Polym. Bull. (2010) 64:939–951
DOI 10.1007/s00289-009-0230-0

ORIGINAL PAPER

Morphology of carbon/TiC composite films prepared by carbonization of polyimide/titania composites

Yanling Luo · Masaru Matsuo

Received: 26 August 2009 / Revised: 5 December 2009 / Accepted: 17 December 2009 /

Abstract Polyimide/titania (PI/TiO_2) composite was synthesized by in situ sol–gel polymerization, and carbon/titanium carbide (TiC) composite films were prepared by carbothermal reduction of the PI/TiO_2 composite at 1,600 °C under flowing argon. The structure and properties of the composites were studied by wide angle X-ray diffraction (WAXD), Fourier transform infrared spectrometer (FTIR), scanning electron microscopy, and energy dispersive X-ray spectroscopy. The carbon/TiC composite films exhibited metallic luster on the surface and compact structure in cross section with well dispersed TiC particles. WAXD intensity distribution revealed that TiC particles formed by tightly bonding between elemental carbon and titanium formed crystallites which as a filler provided tough films. The results indicated that heat treatment of PI/TiO_2 under argon is a promising method for preparing tough carbon composite films.

Keywords In situ sol–gel polymerization · Carbon/titanium carbide composite films · Heat treatment · Metallic luster · Tough films

Introduction

Carbon-based composites have been widely studied as potential candidates for plasma facing materials [1, 2]. Carbon composites filled with boron, silicon, or titanium have attracted research interest in the reduced chemical erosion of the fillers [3–8]. Titanium carbide (TiC), in particular, shows high electrical conductivity and

---

Y. Luo · M. Matsuo (✉)
Department of Textile and Apparel Science, Faculty of Human Life and Environment,
Nara Women's University, Nara 630-8506, Japan
e-mail: m-matsuo@cc.nara-wu.ac.jp

mechanical stiffness, low density, and catalytic activity resembling that of metals [9]. Very small TiC particles embedded in a matrix of amorphous carbon can improve the electrical and mechanical properties of carbon composites [10].

In general, TiC has been prepared by mechanical milling, solid state metathesis, organometallic reactions, and carbothermal reduction from polymer/titanium oxide composites [11]. Compared with carbothermal reduction of titanium oxides by carbon powder, the carbothermal reduction of polymer composite is a promising method because of easy control of the composition ratio and uniform dispersion of TiC in the final composite [12]. As far as we are aware no research has been reported on the preparation of carbon/TiC composite by carbothermal reduction of polyimide/titania (PI/TiO_2) composite.

In the present study, PI/TiO_2 composites were synthesized by an in situ sol–gel method, and carbon/TiC composites were prepared by carbothermal reduction of the PI/TiO_2 composites at 1,600 °C under argon. The carbon/TiC composite films were composed of a compact amorphous carbon matrix with ca. 100 nm TiC particles dispersed homogeneously in the matrix. The effect of titania on the carbothermal reduction is discussed in terms of morphological aspects of the composites.

Experimental section

Materials

4,4′-Oxydianiline (ODA) and 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) were purchased from Tokyo Chemical Industry Co. Ltd., Japan and dried under vacuum for 10 h at 150 °C before use. *N*-methyl-2-pyrrolidone (NMP) was purchased from Nacalai Tesque Inc., Kyoto, Japan, and dried with molecular sieve for 3 days. Titanium isopropoxide (TIP) was purchased from Tokyo Chemical Industry Co. Ltd. in Japan.

Preparation of PI/TiO_2 composite films

The PI/TiO_2 composites were synthesized using in situ sol–gel methods [13, 14]. In a typical synthesis ODA (1.0 g) was mixed with an appropriate amount of NMP solvent in an N_2 atmosphere. After complete dissolution of ODA, the TiO_2 precursor TIP (0.54 g) was added, then BTDA (1.62 g) was added in three aliquots at 30 min intervals. After stirring the mixture for a further 12 h at room temperature, a golden yellow solution was obtained.

The solution was cast on a glass plate and cured by heating in N_2 for ca. 4 h at 70 °C until a rigid film formed. The film was then heated gradually to remove NMP and promote imidization. Heating was carried out in four stages (temperature, time): 100 °C, 1 h; 150 °C, 1 h; 250 °C, 1 h; and 300 °C, 2 h. The resulting highly transparent film was then cooled to room temperature. The mass of titania in the PI/TiO_2 composite films was calculated from the mass of TIP used.

