RAMAN SPECTRUM OF GROUND NATURAL GRAPHITE

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Introduction

Carbons and polycrystalline graphites show two Laman lines at 1580 cm⁻¹ and 1360 cm⁻¹ which originate from the in-plane vibrational motion of carbon atoms within graphite layer planes[1]. The 1360 cm⁻¹ Raman line disappears in natural graphite and stressarmealed pyrolytic graphites which possess a perfect reragonal lattice belonging to the space group Dgh. However, the 1360 cm⁻¹ vibrational mode becomes Raman active when defective structures are present in the layer planes, i.e., a defect-induced Raman mode. Therefore, it can be considered that the intensity of the 1360 cm⁻¹ line is structure-sensitive and proportional to the amount of structural defects in the hexagonal layer planes.

Inagaki has reported from his X-ray works that the effective Debye parameter B_{eff} is sensitive to a small amount of deformation of crystal structure and tan be used as a measure of imperfection of the layer planes for polycrystalline graphites[2]. The parameter B_{eff} represents the displacement of carbon atoms from the ideal positions of hexagonal lattice along the direction of the c-axis which may result from lattice defects.

The present study has been made to find the behavior of the 1360 cm⁻¹ Raman line when structural defects are introduced into Ceylon natural graphite by grinding and to compare Raman results with the effective Debye parameter Beff obtained on the same sample.

Experimental

Ceylon natural graphite was purified in a flowing halogen gas at 2700°C. About 2 grams of the graphite sample was ground in an agate mortar in air at room temperature for various times extending over 200 hr. Raman spectra of the ground samples of graphite were recorded on a JEOL Raman spectrophotometer JRS-S1 equipted with a photon-counting detector and a Coherent Radiation argon-ion laser CR-2. Most of the measurements were carried out on pressed powder pellets using the 488 nm argon line providing 400 mW at the sample. The intensity of the 1360 cm⁻¹ line was measured with its line height relative to that of the 1580 cm⁻¹ line and is expressed by R.

The effective Debye parameter Beff was determined from the observed slope of the plots of X-ray diffraction intensities of (OOL) lines against $\sin^2\theta/\lambda^2$ [3]. The C_o spacing and specific surface area of the ground graphite were measured according to the ordinary procedures.

Results and Discussion

Fig. 1 shows Raman spectra of the ground samples of Ceylon natural graphite for various times up to 200 hr. The original sample exhibits an intense graphite line at 1580 cm⁻¹. The 1360 cm⁻¹ Raman line also appears very weakly in this sample, suggesting the existence of structural defects which may have been introduced in the course of sample preparation.

When the natural graphite is ground for several tens of hours, the 1360 cm^{-1} line increases gradually its intensity and becomes much stronger than the 1580 $\rm cm^{-1}$ line at 200-hr grinding. This indicates that defective structures increase in the graphite samples as grinding time is increased and that the crystal lattice of graphite is remarkably destroyed by grinding. As is obvious in Fig. 1, another Raman line appears around 1620 $\rm cm^{-1}$ which is clearly seen in the sample ground for 200 hr. The exact nature of this Raman line can not be explained at present but may be associated with the existence of finely ground particles of graphite containing extremely defective structures. However, all the spectral lines of the sample ground for long time are still sharp compared to Raman lines of various carbons obtained at heat treatment temperatures below 2000°C [4,5]. One of the possible expanations is to assign the 1620 cm^{-1} Raman line to the stretching vibration of conjugated carbonyl groups attaching to the edge carbon atoms of the graphite layer planes, because fine grinding leads to an increase in surface area of the graphite particles and oxygen in air is easily chemisorbed on the free valence bonds of the edge carbon atoms [6].

Fig. 2 shows changes of the relative intensity ratio R for two Raman lines, effective Debye parameter $B_{\mbox{\scriptsize eff}},\ C_{\mbox{\scriptsize o}}$ spacing and specific surface area of the ground graphites with grinding time. All but Co spacing increases gradually with increasing grinding time up to 30 hr. For grinding times more than 30 hr, all the values of these parameters increase very rapidly. The Co spacing of the ground samples remains constant(6.708 A) up to 30-hr grinding. From the analysis of the X-ray diffraction profiles, the first 30-hr grinding leads to a transformation of the hexagonal form of the graphite lattice to the rhombohedral form, and the amount of the latter form reaches about 30 wt% of the ground graphite [7]. During this transformation process in which $\ensuremath{C_{\mathsf{O}}}$ spacing remains unchanged, the values of both R and Beff increase gradually, suggesting a partial destruction of the graphite lattice within the layer planes by grinding. This indicates that the parameter, C_0 spacing is less sensitive than R and Beff to a small structural change in the graphite lattice.

As mentioned in the first section, both the parameters R and Beff are associated with structural defects and increase in proportion to their amounts present in the graphite layer planes. It is, therefore, expected that there exists a certain relationship between R and Beff. Plots of R and Co against Beff for the ground graphite are shown in Fig. 3 where for comparison the same plots are also included for various graphitized cokes [8]. As is evident from the figure, a linear relationship exists between the parameters ${\ensuremath{\mathsf{R}}}$ and Beff for both the ground graphite and the graphitized cokes. The difference in the slope between two curves indicates that structural defects introduced into the natural graphite in the grinding process are different from those which are present originally in the cokes and can be gradually removed

in the graphitization process. A similar difference between both the processes is seen for the plots of C_0 spacing against Beff, showing a rapid decrease in the $\ensuremath{C_O}$ spacing of the cokes and a gradual increase in the C_0 spacing of the ground graphite as each process proceeds along the direction indicated by arrow. In other wards, the $\ensuremath{\mathtt{C}}_{0}$ spacing of the cokes decreases very rapidly as the structural defects are removed by graphitization, while that of the ground graphite increases gradually as the defects are introduced by grinding.

For the same value of Beff, different values of R and Co are obtained between the grinding and graphitization processes. This indicates that both the parameters R and B_{eff} can be used along with C_0 spacing to characterize graphite and carbon materials, Various types of structural defects need to be investigated further for the structural characterization of those materials.

References

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Raman Shift, cm⁻¹







Fig. 3 Plots of R and Co against $B_{\mbox{\scriptsize eff}}$ for the grinding and graphitization processes

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