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Compatibility studies between pyrolytic carbon and nickel

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It is well known that carbon is graphitized by foreign substances. In previous work, graphitization of carbon fibre by nickel was found at temperatures as low as 700° C, but it was difficult to establish the graphitization rate because of the fibre's round cross-section and the variable orientation of the crystallites. In this work, pyrolytic carbon was used instead of the carbon fibre because of its flat surfaces and the preferred orientation of the carbon networks. The pyrolytic carbon which was electro-deposited with nickel, was held at high temperatures. A nickel layer was observed in the pyrolytic carbon, and the carbon area through which the nickel layer passed became graphitized. The graphitization rates were constant at each temperature. And activation energy of 39.7 kcal mol^{-1} was obtained from the graphitization rates, which agrees well with the activation energy for diffusion of carbon atoms in nickel. No obvious difference of the graphitization rates was recognized between the directions parallel and normal to the carbon networks.

1. Introduction

There are many previous works on the graphitization of carbon with foreign substances [1–9]. For example, it is well known that carbon with silicon [1], iron, nickel, cobalt [2, 3], or titanium, zirconium [4] is readily graphitized at high temperature. Petroleum coke including ferrosilicon grains also becomes graphitized at relatively low temperature [5]. Although different from these solid–solid reactions, carbon obtained from a gaseous mixture of methane and titanium chloride can be graphitized easily at high temperatures when the carbon contains 5 to 7 wt% titanium [6]. From these examples, it is obvious that the foreign substances in carbon can promote its graphitization. Previous explanations of the graphitization mechanisms of carbon can be summarized as follows: (1) carbon atoms dissolve into a foreign substance, diffuse in it and then are deposited as graphite; (2) a metal carbide is formed which decomposes to graphite; (3) a foreign substance dissolves in carbon producing a driving force to lessen lattice distortion of the carbon by graphitization; (4) carbon atoms dissolve into a foreign substance and the carbon remains as graphite after evaporation of the foreign substance.

In previous work, however, it was difficult to observe the produced graphite quantitatively, because the graphite grew around the foreign particles which were dispersed in the original carbon. Jackson *et al.* [7] attempted to observe the process by investigating the deterioration in strength of nickel-coated carbon fibre at high temperatures as an indicator of graphitization. However, it is desirable to observe quantitatively and directly the amount of graphite produced.

In our previous studies, a nickel ring in a carbon fibre migrated to the fibre centre [10, 12] and the area of carbon through which the nickel passed was graphitized [11, 12]. A similar study was later carried out by Warren and Wood [13]. From these results, we believed that the graphitization was caused by diffusion of carbon atoms through the nickel. However, it was difficult to determine the amount of graphite produced as a function of time and temperature, because of the round cross-section of the carbon fibre. In addition, we could not determine the difference in graphitization rate between the directions parallel and normal to the carbon atom network, as the carbon fibre had a variable orientation of crystallites.

Pyrolytic carbon is very useful for the purpose of examining these points, because of its flat carbon atom network and preferred orientation. In this work, migration of a nickel layer at high temperature were observed both parallel and normal to the carbon atom network by scanning electron microscopy, electron probe microanalysis and optical microscopy. The structure of carbon affected by the nickel layer was observed by transmission electron microscopy.

2. Experimental details

A pyrolytic carbon, which was produced by decomposition of methane at 1850° C for 10h under 10 Torr was used. This carbon had a preferred orientation of crystallites, but the unit cell height (C_0) was 6.85 Å, rather larger than that of a natural graphite ($C_0 = 6.70$ Å). The apparent density was 1.8 g cm^{-3}. Another pyrolytic carbon, which was produced by heat-treatment of the first pyrolytic carbon at 2900° C under 10^{-3} Torr for 30 min, was examined to determine the effect of C_0 on graphitization. This heat-treated carbon had $C_0 = 6.75$ Å, which was much closer to that of natural graphite. These carbons were cut into samples 20 mm long, 3 mm wide and 1.5 mm thick and all surfaces of each sample were polished. A few samples were polished to 0.1 mm thickness, and used to observe the apparent density of the carbon affected by nickel. All specimens were electro-coated with nickel at room temperature at 0.2 A dm^{-2}, using nickel plating bath based on nickel sulphate. The thickness of the plated nickel was 0.8 μm. The nickel-plated samples were held at various temperatures between 600 and 1200° C for up to 48 h in a vacuum of 2×10^{-5} Torr. After holding at each temperature and time, the samples were sectioned and polished normal to the nickel layer.