Preparation of carbon/TiC composite films

The PI/TiO_2 composite film was cut into several pieces, sandwiched between graphite plates and heated at an optimized heating rate of 400 °C h^{-1} to 600, 900, 1,200, or 1,600 °C under a flow of argon. Some of the pieces were kept at one of the above temperatures for 1, 3, or 5 h. Carbonized films were obtained on cooling to room temperature. The carbon/TiC composite films prepared by heat treatment at 1,600 °C of PI/TiO_2 composites containing 2, 5, 7, and 10 wt% TiO_2 are denoted by TC-2w, TC-5w, TC-7w, and TC-10w, respectively.

Measurements

FTIR spectroscopy was performed in the 400–4,000 cm^{-1} range; 20 scans were averaged for each spectrum.

Thermogravimetric analysis (TGA) was carried out using a TG/DTA 6300 (SII Nano Technology Inc.) instrument, at 10 °C min^{-1} heating rate under nitrogen. Wide angle X-ray diffraction (WAXD) was conducted with a 12 kW rotating anode X-ray generator (Rigaku RDA-rA) operated at 150 mA and 40 kV. The CuKα X-ray beam was monochromatized with a graphite monochromator.

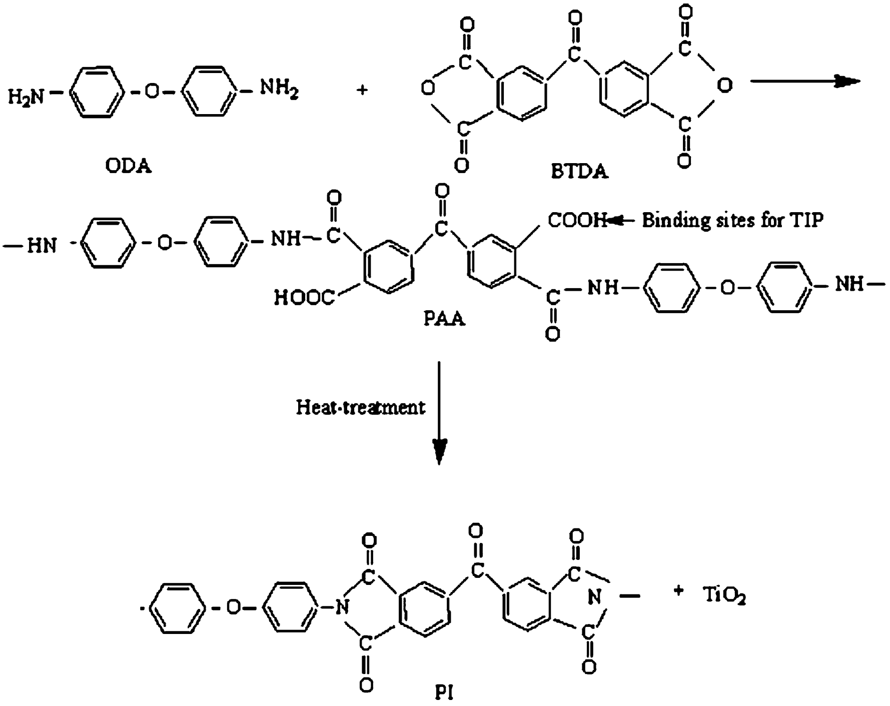
Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were carried out using JSM-6700F and JSM-B300 (JEOL Co. Ltd.) instruments.

Characteristics and morphology of PI/TiO_2 composite

The preparation of PI/TiO_2 composites is summarized schematically in Scheme 1. In this reaction, polymerization of ODA and BTDA generates the polyamide acid precursor (PAA) whose carboxylic acid groups act as binding sites for the titania precursor TIP [13, 14]. The subsequent imidization ring closure led to hydrolysis of the TIP and generated titanium clusters. The rigid polyimide backbone reduced the mobility of titania clusters and prevented agglomeration of large titania particles [13, 14].

By comparing the FTIR absorption peaks of PI and PI/TiO_2 composite, it was confirmed that the structure of the PI matrix remained chemically invariant and coordination of polymer carbonyl groups with TiO_2 did not occur in PI/TiO_2 composite film. SEM of the PI/TiO_2 composite did not show the TiO_2 particles with very small size, even at high power, because of the low conductivity of the polyimide matrix.

The influence of the titania on the viscoelastic behavior of PI/TiO_2 composites was studied using a viscoelastic spectrometer (VES-F; Iwamoto Machine Co. Ltd.) at 10 Hz frequency in the temperature range -130 to 310 °C. The storage modulus of PI film and PI/TiO_2 composites films increased in a sigmoidal manner as temperature decreased. The storage modulus of PI/TiO_2 composites increased slightly with increasing TiO_2 content, indicating a filler effect [15–18]. The storage modulus at 20 °C was in the range 2.7–3.3 GPa.



