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Oxidation characteristics of the graphite micro-coils, and growth mechanism of the carbon coils

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The oxidation characteristics of the graphite coils obtained by high-temperature heat treatment of the vapor grown carbon micro-coils were examined, and the growth mechanism of the carbon micro-coils is discussed. The ruptured cross section of the graphite coils with a circular cross section (circular graphite coils) exposed in air or an Ar atmosphere at 800–1400°C have generally negative or positive trigonal cone-forms. On the other hand, that of the graphite coils with flat or rectangular cross sections (flat graphite coils) have negative or positive rectangular cone or roof-like forms. The edge between two graphite layers was preferentially oxidized to form three deep striations that extended in the direction of the fiber axis, and then formed six coils from the double circular graphite coils. It is reasonably considered that eight thin coils are formed from the double flat graphite coils. These observations strongly supported the growth mechanism based on the catalytic anisotropy between the catalyst crystal faces.

1. Introduction

Carbon fibers commercially obtained from precursor fibers or by the CVD process have generally straight or slightly curled forms. Other commercially obtained fibers or whiskers have also generally straight forms, therefore we can not obtain fibers or whiskers with micro-coiled forms. However, micro-coiled fibers, such as carbon [1–4], SiC [5–7], and Si_3N_4 [8–11] were experimentally obtained, but the reproducibility and yield were very poor. We have prepared, with high yield and good reproducibility, regularly micro-coiled carbon fibers (referred to as "carbon coils" hereafter) by the catalytic pyrolysis of acetylene [12–15]. The carbon coils are considered to be grown by an anisotropic mechanism [16]. The carbon coils have an amorphous structure and change to a herring bone-like graphite structure by heat treatment at 3000°C (referred to as "graphite coils" hereafter) [17].

In this study, the graphite coils obtained by the heat treatment at 1300–3000°C were exposed in air or an Ar atmosphere at 800–1400°C, and the oxidation characteristics and morphology were examined in detail. The growth mechanism of the carbon coils is then discussed.

2. Experimental

The carbon coils obtained by the heat treatment of the as-grown carbon coils at 3000°C were used as the source graphite coil. The graphite coils of about 0.5 g were heated in air using a rotating reaction tube (34 mm i.d.). The rotating speed was fixed at 60 rpm. The graphite coils as well as the as-grown carbon coils were also heated from room temperature to 1400°C in air or an Ar atmosphere at an increasing rate of 10°C/min by the TG analyzer.

3. Results and discussion

3.1. Oxidation characteristics and morphology

Fig. 1 shows the representative regular graphite coils obtained by the heat treatment of the carbon coils at 3000°C for 5–6 hrs in a $CO + CO_2$ atmosphere. It can be seen that there are two kinds of side wall-forms of the graphite coils reflecting the form of the cross section of the fibers that constructed the coils; circular or eliptical-forms (referred to as "circular graphite coils" hereafter) and flat or rectangular-forms (referred to as "flat graphite coils" hereafter). The ruptured patterns of the partially oxidized graphite coils are different

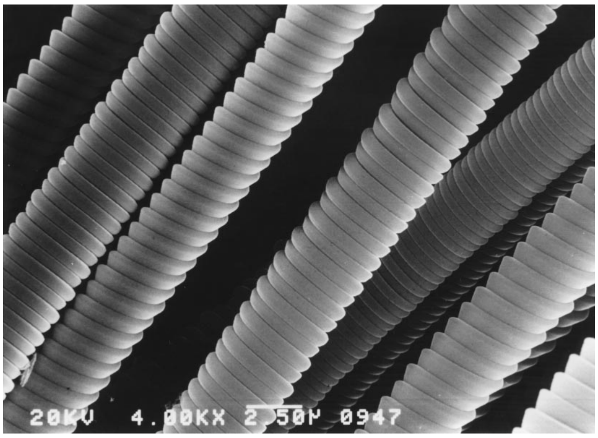


Figure 1 Representative SEM image of the graphite coils.

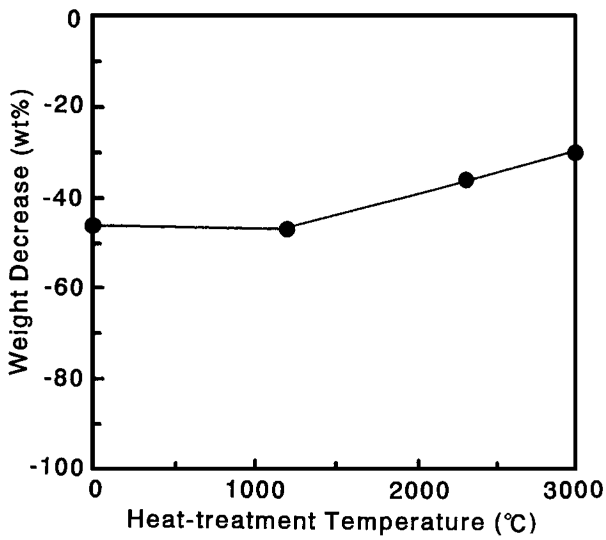


Figure 2 Effect of heat treatment temperature on the weight decrease after exposure in air at 800°C for 12 min. Heat treatment time: 5–6 hrs.

from the circular graphite coils to flat graphite coils as will be shown later. Fig. 2 shows the weight decrease in the graphite coils exposed in air at 800°C for 12 min using the rotating reaction tube. The weight decrease in the carbon coils heat treated at 1300°C was the same as that of the as-grown carbon coils, and then decreased

