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Preparation and properties of TaC/C/TaC ~ TaC composite micro-tubes by vapor phase tantalizing of the regular carbon micro-coils/micro-tubes

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TaC/C/TaC ~ TaC composite micro-tubes were prepared by the vapor phase tantalizing of the regular carbon micro-coils/micro-tubes, and the preparation conditions and some properties were examined. The carbon micro-coils with a tube-like morphology were tantalized from the surface to the core of the carbon fibers with full preservation of the tube-like morphology to form TaC/C/TaC ~ TaC composite micro-tubes. The bulk electrical resistivity and specific surface area of the TaC/C/TaC ~ TaC composite micro-tubes were 4×10^{-3} to 5×10^{-4} Ω·m and 5×10^{3} to 2×10^{4} m^2/kg, respectively, depending on the tantalized ratio and the bulk density.

1. Introduction

Microscopic hollow tubes of various materials, such as carbon, carbides, nitrides, etc., are potential candidates for lightweight, thermal barrier, and heat exchange materials, micro-sensors, electron emitter, electromagnetic absorbers, etc. Microscopic hollow tubes have been generally prepared by appling a surface coating on the microscopic fibers with outer diameter of microns which is then removed [1]. However, this coating process has some difficulties when removing the core fibers on the surface of which the thin or thick coating layers are present.

We have prepared micro-coiled carbon fibers (referred to as "carbon micro-coils" hereafter) by the catalytic pyrolysis of acetylene [2–5]. Among them, there are micro-pipe like carbon coils which have a constant coil diameter with no coil cap (referred to as "carbon micro-tubes" hereafter). Thin pyrolytic carbon layers are deposited in the coil gap as well as on the surface of the carbon coils and connect each coil to form a tube-like morphology. We have also obtained micro-coiled or micro-tubed fibers of SiC [6], TiC [7, 8], and ZrC [9], by the vapor phase metallizing of the regular carbon micro-coils/micro-tubes with full preservation of the coiling and tube-like morphology.

In this study, carbon micro-coils/micro-tubes obtained by the Ni-catalyzed pyrolysis of acetylene were vapor-phase tantalized to form TaC/C/TaC ~ TaC composite micro-tubes, and the reaction conditions and some properties were examined.

2. Experimental

Regular carbon micro-coils/micro-tubes were prepared by the Ni-catalyzed pyrolysis of acetylene. The detailed preparation procedures and conditions are shown in ref. [3]. The carbon micro-coils/micro-tubes used as the starting point for the proportions described here have a regular coil diameter of 3–5 μm, a coil gap of zero and a coil length of 1–5 mm, and they were tantalized under a $TaCl_5 + H_2$ atmosphere at 900–1200°C. The gas flow rates of $TaCl_5$ and H_2 were fixed at 5×10^{-7} m^3/min and 1×10^{-4} m^3/min, respectively. The rotating apparatus used for tantalizing the carbon coils is the same as that shown in ref. [8].

3. Results and discussion

3.1. Tantalizing conditions and morphology

The weight gain caused by tantalizing of the carbon micro-coils/micro-tubes was observed above 800°C, and increased with increasing reaction temperature and reaction time. The conversion ratio of the carbon micro-coils/micro-tubes to TaC micro-tubes, which was estimated from the weight gain, increased with increasing reaction time at a rate according to the square root law as shown in Fig. 1. This suggests that the rate-determining step is the diffusion of Ta or carbon through the deposited TaC layers.

X-ray diffraction profiles showed that the phase formed by the tantalizing of the carbon micro-coils/micro-tubes is a single TaC phase irrespective of the

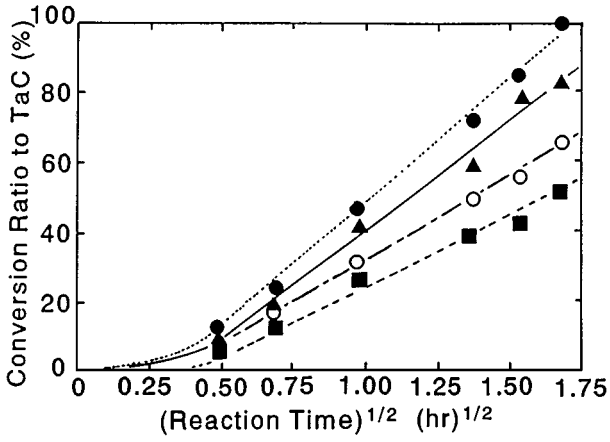

Figure 1 Relationship between conversion ratio of the carbon micro-tubes to TaC micro-tubes and square root of reaction time. Reaction temperature: (●) 900°C, (▲) 1000°C, (○) 1100°C, (■) 1200°C.