The behaviour of the nickel layer was observed using a scanning electron miscroscope and the distribution of nickel and carbon was examined by electron probe microanalysis. The carbon affected by the nickel was taken from the surface of the sample and its structure examined in a transmission electron microscope. The apparent density of this carbon was examined by comparing the thickness before and after holding at high temperature.

3. Results and discussion

Nickel over 1 μm thickness could not be plated on the pyrolytic carbon, as the interfacial bonding between nickel and carbon was not strong enough. No morphological change in the nickel-plated pyrolytic carbon was observed after being held at 600° C for 48 h, although slight grain growth of plated nickel was recognized and the surface of the plated nickel became slightly rough.

Very little morphological change of the carbon–nickel interface was observed after holding at 700° C for 48 h, although the grains of the plated nickel grew more remarkably.

A white layer was observed in the sample which was held at 800° C. This phenomenon is rather similar to the case of the nickel-plated carbon fibre [10, 13]. The migration rate, however, was 0.5 μm in 16 h, much smaller than the case of the carbon fibre in which a nickel ring migrated at a rate of about 2 μm in 2 h at 800° C. When the temperature became higher (1000° C), the nickel on the pyrolytic carbon migrated very quickly and reached 1 μm depth after 2 h as shown in Fig. 1. All the plated nickel of 0.8 μm thickness migrated into the pyrolytic carbon, which was different from the case of the fibre [10, 13]. A scanning electron micrograph of a higher magnification of the same sample as Fig. 1 is shown in Fig. 2. The boundary between carbon and the white layer is not clear, which again is similar to the case of the fibre. The area of pyrolytic carbon which was passed through by the white layer was changed to a flaky appear-

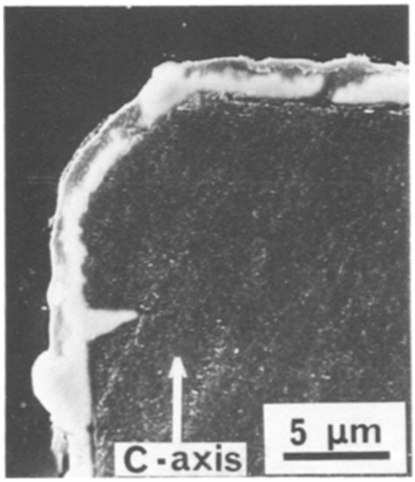

Figure 1 A migrated white layer in the pyrolytic carbon seen by SEM (held at 1000° C for 2 h).

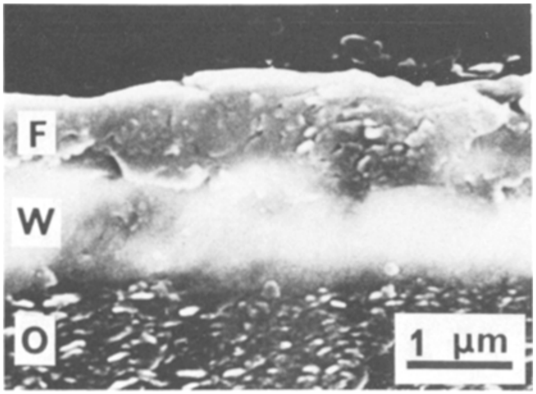

Figure 2 A higher magnification of the direction normal to the *C*-axis of Fig. 1. F, flaky area; W, white layer; O, original pyrolytic carbon.

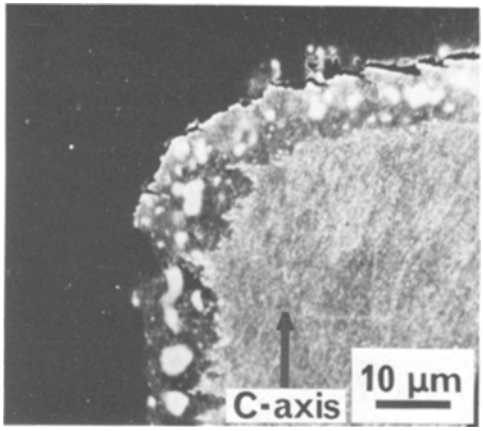

Figure 3 The flaky area which ceased to increase after reaching 8 μm (held at 1000° C for 16 h).