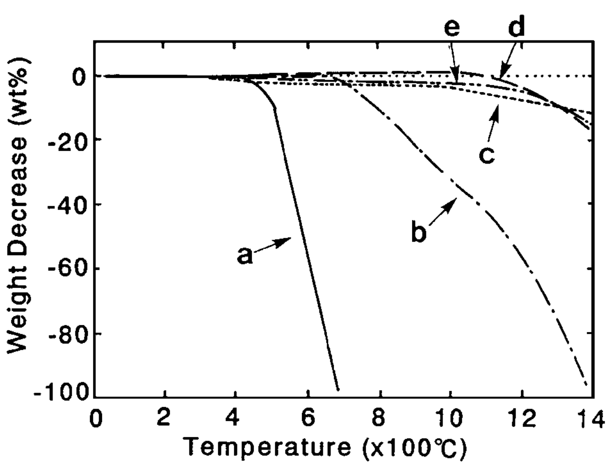
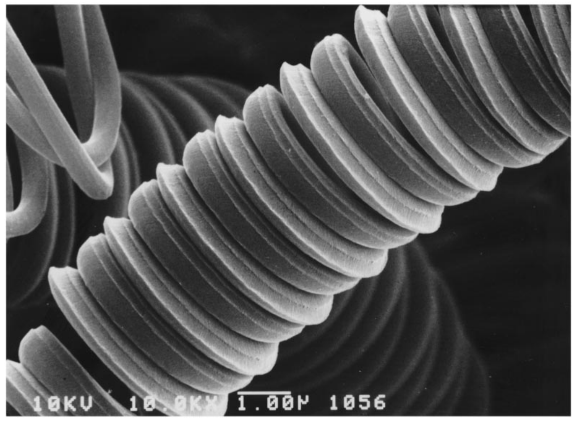
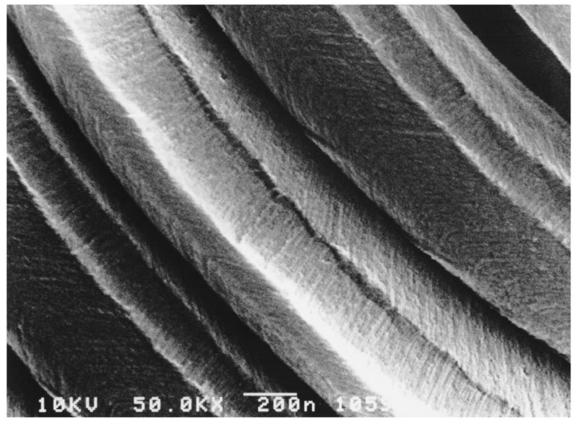


Figure 3 Effect of temperature on the weight decrease. Increasing temperature rate: 10°C/min by TG analyzer. (a) As-grown carbon coils exposed in air, (b) graphite coils in air, (c) as-grown carbon coils in Ar, (d) graphite coils in Ar, (e) commercial graphite powder, (- - - -) base line.



(a)



(b)

Figure 4 Surface of the circular graphite coils exposed in air at 800°C for 12 min (a) and the enlarged view (b).

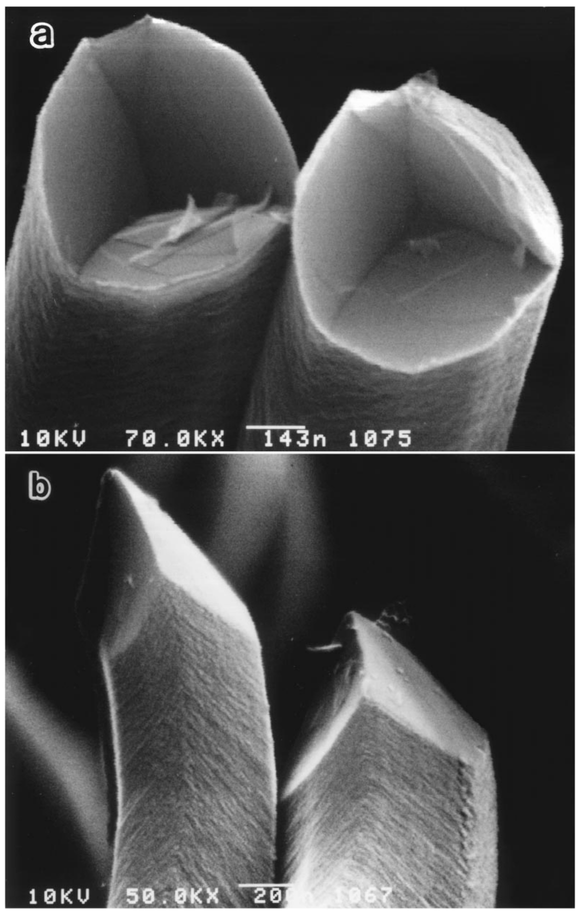


Figure 5 Ruptured tip part of the circular graphite coils exposed in air at 800°C for 12 min. (a) Trigonal hollow, (b) trigonal pyramid.

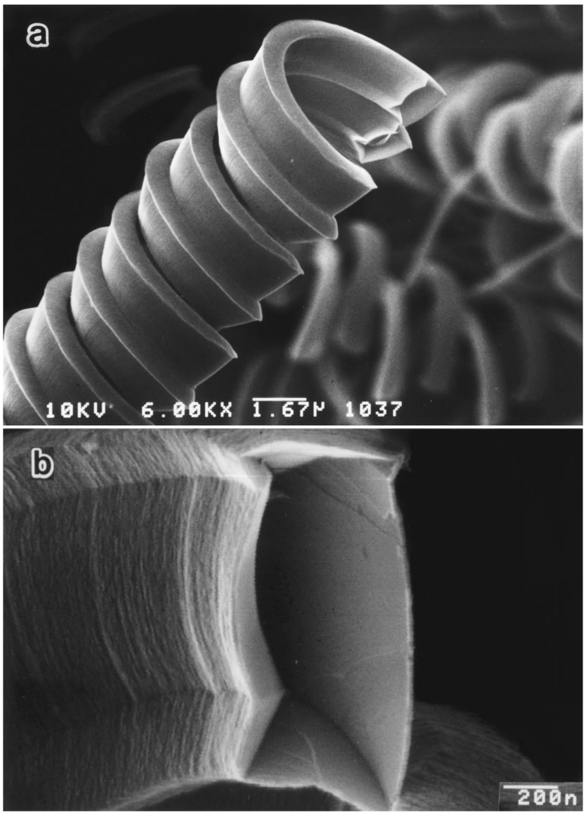


Figure 6 Ruptured tip part of the flat (rectangular) graphite coils exposed in air at 800°C for 12 min (a) and the enlarged view (b).