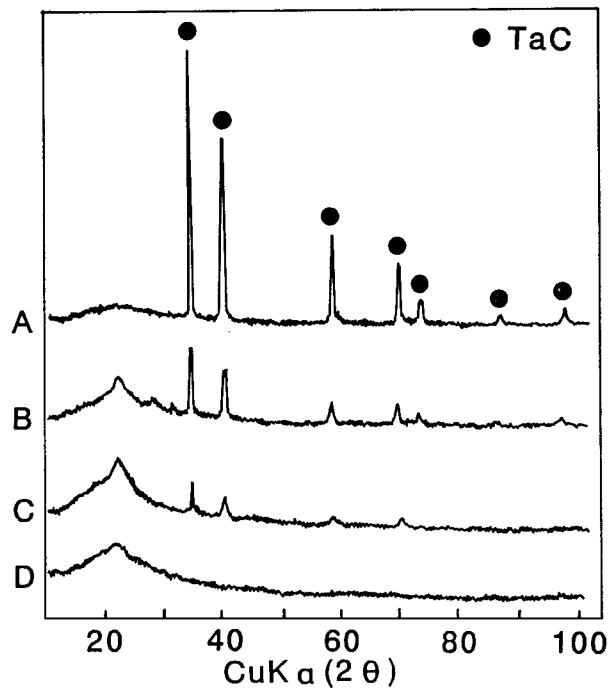

Figure 2 X-ray diffraction profiles. Reaction temperature: 1200°C, reaction time: (a) 3 hr, (b) 2 hr, (c) 1 hr, (d) source as-grown carbon micro-tubes.

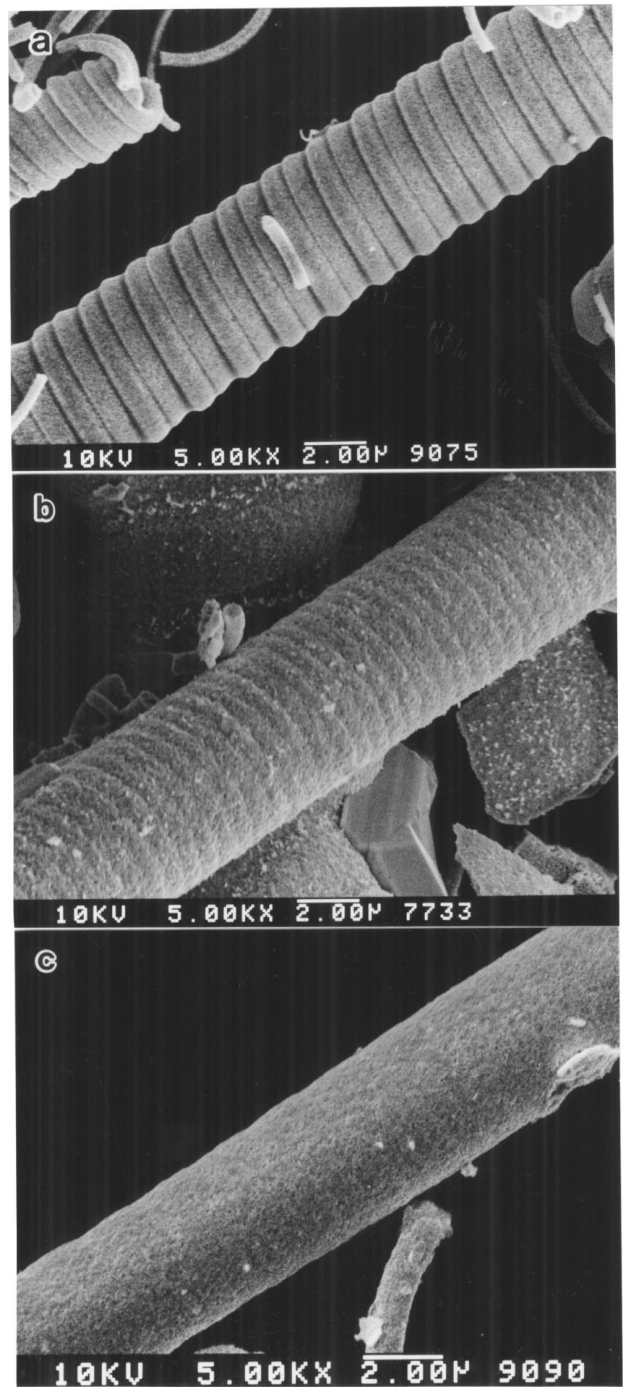

Figure 3 Surface morphology of the TaC micro-tubes. Reaction temperature: 1200°C, reaction time: (a) 1 hr, (b) 2 hr, (c) 3 hr.

reaction temperature and reaction time used in this work as shown in Fig. 2.