Scheme 1 Synthesis scheme for the preparation of PI/TiO_2 composite

Results and discussion

Figure 1 shows an example of a carbon/TiC composite film prepared by heat treatment for 5 h at 1,600 °C of a PI/TiO_2 composite with 10 wt% TiO_2. The carbon and titanium were thought to be combined tightly which is discussed later. The composite formed a very tight film with no cracks. The same morphology was found for carbon/TiC composites prepared from PI composites with varying content (2, 5, and 10 wt%) of TiO_2 particles. The composite film exhibited a metallic luster on the smooth surface and this characteristic was enhanced with increasing TiO_2 content.

Fig. 1 Carbon–TiC composite film (TC-10w) produced by heat treatment, for 5 h at 1,600 °C, of PI/TiC composite with 10 wt% TiO_2

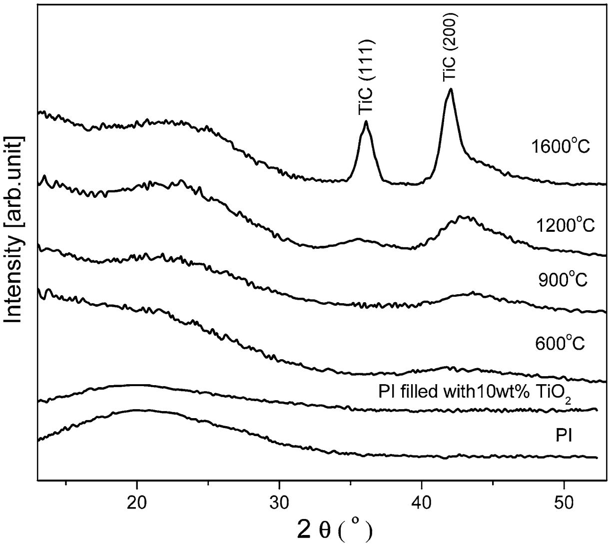


Fig. 2 WAXD patterns of carbon/TiC composite films (TC-10w) prepared from PI composite with 10% TiO_2 heat treated for 1 h at different temperatures

Further experiments showed that it was not possible to incorporate more than 20 wt% TiO_2 in the PI matrix.

To elucidate the effect of heat treatment on PI/TiO_2 composite films, WAXD was carried out for carbon composite films obtained from PI composite with 10 wt% TiO_2 that had been heat treated for 1 h at different temperatures. The diffraction patterns were corrected for air scattering, background noise, polarization, and absorption: the procedure has been described in detail elsewhere [19]. The WAXD pattern of PI/TiO_2 composite film (before heat treatment) shown in Fig. 2 displayed a very broad peak with maximum at ca. 20° (2θ) attributable to scattering from the amorphous PI backbone [20]. This broad peak appeared at a slightly smaller value of 2θ for PI/TiO_2 composite, which has been generally observed, indicating a larger lattice distance between the (100) planes of the PI backbone in the composite than in PI [21]. This broad peak implies that no crystallization of PI matrix in the original composite occurred, and the incorporation of TiO_2 in the matrix hampered ordering of the PI backbones.

The WAXD pattern for carbon film obtained from PI/TiO_2 composite heated at 600 °C does not show the (002) reflection of graphite crystallites, indicating no conversion to ordered carbon. When the PI/TiO_2 composite was heated at 900 °C, two broad peaks appeared at 22 and 44°, indicating that the resultant carbon/TiC composite film was amorphous. The carbon/TiC film obtained from PI/TiO_2 composite heat treated at 1,200 °C shows two broad peaks corresponding to TiC (111) and (200) reflections, at about 36 and 42°, respectively. These results suggest that the carbothermal reaction ($TiO_2 + 3C \rightarrow TiC + 2CO$) occurred during pyrolysis [22]. As the heat treatment temperature increased to 1,600 °C, the resultant carbon/TiC composite showed relatively sharp, narrow peaks from the TiC (111) and (200) reflections, at 36.1 and 41.9°, respectively. Thus, heat treatment at ca. 1,200 °C led to the formation of TiC, and heat treatment at 1,600 °C is thought to promote formation of TiC crystallites.