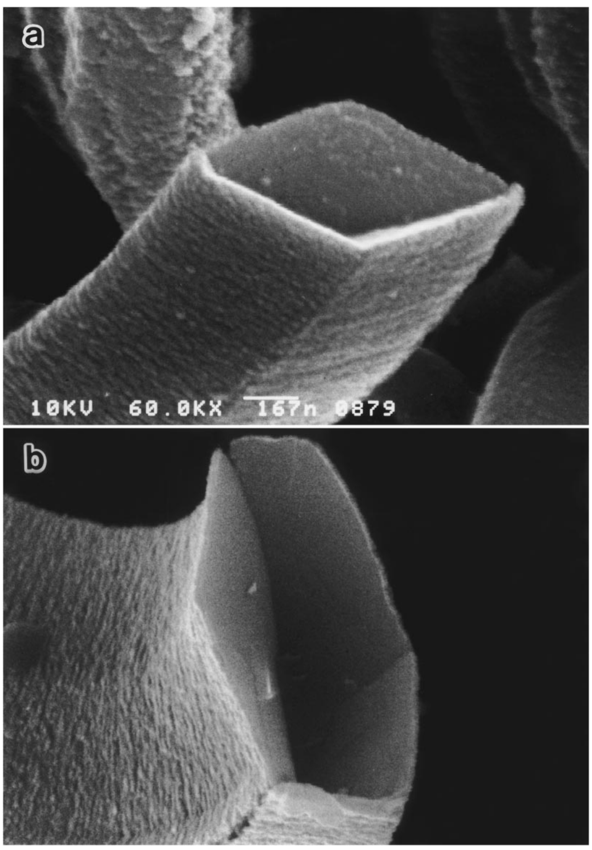


Figure 7 Regular rhombohedral (a) and deformed hexagonal (b) hollow tips.

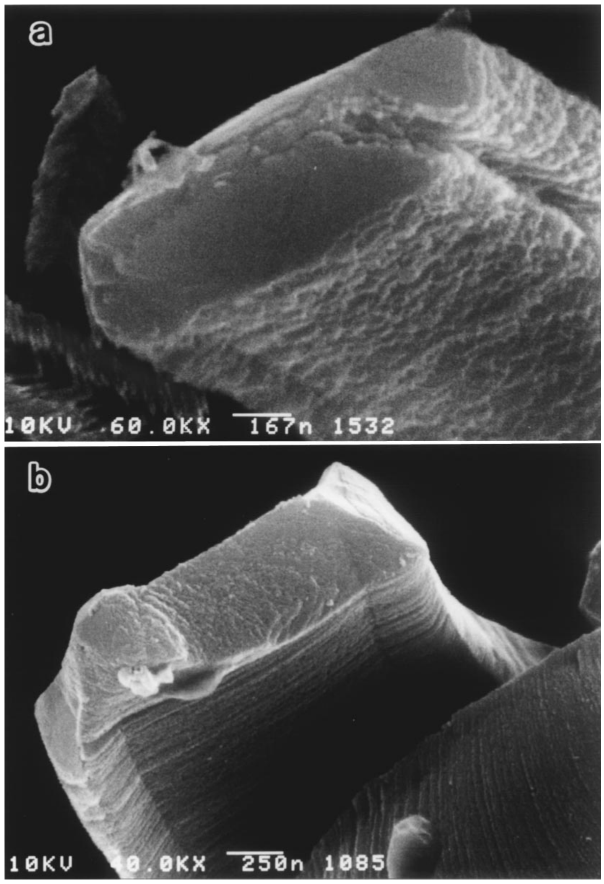


Figure 8 Ruptured tip part of the flat (rectangular) graphite coils exposed in air at 800°C for 12 min. (a) Roof-like tip, (b) flat tip.

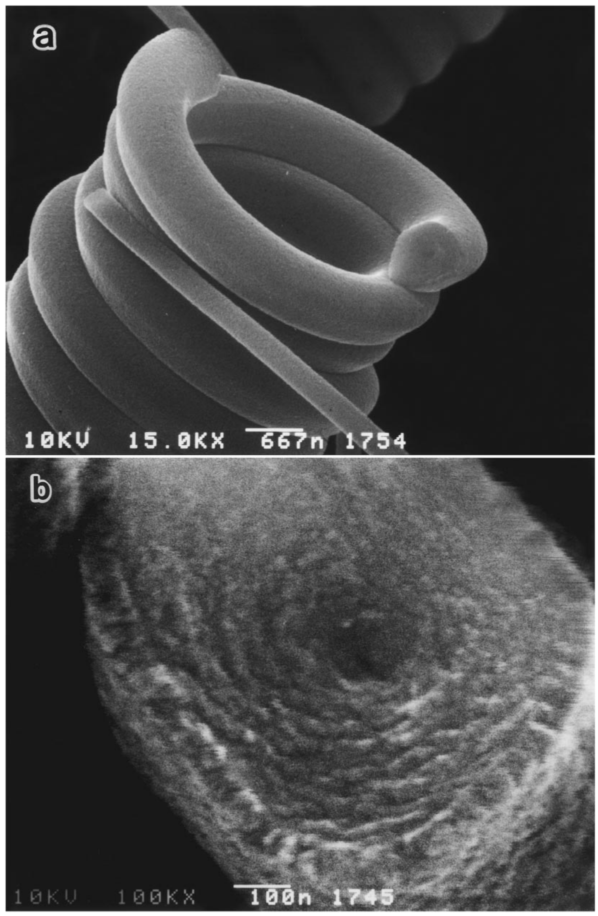


Figure 9 Ruptured tip part of the as-grown carbon coils exposed in Ar up to 1400°C (a) and the enlarged view (b).

with increasing heat-treatment temperature, probably caused by the graphitizing.