The carbon micro-tubes/micro-pipes could be tantalized from the surface to the core of the carbon fibers with full preservation of the coiled-tube morphology. The outer surface morphology of the obtained TaC micro-tubes at 1200°C at different reaction times is shown in Fig. 3. The TaC grains formed on the surface increased with increasing reaction time, and the coiling pattern gradually disappeared with increasing reaction time, and then completely disappeared after 3 hrs to form apparently straight fibers with a smooth surface as shown in Fig. 3c. Fig. 4 shows the ruptured cross section of the TaC micro-coils obtained at 1200°C for 1 hr. Fine TaC layers of about 100 nm thick are deposited on the surface. A conical cavity can be seen in the central part of the unreacted carbon fibers. The presence of the conical cavity in the central part of the carbon coil axis may reflect the unique growth mechanism of the carbon micro-coils as proposed in ref. [10]. Polished cross sections of the TaC coils obtained at 1000°C for 1 hr are shown in Fig. 5. It can be seen that uniform thin TaC layers were formed on the inner surface as well as on the outer one of the carbon micro-tubes, in which the outer and inner white thin layer parts are the formed TaC layers and the black and/or transparent parts enclosed by the white parts are the unreacted carbon micro-tubes with coiling morphology, thus forming the TaC/C/TaC composite micro-tubes. The thickness of the TaC layers increased with increasing reaction

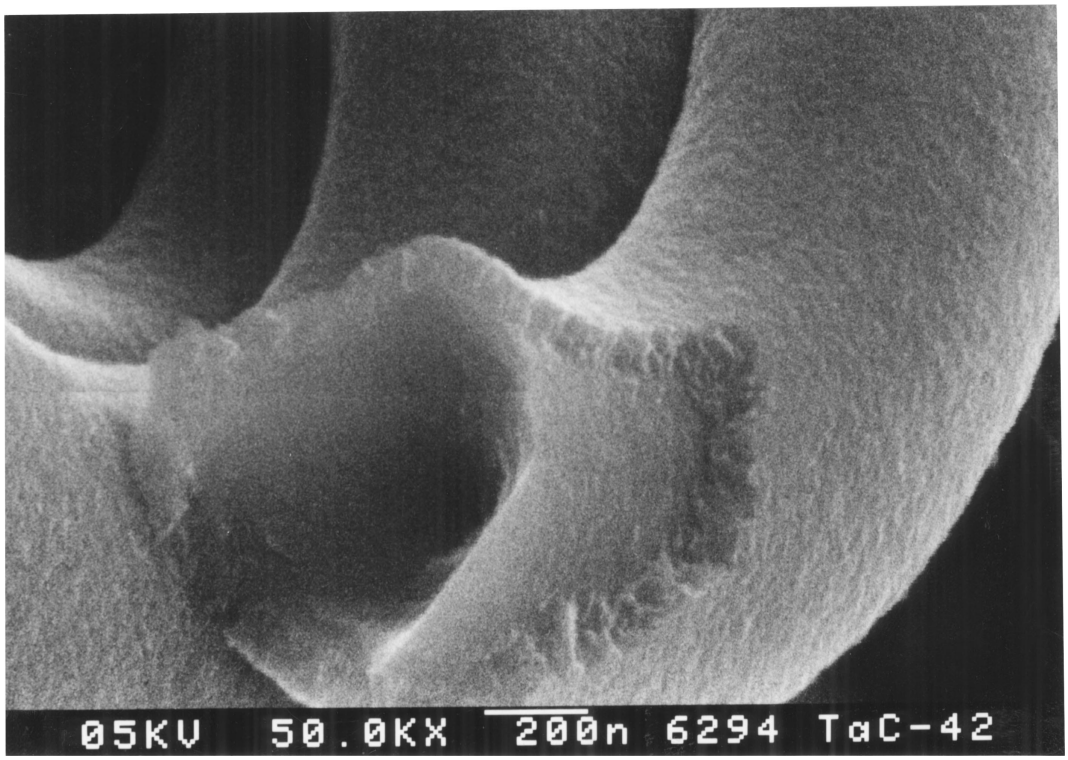

Figure 4 Ruptured cross section of the TaC micro-tubes. Reaction temperature: 1000°C, reaction time: 1 hr.