It has been reported that the reaction between TiO_2 and carbon becomes thermodynamically spontaneous at 1,087 °C [22]. The formation of TiC by heat treatment coupled with carbothermal reduction can be represented by the following chemical equation [23].

$$TiO_2(s) + 3C \rightarrow TiC(s) + 2CO \tag{1}$$

According to a DSC study of this process [22], the following series of reactions is proposed:

$$4TiO_2(s) + C(s) \rightarrow Ti_4O_7(s) + CO(g) \tag{2}$$

$$3Ti_4O_7(s) + C(s) \rightarrow 4Ti_3O_5(s) + CO(g) \tag{3}$$

$$Ti_3O_5(s) + 8C(s) \rightarrow 3TiC(s) + 5CO(g) \tag{4}$$

Figure 3 shows FTIR spectra in the range 400–4,000 cm^{-1} measured for carbon/TiC composite films formed from PI/TiO_2 composite that was heat treated for different times. For the carbon composite formed by heat treatment at 1,600 °C for 3 h absorption peaks in the range of 1,000–2,000 cm^{-1} were observed, which are attributable to the absorption bands of organic structures. With an increase in pyrolysis time from 3 to 5 h, the organic absorption intensity became weaker but did not vanish, indicating that carbonization is a very slow process, and prolonged heat treatment is needed to complete the process. After complete carbonization TiO_2

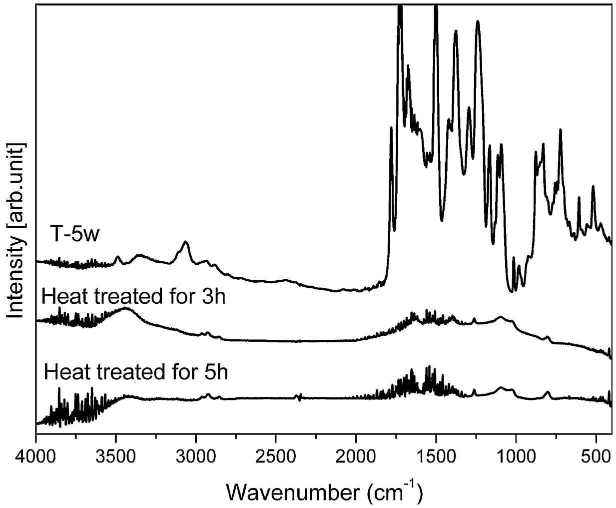


Fig. 3 FTIR spectra of carbon/TiC composite films obtained from PI composite with 5 wt% TiO_2 by heat treatment at 1,600 °C

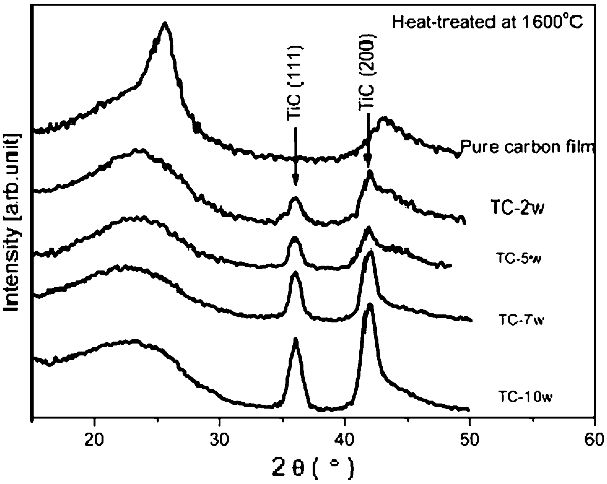


Fig. 4 WAXD intensity distributions for carbon/TiC composite films prepared from PI composite with different TiO_2 contents by heat treatment for 5 h at 1,600 °C

absorption bands in the range 400–1,000 cm^{-1} were not observed, indicating that TiO_2 particles disappeared in the carbonization process.

Figure 4 shows WAXD profiles for carbon/TiC composite films obtained by heat treatment of PI/TiO_2 composite for 5 h at 1,600 °C. TiC (111) and (200) diffraction peaks appear at 36.1° and 41.9° for this sample. The WAXD pattern for carbon film prepared from pure PI film displays a relatively strong reflection from the (002) plane at ca. 26°, which is probably because of a quasi-graphite structure (T-carbon) [24]. On the other hand, the carbon/TiC composite shows a broad reflection from the (002) plane of T-carbon, which indicates that titanium does not catalyze the carbonization process from amorphous carbon to ordered carbon. The decrease of crystallinity for T-carbon is considered to be because of the reduction of the regularity of the PI backbone in PI/TiO_2 composite before heat treatment.

From the XRD profiles of carbon/TiC composites in Fig. 5, together with the WAXD profile of TC-10w prepared by heat treatment for 1 h (Fig. 2), the broad peak with maximum at about 42° can be considered as having two components, one from the (200) plane of TiC and the other corresponding to the overlapping diffraction from the (100) and (101) planes of T-carbon, which is often called the (10) peak [25]. With increase of TiC content the (10) diffraction peak of carbon becomes broader and the intensity decreases, which suggests a decrease in the grain size of carbon with increasing TiC content. Thus, TiO_2 has no catalytic effect on the graphitization process.