The graphite coils were heated to 1400°C in an Ar atmosphere, and the weight decrease versus temperature is shown in Fig. 3, together with the reference data of the as-grown carbon coils and the graphite coils heated in air. The as-grown carbon coils became oxidized at about 450°C in air and the weight significantly decreased with increasing temperature and burned out at 700°C. The graphite coils began to oxidize at about 700°C in air and were then burned out at 1400°C. On the other hand, the weight decrease of the as-grown carbon coils, graphite coils as well as commercial graphite powder were 10–15 wt% at 1400°C in an Ar atmosphere. The weight decrease in the Ar atmosphere may be caused by the partial oxidation due to the small oxygen contaminant present in Ar or the measurement atmosphere and/or by the thermal decomposition of organic residues.

Fig. 4 shows the surface of the circular graphite coils exposed in air at 800°C for 12 min. The formation of some continuous dents are observed along the fiber axis, probably caused by the oxidation consumption of carbon from the surface. Fig. 5 shows one side of the ruptured cross section of the circular graphite coils. It can be seen that two fibers, which form the double coils, have a trigonal cavity enclosed by three mirror-like crystal faces (Fig. 5a). On the other hand, the other side of the ruptured cross section of the graphite coils with a trigonal cavity in one side always have trigonal pyramid-like forms which was also constructed from the three mirror-like planes as shown in Fig. 5b. The outer surface of the graphite coils have many striations with an inclination against the fiber axis.

Fig. 6 shows the ruptured cross section of the flat graphite coils with a deformed rectangular cross

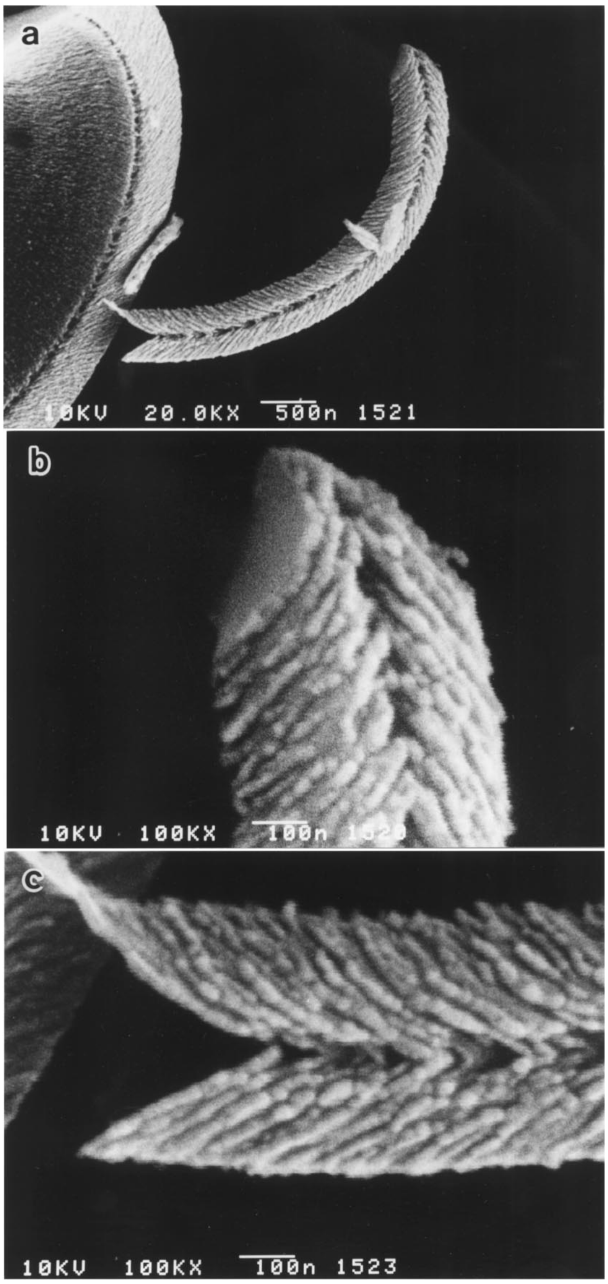


Figure 10 Thin graphite coils expose in Ar up to 1400°C (a) and the enlarged views (b and c). Increasing temperature rate: 10 °C/min.