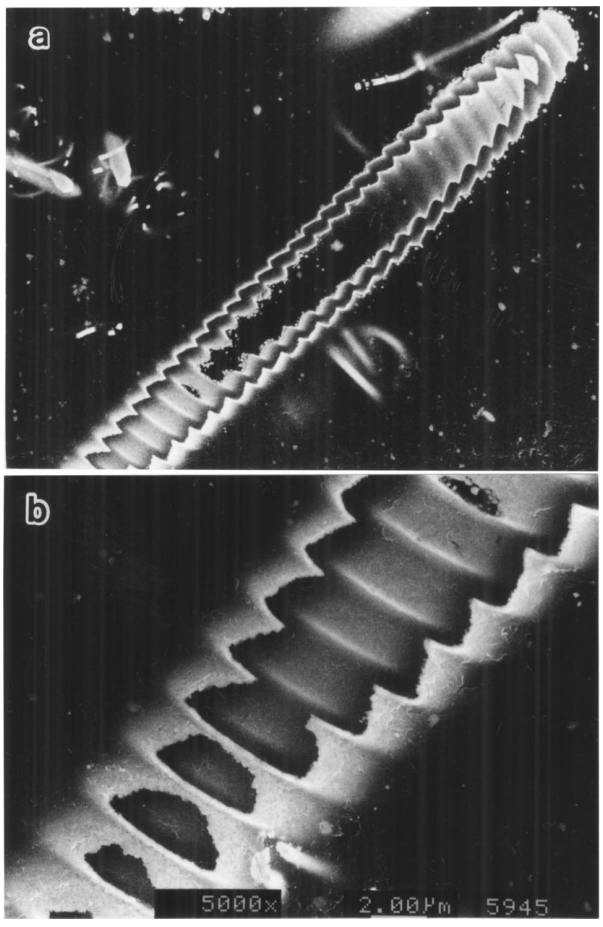

Figure 5 Polished cross section of the TaC micro-tubes (a) and the enlarged view (b). Reaction temperature: 1000°C, reaction time: 1 hr. The outer and inner white thin layer parts are the formed TaC layers, and the black and/or transparent part enclosed by the white part is the unreacted carbon micro-tubes.

time as shown in Fig. 6a–c. The carbon coils were tantalized to the fiber cores after a 3 hr reaction time and the formed TaC layers coalesced with each other to form the pure TaC micro-tubes as shown in Fig. 6d. The presence of Ta was identified in the white part by electron probe microanalysis (EPMA) on the vertical cross section of the TaC micro-tubes as shown in Fig. 7.

3.2. Properties

The bulk (powder) electrical resistivity was measured using a 0.01 m i.d. cylindrical measurement glass cell at room temperature in air. The bulk electrical resistivities of TaC/C/TaC ∼ TaC composite micro-tubes with different Ta/C ratios are shown in Fig. 8 in relation to the bulk density. The Ta/C ratio of the TaC composite micro-tubes was obtained from the weight gain by the tantalizing. The original carbon micro-tubes/micro-pipes have a bulk electrical resistivity of 1×10^{-2} to 4×10^{-3} Ω·m for a bulk density of 4×10^2 to 6×10^2 kg/m^3. The bulk electrical resistivty of the TaC/C/C/TaC ∼ TaC composite micro-tubes decreased with increasing Ta/C ratio and also with increasing bulk density, and the TaC micro-tubes of Ta/C = 1 have a 1×10^{-3}–5×10^{-4} Ω·m electrical resistivity for a bulk density of 3×10^3–5×10^3 kg/m^3. The fine TaC powder (1 μm) shows a higher resisitivity thant that of the TaC (Ta/C = 1) coils. This may be caused by the oxide layers formed on the surface of the TaC powders as shown in the case of the ZrC coils.