The *d*-spacings for TiC (111) (d_{111}) and TiC (200) (d_{200}) for carbon/TiC composite obtained by heat treatment at 1,600 °C were calculated using Bragg's equation. The calculated values, shown in Table 1, for d_{111} and d_{200} are slightly smaller than the standard values for TiC crystallites (0.2499 and 0.2163 nm, respectively). The crystallite size along the (111) and (200) crystallographic

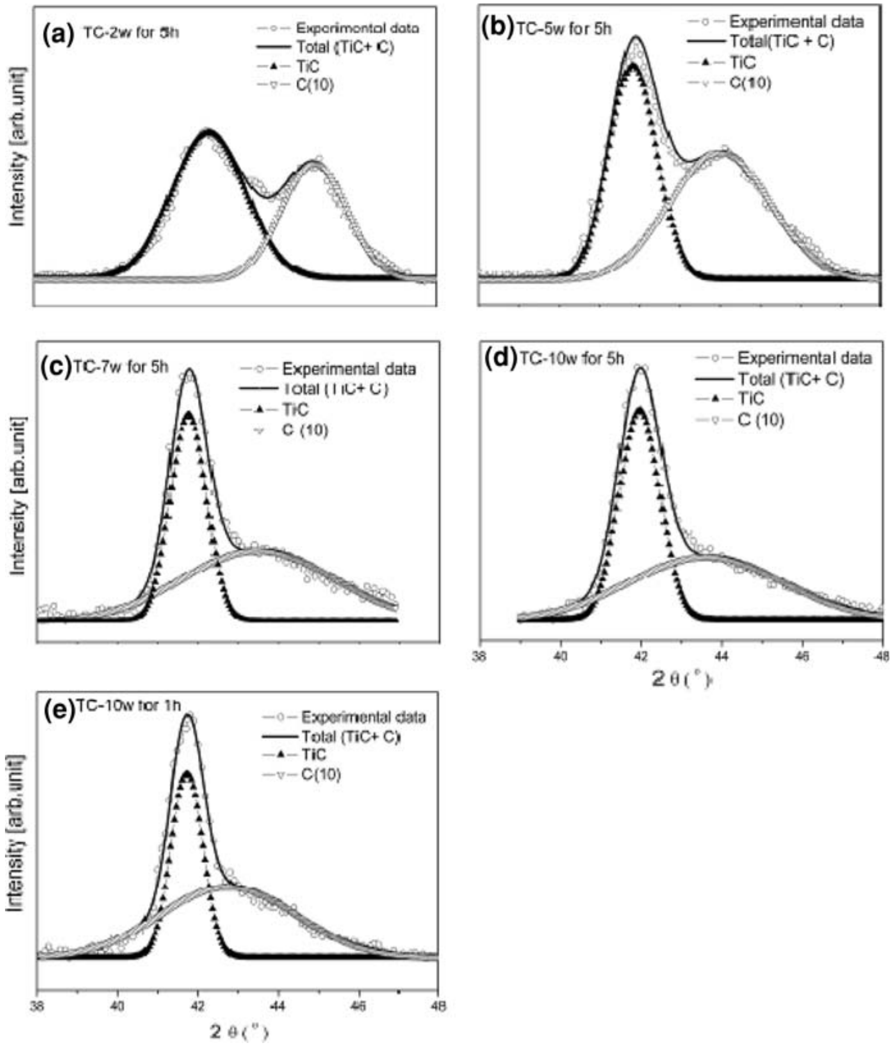


Fig. 5 WAXD profiles for carbon/TiC composite films

directions of TC-10w obtained by heat treatment at 1,600 °C for 1 h was calculated from the Scherrer equation and was shown in Table 1. It should be noted here that the fitted profile of the (200) peak was used to calculate *d*-spacing and crystallite size.