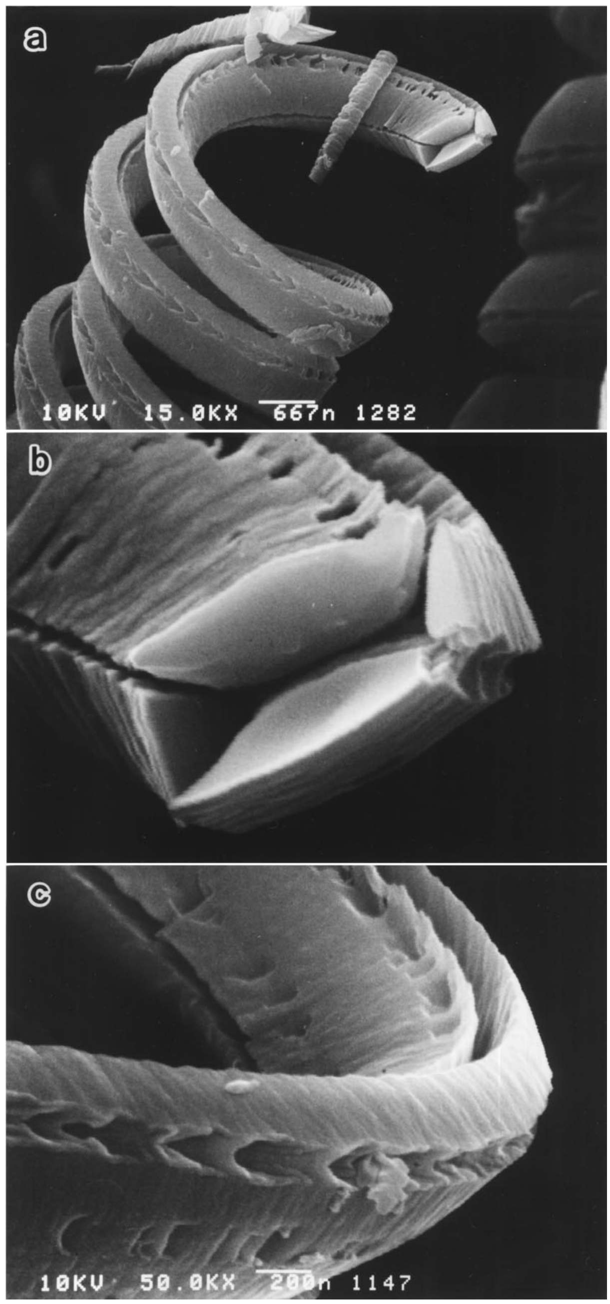


Figure 11 Ruptured tip part (a), enlarged view of (a) (b) and surface (c) of the flat graphite coils exposed in Ar up to 1400°C.

section. The ruptured cross section generally has a rectangular cavity with a smooth inner wall, while the outer surface of the coils have many striations perpendicular to the fiber axis. The four edges are sharpened to form a polygonal cavity. Fig. 7 shows the regular rhombohedral (a) and deformed hexagonal (b) cavities sometimes observed in the ruptured cross section. On the other hand, the other ruptured cross section of the flat graphite coils generally have a roof-like form as shown in Fig. 8a. A flat ruptured cross section as can be seen in Fig. 8b was rarely observed while many distinct striations were observed on the outer surface of the coils.

Fig. 9 shows the ruptured cross section of the as-grown carbon coils heated to 1400°C in an Ar atmosphere in the TG analyzer. The outer surface of the coils are smooth and no striations or hollows are observed

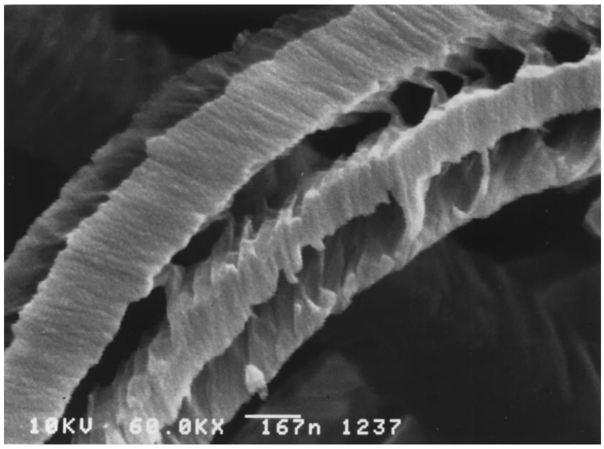


Figure 13 Surface of the flat graphite coils exposed in Ar up to 1400°C.

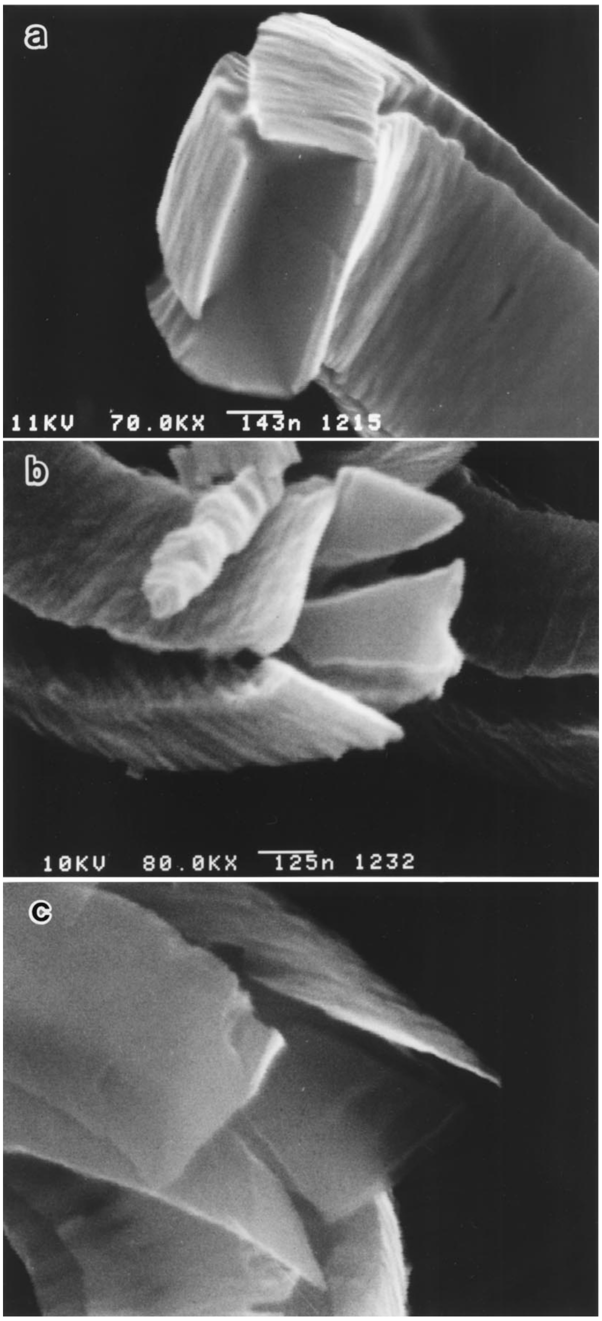


Figure 12 Interesting tip parts of the flat graphite coils exposed in Ar up to 1400°C.