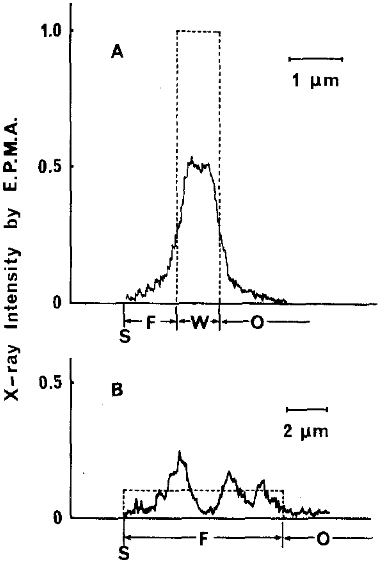

Figure 4 X-ray intensity of nickel by EPMA. A and B correspond to Figs. 2 and 3, respectively. The broken line in Fig. A shows the real distribution of nickel after correction. The broken line in B shows the average nickel portion. S, surface; F, flaky area; W, white layer, i.e. nickel layer; O, original pyrolytic carbon.

ance. The features of the normal direction to the carbon atom network were similar to those of the parallel direction shown in Fig. 2.

The affected carbon was taken from the original carbon and was examined in a transmission electron microscope. The C_0 of the affected carbon was 6.72 Å, and thus graphitization of the pyrolytic carbon by nickel was confirmed.

The flaky area affected by nickel increased in proportion to the holding time at each temperature, and ceased to increase when it reached about 8 μm (Fig. 3). No morphological change was observed after that. The white layer broke up into many pieces during migration and the pieces were gradually left in the flaky area as migration proceeded. When the flaky area increased to 8 μm, the white layer disappeared, as the separated pieces of the layer had been gradually left behind in the flaky area.

This result is different from the case of carbon fibre in which the migration of a layer was approximately proportional to the square root of the holding time [11]. In the case of carbon fibre, the thickness of the layer increased as the diameter of the nickel ring was reduced during migration without reduction of the total volume of the nickel. In the present case, the thickness of the layer did not vary so much, because the layer was flat.

The distribution of the elements corresponding to Figs. 2 and 3, was examined by electron probe microanalysis. As there were only two elements in the samples, carbon and nickel, the distribution of nickel is shown as a black line in Fig. 4. The intensity does not show 100% nickel as an electron beam diameter of 2 μm was used and the diameter of the electron beam was larger than the thickness of the nickel layer. The intensity should therefore be corrected by a factor of a ratio of the area of the electron beam and the area of the element (in this case, Ni) which was covered by the electron beam. The nickel distribution obtained after correction of the X-ray intensity is shown as a broken line in Fig. 4. From this result, it is confirmed that the migrating white layer and the white particles dispersed in the flaky area are almost pure nickel. The portion of the nickel remaining in the flaky area is about 10%, which corresponds to the fact that the initial nickel layer of 0.8 μm was dispersed in 8 μm of carbon. This ratio is approximately the same as in the case of carbon fibre.

The apparent density of the flaky area was examined by comparing the total thickness before and after holding at high temperature. The total thickness of the plated nickel layer and the pyrolytic carbon after holding at high temperature was approximately equal to the thickness before holding at high temperature. Thus the flaky carbon had the same apparent density of 1.8 g cm^{-3} as the original pyrolytic carbon.

From these results, the amount of graphitized pyrolytic carbon from $C_0 = 6.85$ to 6.72 Å can be obtained directly from the migration depth in Fig. 5. The initial gradients imply the graphitization rates at each temperature. The graphitization rate was constant, as the migrating depth was proportional to the holding time at each temperature. The amount of graphitized carbon per unit area and per unit time plotted as a inverse function of temperatures is shown in Fig. 6. The points can be connected by a straight line. Thus, the graphitization process from $C_0 = 6.85$ to 6.72 Å by nickel between 600 and 1200° C is governed by only one rate-determining step. The activation energy obtained from the straight line in Fig. 6 is 39.7 kcal mol^{-1}, and this agrees well with the activation energy of 38.5 to 40.0 kcal mol^{-1} [14] for diffusion of carbon atoms in nickel. As graphitization of a carbon without any co-existing materials passes through many intermediate steps, a variety of processes are involved. However, in the present experiments, there are few intermediate states and only two types of carbon: $C_0 = 6.85$ Å and $C_0 = 6.72$ Å for the initial and final states. Therefore, the transition in this case is caused by diffusion of carbon atoms through nickel, and this is the rate-determining step.

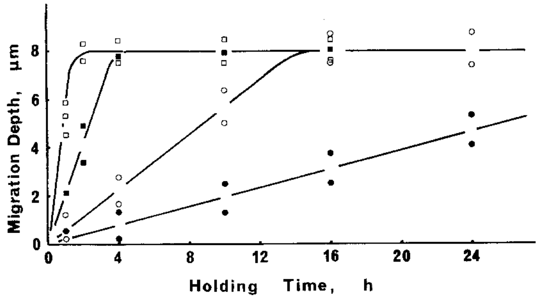

Figure 5 Migration depth after being held at high temperatures.