Fig. 9 shows the specific surface area of the single TaC micro-tubes measured using the BET method. The specific surface area was significantly decreased with increasing reaction time and reaction temperature,

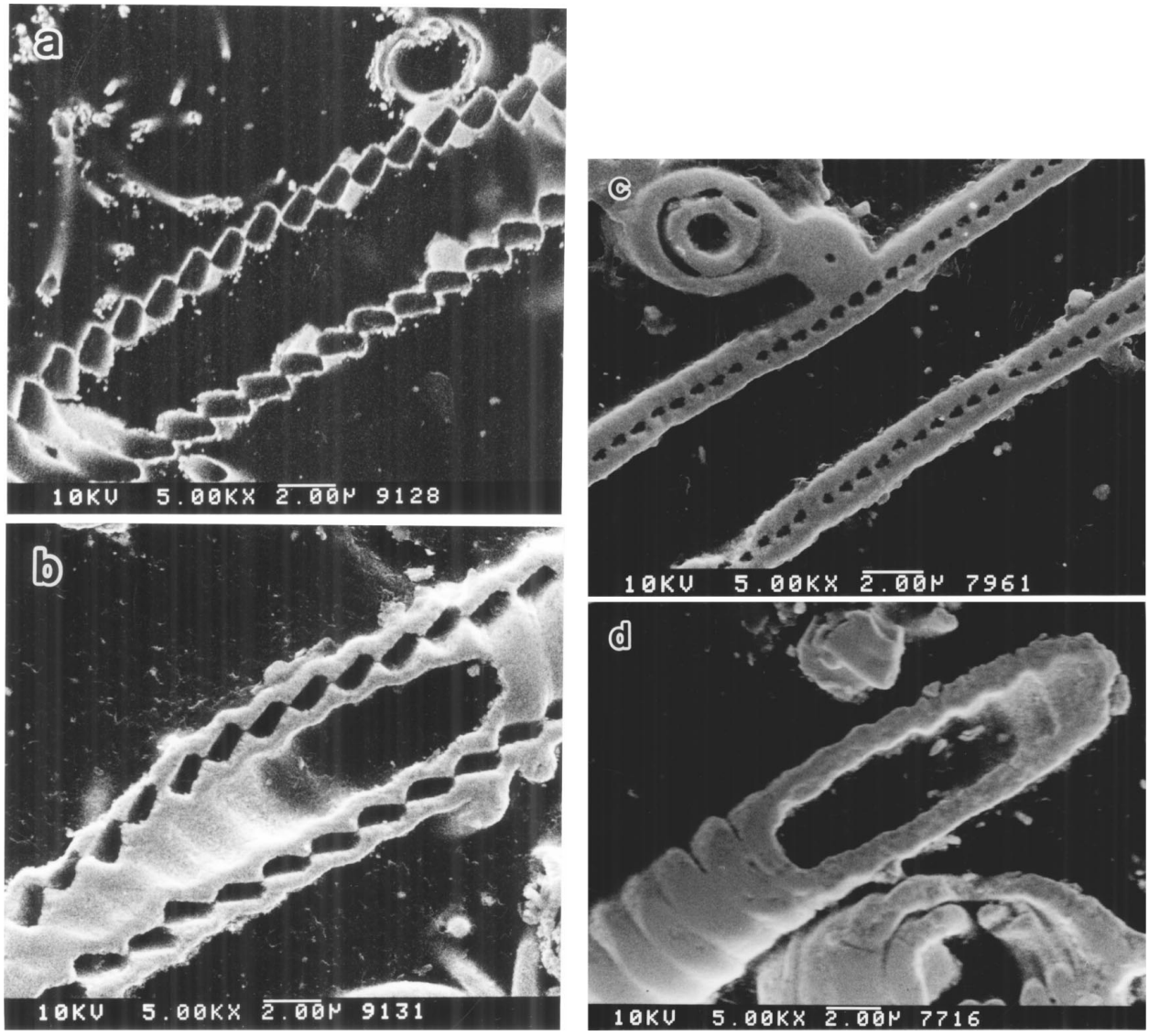

Figure 6 Polished cross section of the TaC micro-tubes. Reaction temperature: 1200°C, reaction time: (a) 0.5 hr, (b) 1 hr, (c) 2 hrs, (d) 3 hrs.