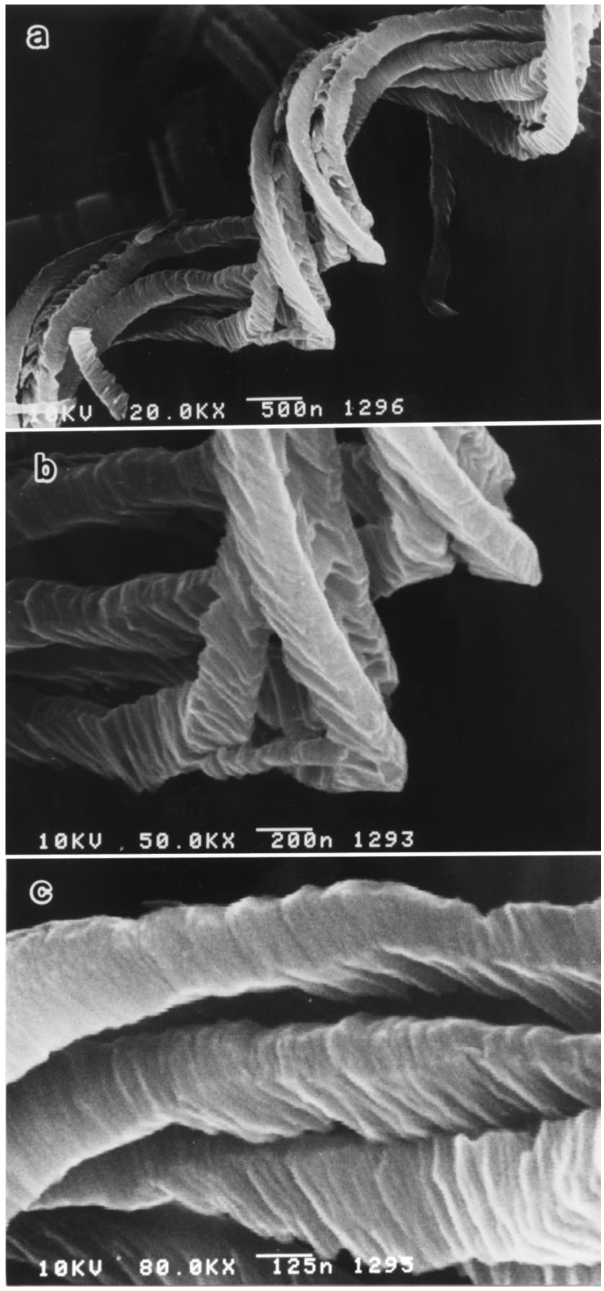


Figure 14 Graphite thin coils formed from the partial oxidation of the circular double graphite coils by exposing in Ar up to 1400°C. Six thin graphite coils (a) and the enlarged view (b) formed from the double coils. Enlarged view of three thin graphite coils formed from a piece of coil.

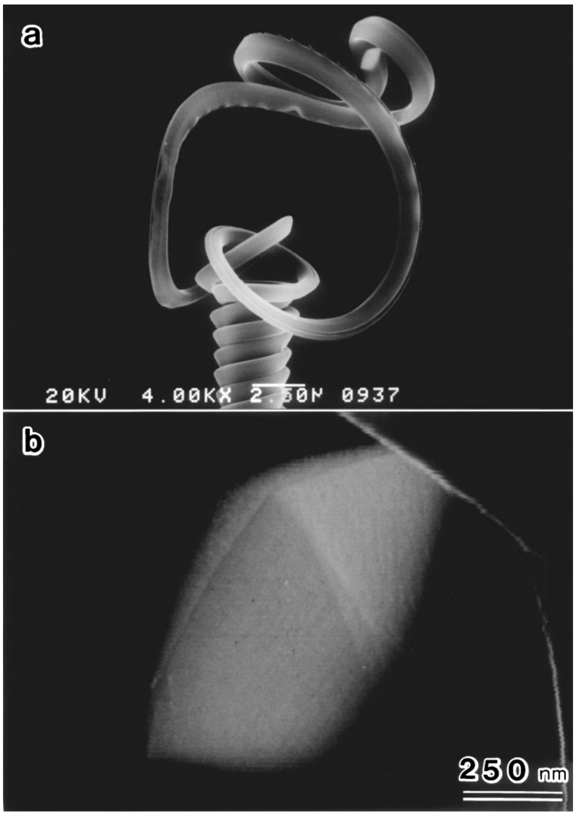


Figure 15 A catalyst grain present on the tip part of the as-grown flat carbon coils (a) and the enlarged view (b).