TiC has a cubic close packed structure (fcc, NaCl type) [26]. The lattice parameter (a_0) values, calculated from the Debye–Scherrer equation from the XRD results shown in Figs. 2 and 4, are shown in Table 1. According to the Joint Committee of Powder Diffraction Standard (JCPDS) card, the TiC lattice parameter is 0.4328 nm (JCPDS 32-1383), which is for a unit cell with the stoichiometric composition. Thus, the calculated lattice parameter is slightly smaller than the standard value. It was

Table 1 Spacing distance, crystallite size, and lattice parameter (a_0) of TiC in carbon/TiC composites with varying TiC content

TiC sample	(hkl)	$d_{(hkl)}$ (nm)	Crystallite size (nm)	a_0 (nm)
TC-2w for 5 h	(111)	0.249	12.4	0.428
	(200)	0.213	8.9	
TC-5w for 5 h	(111)	0.249	13.3	0.431
	(200)	0.216	12.6	
TC-7w for 5 h	(111)	0.249	16.5	0.432
	(200)	0.216	16.8	
TC-10w for 5 h	(111)	0.249	19.5	0.432
	(200)	0.216	19.5	
TC-10w for 1 h	(111)	0.249	13.8	0.430
	(200)	0.215	14.0	

reported by Pearson [27] that TiC has a very wide homogeneous region ranging from 28 at% C ($a = 0.4269$ nm) to 50 at% C ($a = 0.4327$ nm); consequently the carbon content of the present TiC crystallites should be smaller than for the ideal stoichiometry. It can be concluded from the measured X-ray diffraction patterns that the TiC phase in carbon/TiC composite films changes from amorphous to cubic NaCl type with increasing heat treatment temperature.

Figure 6a shows an SEM image of the cross section of carbon/TiC composite film; the framed part of the image is enlarged in Fig. 6b. Some bright areas with length ca. 100 nm are visible in Fig. 6b. EDS was performed to identify the component elements in the bright areas, with the results shown in Fig. 6c. The spectrum shows peaks from elemental carbon and titanium but not oxygen in the bright areas of the cross section image. Thus, after carbonization titanium was converted without oxidation to TiC particles in the amorphous carbon matrix, in accordance with the FTIR and WAXD data in Figs. 3, 4, respectively. As discussed above, the WAXD intensity distribution curves revealed crystallization of TiC particles and a matrix of amorphous carbon.

The thermal stability of composite films heat treated at 1,600 °C for 5 h was determined in air and nitrogen atmospheres by TGA at heating rate 10 °C min^{-1} from room temperature to 1,000 °C. Figure 7a shows the weight loss curves obtained under nitrogen. The weight loss of carbonized film prepared from pure PI was almost zero, indicating that the carbonized film was stable in nitrogen. The carbon/TiC composite films showed weight loss at temperatures lower than 200 °C, but at higher temperatures the weight loss recovered gradually up to ca. 100% with increasing temperature. This behavior is attributable to release of adsorbed gas at low temperatures and re-adsorption of nitrogen by the carbon/TiC composite films at higher temperature. The percentage weight loss at temperatures below ca. 200 °C reflects the adsorptivity of the carbon/TiC composite films. With increase in TiC content, the adsorptivity of the carbon film is enhanced, which indicates that the carbon structure becomes less compact in the carbon/TiC composite.

The TGA curves determined in air (Fig. 7b) show that drastic weight loss occurred in air at ca. 600 °C for the carbon/TiC composite films, indicating that