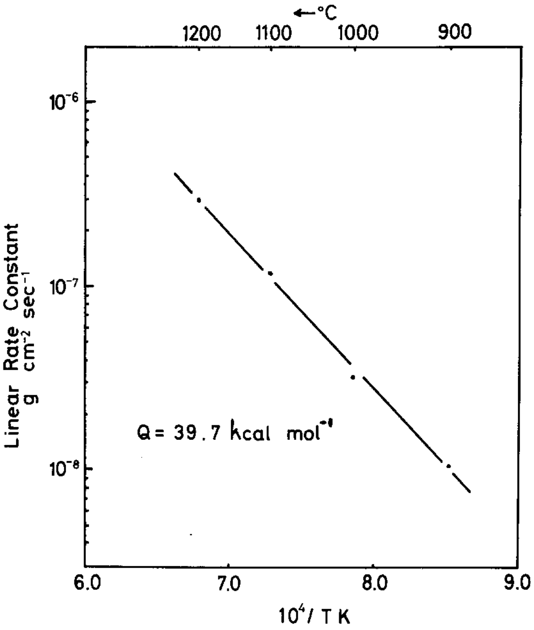

Figure 6 Arrhenius plot of the graphitization rates obtained from the initial gradients in Fig. 5.

It is expected that the reaction rate of the normal direction to the carbon network would be different from that of the parallel direction. In the graphite structure of carbon, three σ electrons of $2s$, $2p_x$ and $2p_y$ make a sp^2 hybridized orbit to produce a strong hexagonal network of covalent bonding. Another π valence electron of $2p_z$ can move freely parallel to the network, and the bonding between the hexagonal network planes is very weak. Therefore, removing an atom from the perfect network which is surrounded by strong covalentic bonding should be more difficult than removing one which has a free end at the edge of the network. Nevertheless, no obvious difference in migration rates was observed parallel to and normal to the network, as shown in Fig. 1. This is explained as follows: the dissolving rate of carbon atoms in nickel should be equal to their deposition rate from the nickel, as no change in the concentration of carbon in nickel with time was observed. The C_0 of graphitized carbon from the carbon parallel to the network was similar to that from carbon normal to the network. The thicknesses of the plated nickel of both directions are virtually equal. Therefore, if there was some difference in graphitization rates between two directions, it would be caused by a difference in the structures of the two directions. However, in the case of the oxidation of carbon, the oxidation activity of the carbon network is much higher that the theoretically expected one for ideal crystal, and the oxidation rate from the network is nearly equal to the rate from the edge of the network [15, 16]. This means that there are many defects and dislocations in the network, and they play an active role in the sites of oxidation as shown by Henning [16]. Thus, in a similar way in the present experiments, the carbon atoms around such weakly bounded sites dissolve into the nickel, so there was no obvious difference of graphitization between the two directions.

No graphitization was observed on the pyrolytic carbon which was heat-treated at 2900° C for 30 min. It is similar to the case of the high-modulus carbon fibres. As the carbon was already graphitized by heat-treatment, the gradient of the chemical potential, i.e. the driving force for graphitization, is small. Thus it was difficult for the carbon to be graphitized. Carbon itself can be graphitized by heat-treatment at high temperature (2000 to 2500° C depending on the original carbon) and the activation energy is 100 to 260 kcal mol^{-1} [17, 18]. The graphitization with nickel occurred at very low temperatures, below 1000° C, and the activation energy in the present experiment is much smaller than that. In this case, carbon atoms dissolved into nickel to decrease the free energy of the system, and diffused through the nickel and were deposited as graphite.

4. Conclusions

When a pyrolytic carbon with $C_0 = 6.85$ Å which was electroplated with nickel was held at various temperatures between 600 and 1200° C, a white layer or white particles were observed inside the carbon. The white layer or particles were almost pure nickel. The carbon through which the nickel passed became flaky, and this area was found to be graphitized carbon ($C_0 = 6.72$ Å).

The apparent density of the graphitized carbon was 1.8 g cm^{-3}, which was approximately equal to that of the original pyrolytic carbon. The amount of graphitized carbon at each temperature increased proportionally with time. The activation energy of the graphitization was 39.7 kcal mol^{-1}, thus graphitization is controlled by diffusion of the carbon atoms through the nickel. No obvious difference in graphitization rates was observed between the directions parallel and normal to the carbon network, and no morphological change was observed in a pyrolytic carbon which was previously heat-treated at 2900° C.

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