so that the ratio of the triplet radicals is increased in comparison with the case with no magnetic field. Then, main reactions take place through the loop Ⓑ instead of the termination of the polymerization so that escaped radicals are increased and the polymerization Ⓒ is more propagated in comparison with the case with no magnetic field. Hence, the carbonization reaction takes place by accompanying with the removal of low molecular components like a hydrogen and the growth of the carbonaceous mesophase. On the basis of the above theoretical consideration, we can explain the reason why the peaks of 750cm^{-1} seen in the case with the imposition of a magnetic field are decreased, as shown in Fig.2.

When a molecular size becomes large, the effect of the magnetic alignment due to the anisotropy in the magnetic susceptibility appears. As carbonaceous mesophases have the structure similar to a graphite, which is hexagonal and diamagnetic, and the magnetic susceptibility of which is about 43 times larger in the direction of c axis than that of a and b axis, the magnetization energy given in $U = -\frac{\mu_0 \chi}{2(1+N\chi)^2} H_{ex}^2$ is smaller in the case where the magnetic field line is parallel to a and b axis than in the case where it is parallel to c axis. That is, it can be understood that the magnetic field makes the carbonaceous mesophase rotate to align its c axis to the magnetic field lines. As this arrangement of carbonaceous mesophase planes along magnetic field lines takes place, while the radical pair mechanism in the magnetic field still works, the mesophase spherules of Brooks & Taylor type[6] are remarkably propagated by the imposition of a high magnetic field.

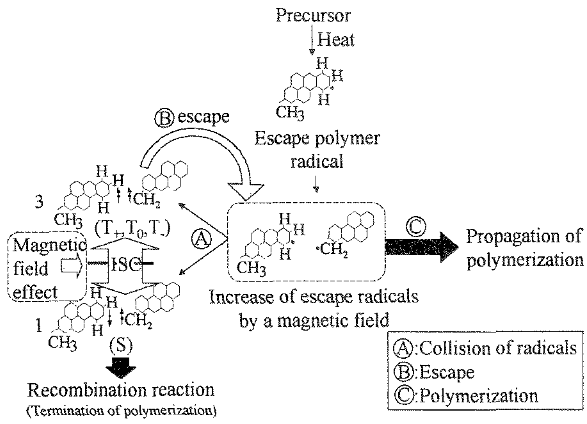

Fig.3 The cross-linking mechanism in carbonization process of pitch.

3. Conclusion

A high magnetic field was imposed in the carbonization process of pitch. The effect of the magnetic field on the formation of mesophase spherules was examined by use of a SEM and a FT-IR. And the formation mechanism of mesophase spherules has been theoretically studied. The results obtained in this study is summarized as follows:

1. The imposition of a high magnetic field in the carbonization of pitch strongly promotes to increase the size of mesophase spherules.
2. The formation mechanism of mesophase spherules has been explained by use of the radical pair theory in a magnetic field and the magnetic alignment theory due to the anisotropy in a magnetic susceptibility.

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