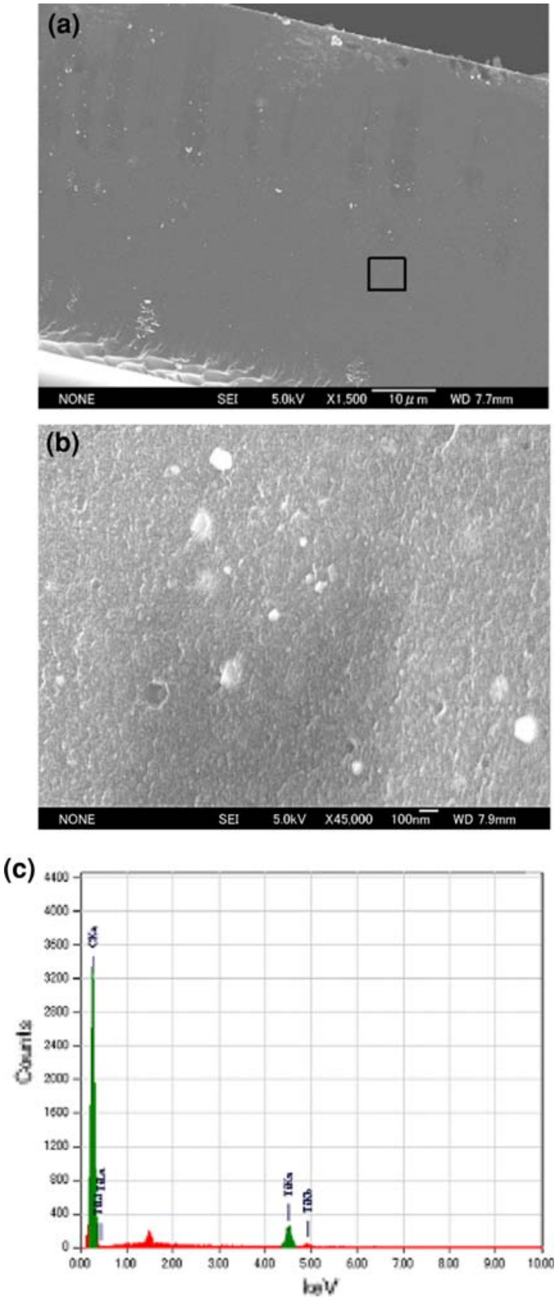


Fig. 6 **a** SEM photos of the cross section for carbon/TiC film (TC-5w) obtained by heat treatment of PI composite with 5% titania at 1,600 °C for 5 h. **b** Enlargement of a typical area in cross section of the carbon/TiC composite film. **c** EDS spectrum of the above specimen

oxygen caused oxidative decomposition. The residue at ca. 900 °C is because of formation of titanium oxide. The decomposition temperature decreased slightly with increase in TiC content, probably because of formation of TiC decreasing the

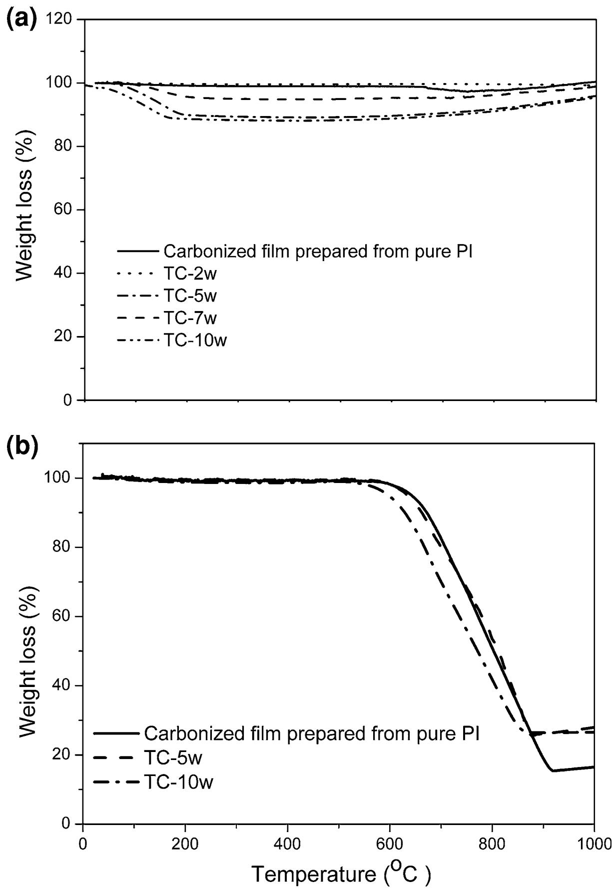


Fig. 7 Thermogravimetric study for carbonized films obtained from PI and PI/titania composites **a** in nitrogen atmosphere **b** in air atmosphere

crystallinity of the carbon matrix and thus decreasing the thermal stability of the carbon framework.

Conclusion

PI/TiO_2 composite was prepared by in situ sol–gel polymerization. Titania formed an inorganic network with carbon chains, and played an important role in increasing the rigidity of the film. Carbothermal reduction of the PI/TiO_2 composite at 1,600 °C under argon produced an amorphous carbon matrix with dispersed crystalline TiC particles formed by tightly bonding between carbon and titanium. The crystallinity of T-carbon in the matrix decreased with increasing TiO_2 content in the PI/TiO_2 precursor, and the matrix was composed of amorphous carbon. The carbon/TiC composite films exhibited metallic luster on the surface and relatively compact structure in cross section. A series of results show that carbothermal reduction of PI/TiO_2 composite is an effective method for obtaining carbon/TiC composite films.