(Fig. 9a). A fiber which forms the coil is vertically ruptured against the fiber axis while the central part is slightly hollowed. (Fig. 9b). Fig. 10 shows a piece of the ruptured thin graphite coils heated to 1400°C in an Ar atmosphere. It can be seen that the fiber is composed of many thin plates of 10–30 nm thick which declined about 20–40° against the fiber axis, and have a cavity and an apex in both ruptured faces. Fig. 11 shows the tip part of the ruptured flat graphite coils. It can be seen that the hollow observed on the tip have rectangular cones or negative roof-like forms which were enclosed by the smooth and oblique four crystal faces, while the corner of the respective faces were etched (oxidized) out. Deep valley-like striations and cavities can be seen on the outer surface of the coils. Fig. 12 shows an other interesting ruptured tip of the flat graphite coils. It can be seen that one coil is composed of four parts. Fig. 13 shows the middle part of one flat coil. Four thin fibers divided by four deep valley-like cavities can be seen. These results suggest that the flat graphite coils with a rectangular cross section are composed of four parts and separated into four thin coils by the partial oxidation burned out of the corner. Fig. 14 shows the double circular graphite coils which were completely divided into thin coils. It can be seen that one coil is divided into three thin coils, and thus a total six of thin coils are formed from the double circular graphite coils. Furthermore, it can be seen that the respective thin coils are

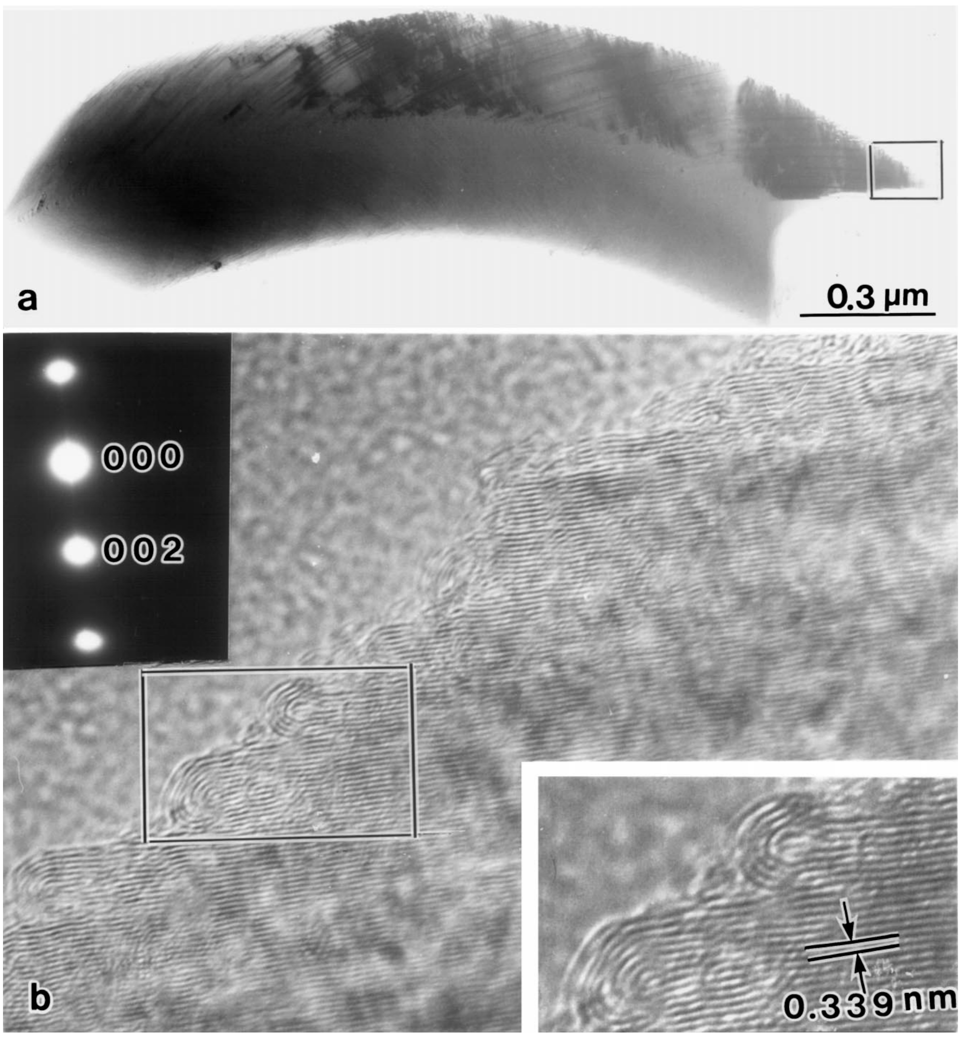


Figure 16 TEM image (a) and lattice image (b) of the graphite coils.

composed of thin plate-like (graphite) crystals whose orientation is helically changed (Fig. 14c). Very interesting phenomena of the exclusive oxidation burned out of the edge part of the two graphite layers of the flat graphite coils are not observed in the as-grown carbon coils as shown in Fig. 9. It may be considered that the edge part is concentrated by strong stresses accompanied by the helical growth of two graphite layers, and thus exclusively oxidized, while the as-grown carbon coils are uniformly oxidized from the surface because of the amorphous state. It may be reasonably considered that the edge part with strong stresses is oxidized much faster than that of the amorphous parts as well as the graphite layers.