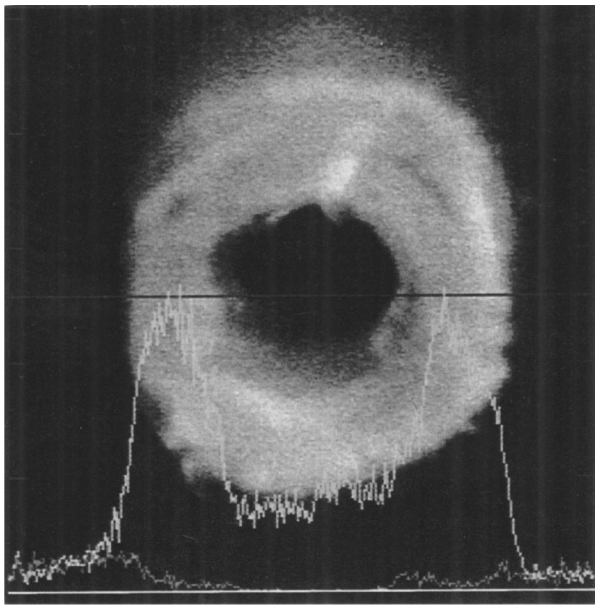

Figure 7 EPMA analysis on the polished vertical cross section of the TaC micro-tubes.

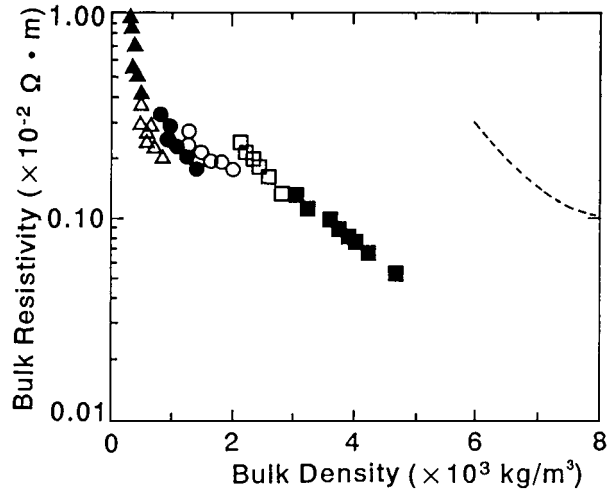

Figure 8 Relationship between bulk electrical resistivity and bulk density. (▲) source as-grown carbon coils. Conversion rate of the carbon micro-tubes to the TaC micro-tubes: (△) 23%, (●) 46%, (○) 69%, (□) 81%, (■) 100%. (- - - - -) TaC powder.

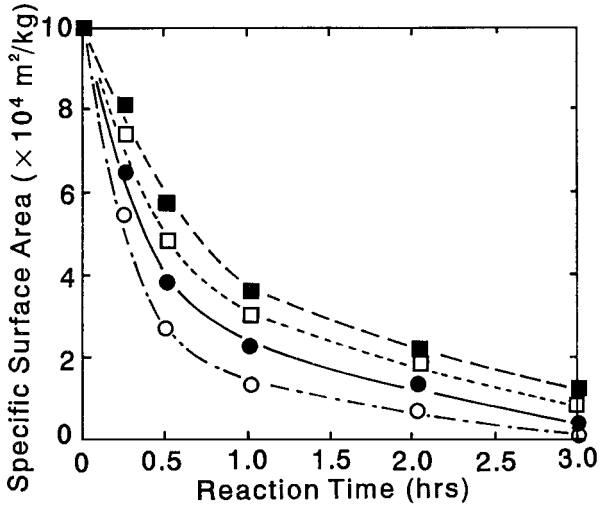

Figure 9 Relationship between specific surface area and reaction time. Reaction temperature: (■) 900°C, (□) 1000°C, (●) 1100°C, (○) 1200°C.

and decreased to a few thousand m^2/kg for the TaC micro-tubes obtained at 1200°C for 3 hrs. The original carbon coil has many micropores of about 4 nm diameter on the surface, and the pores may be sealed by the deposited TaC layers.

4. Conclusions

TaC/C/TaC ~ TaC composite micro-tubes were prepared by the vapor phase tantalizing of regular carbon micro-coils/micro-tubes, and the preparation conditions and some properties were examined. The carbon micro-coils/micro-tubes were tantalized from the surface to the core of the carbon fibers with full preservation of the coiling morphology to form TaC/C/TaC ~ TaC composite micro-tubes. The bulk electrical resistivity and specific surface area of the original carbon micro-coils/micro-tubes were 4×10^{-3} to 5×10^{-4} Ω·m and 5×10^3 to 2×10^4 m^2/kg, respectively, depending on the tantalized rate and bulk density.

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