References

1. Wolf R (1994) Boronized and siliconized graphites—material processing and effects on properties. J Nucl Mater 212–215:1174–1177
2. Hino T, Yamashina T (1992) Evaluation for boron mixed graphite and high Z metal as plasma facing material. J Nucl Mater 196–198:531–536
3. Roth J, Plank H, Schwörer R (1996) Erosion of Si- and Ti doped graphites because of deuterium irradiation. Phys Scr T 64:67–70. doi:10.1088/0031-8949/1996/T64/010
4. García-Rosales C, Roth J (1992) Chemical sputtering of pyrolytic graphite and boron doped graphite USB15 at energies between 10 and 1000 eV. J Nucl Mater 196–198:573–576
5. Davis JW, Haasz AA (1997) Impurity release from low-Z materials under light particle bombardment. J Nucl Mater 241–243:37–51
6. Franzen P, Vietzke E, Haasz AA, Davis JW, Philipps V (1992) Atomic re-emission of hydrogen from pure and boronized graphites at temperatures above 1000 K. Nucl Mater 196–198:967–971
7. Refke A, Philipps V, Vietzke E (1997) Retention and erosion behavior of oxygen implanted in different Si/C-materials. J Nucl Mater 241–243:1103–1109
8. Vietzke E, Haasz AA (1996) Chemical erosion. In: Hofer WO, Roth J (eds) Physical processes of the interaction of fusion plasmas with solids, 4th edn. Academic Press, New York
9. Hwu HH, Chen JGG (2005) Surface chemistry of transition metal carbides. Chem Rev 105:185–212
10. Li DL, Zhou HS, Honma I (2004) Design and synthesis of self-ordered mesoporous nanocomposite through controlled in situ crystallization. Nat Mater 3:65–72
11. Chang YH, Chiu CW, Chen YC, Wu CC, Tsai CP, Wang JL, Chiu HT (2002) Syntheses of nano-sized cubic phase early transition metal carbides from metal chlorides and n-butyllithium. J Mater Chem 12:2189–2191
12. Jiang Z, Rhine WE (1991) Preparation of titanium nitride (TiN) and titanium carbide (TiC) from a polymeric precursor. Chem Mater 3:1132–1137
13. Nandi M, Conklin JA, Salvati L, Sen A (1990) Molecular level ceramic/polymer composites. 1. Synthesis of polymer-trapped oxide nanoclusters of chromium and iron. Chem Mater 2:772–776
14. Wozniak ME, Sen A, Rheingold AL (1992) Molecular level ceramic/polymer composites. 3. Synthesis of polymer-trapped cadmium and copper sulfides starting from the elements and the structure of the intermediate, soluble, cadmium sulfide precursor. Chem Mater 4:753–755
15. Tsai MH, Liu SJ, Chiang PC (2006) Synthesis and characteristics of polyimide/titania nano hybrid films. Thin Solid Films 515:1126–1131
16. Tsai MH, Whang WT (2001) Dynamic mechanical properties of polyimide/poly(silsesquioxane) -like hybrid films. J Appl Polym Sci 81:2500–2516
17. Thompson DS, Thompson DW, Southward RE (2002) Oxo-metal-polyimide nanocomposites. 2. Enhancement of thermal, mechanical, and chemical properties in soluble hexafluoroisopropylidene-based polyimides through the in situ formation of oxo-Lanthanide(III)-polyimide nanocomposites. Chem Mater 14:30–37
18. Tsai MH, Whang WT (2001) Low dielectric polyimide/poly(silsesquioxane)-like nanocomposite material. Polymer 42:4197–4207
19. Bin Y, Oishi K, Koganemaru A, Zhu D, Matsuo M (2005) Catalytic effect of nickel under carbonization of polyimide films. Carbon 43:1617–1627
20. Shen DHWZH, Guo MM, Cheng SZD, Harris FW (2001) Synthesis and properties of polyimides containing multiple alkyl side chains. Macromolecules 40:889–900
21. Han MG, Im SS (2001) Morphological study of conductive polyaniline/polyimide blends. I. Determination of compatibility by small-angle X-ray scattering method. Polymer 42:7449–7454
22. Woo YC, Kang HJ, Kim DJ (2007) Formation of TiC particle during carbothermal reduction of TiO_2. J Eur Ceram Soc 27:719–722

23. Jha A, Yoon SJ (1999) Formation of titanium carbonitride phase through the reduction of TiO_2 with carbon in the presence of nitrogen. J Mater Sci 34:307–322
24. Oya A, Mochizuki M, Otani S, Tomizuka I (1979) Electron-microscopic study on the turbostratic carbon formed in phenolic resin carbon by catalytic action of finely dispersed nickel. Carbon 17(1):71–76
25. Biennier L, Georges R, Chandrasekaran V, Rowe B, Bataille T, Jayaram V, Reddy KPJ, Arunan E (2009) Characterization of circumstellar carbonaceous dust analogues produced by pyrolysis of acetylene in a porous graphite reactor. Carbon 47:3295–3305
26. Hugh OP (1996) Handbook of refractory carbides and nitride. Noyes, New Jersey
27. Pearson WB (1958) A handbook of lattice spacings and structure of metals and alloys. Pergamon Press, New York