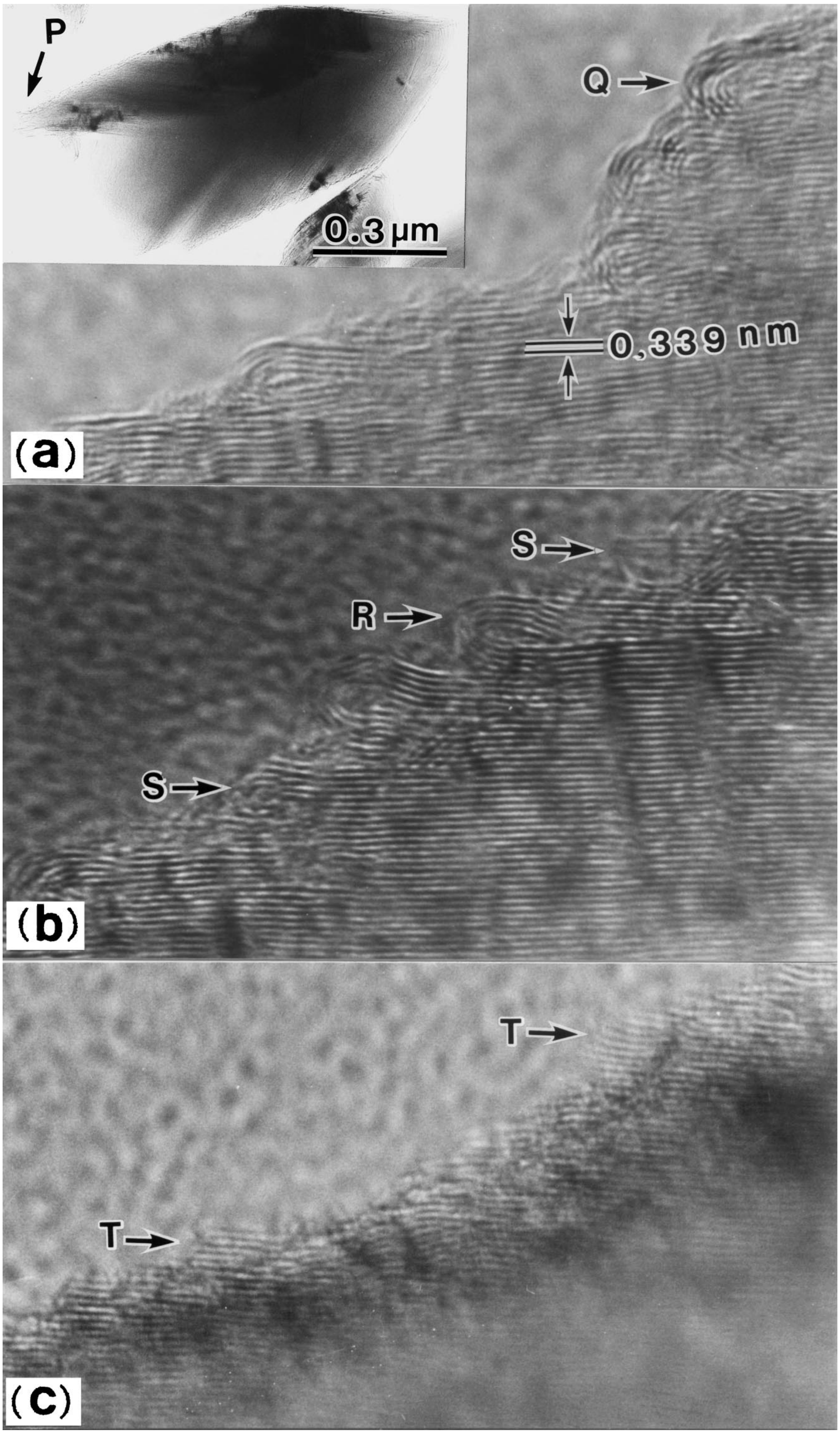


Figure 17 Lattice image of the graphite coils exposed in air at high temperature. Exposed temperature: (a) 800°C, (b) and (c) 1000°C, Exposure time: (a) 12 min, (b) 5 min, (c) 10 min. (Q) completely closed cap, (R and S) partly opened cap, (T) completely opened cap.

We proposed the growth mechanism of the carbon micro-coils based on the catalytic anisotropy between the hexagonal crystal faces of a rhombohedral Ni_3C single crystal [16]. In this mechanism, one carbon coil is composed of three parts which are composed of amorphous carbon grains deposited from three different crystal faces. Furthermore, it is reasonably considered that the circular carbon coils are apt to grow by this mechanism. Fig. 15 shows a Ni catalyst grain present on the tip part of the as-grown flat carbon coils. Tetragonal pyramidal-patterns can be seen. That is, it may be considered that this catalyst grain has octahedral-forms, and two coils grow from one octagonal catalyst grain. Accordingly, it may be reasonably considered that one coil of double flat graphite coils is composed of four parts. This is in good agreement with the above observation of the ruptured tip of the flat graphite coils.

3.2. Microstructure of the oxidized graphite coils

Fig. 16 shows the TEM images of the graphite coils (a) and the lattice images (b). Distinct graphite lattice images can be seen while graphite layers are capped together at the edge. It is important to eliminate the cap for the intercalation of elements, ion, molecules or compounds for obtaining good functionalities. Fig. 17 shows the graphite lattice images of the oxidized graphite coils. Caps of the graphite layers were not eliminated by oxidation in air at 800°C for 12 min as shown in Fig. 17a. On the othe hand, about half of the caps could be eliminated by oxidation in air at 1000°C for 5 min (Fig. 17b), and then completely eliminated after 10 min as shown in Fig. 10c.

4. Conclusions

Graphite micro-coils were exposed in air or an Ar atmosphere at 800–1400°C. The oxidation characteristics and morphology of the graphite coils were examined in detail, and the growth mechanism of the carbon micro-coils is discussed. The surface of the graphite coils was oxidized to form three or four deep striations extending in the direction of the fiber axis as well as the shallow striations caused by the graphite layers developed perpendicular to the fiber axis. The ruptured cross sections of the graphite coils with a circular or elliptical formed cross section (circular graphite coils) exposed in air at 800°C generally have a negative or positive trigonal cone-patterns, while that of the graphite coils with flat or rectangular formed cross section (flat graphite coils) have negative and positive rectangular cone or roof-like patterns. The rupture cross section of the graphite coils exposed in Ar up to 1400°C is generally separated into three or four parts, and then six or eight thin coils were formed from the circular and flat graphite double coils, respectively. These observations strongly supported the growth mechanisms based on the anisotropy of the catalytic crystal faces.

Acknowledgements

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