Journal of Ceramic Processing Research. Vol. 17, No. 6, pp. 581~585 (2016)

J O U R N A L O F
Ceramic Processing Research

Preparation and characterization of oxidation resistive multilayer coating films with yttrium oxide protective layer for ultrahigh temperature applications

Changhun Hwang[a] and Jondo Yun[a,b,*]
[a]*Department of Advanced Engineering, Graduate School, Kyungnam University, 449, Woryeong-dong, Masanhappo-gu, Changwon-si 631-701, Korea*
[b]*Department of Nano Materials Engineering, Kyungnam University, 449, Woryeong-dong, Masanhappo-gu, Changwon-si 631-701, Korea*

Carbon fiber reinforced carbon matrix composites have excellent thermo-mechanical properties, but they are degraded rapidly by oxidation at high temperatures in air. Silicon carbide is the best candidate for the oxidation resistive coating for the carbon composites at high temperature. Multilayer oxidation resistive coating film consisting of three or four layers including silicon carbide has been prepared by chemical vapor deposition method and polymer precurser method. Microstructure and chemical composition of coating films were examined by electron microscopy techniques. It was found that carbon composites with multilayer coating films were stable at high temperature with a weight loss under 1% at 1700 and 1900 °C in high and low oxygen partial pressure environment.

Key words: Sillicon carbide, Carbon composite, Yttria, Multilayer coating, Weight loss.

Introduction

Carbon fiber-reinforced carbon matrix composites (hereafter carbon composites) have light weight, high heat resistance, high elastic modulus, high thermal conductivity, low thermal expansion coefficient, and high fracture toughness. They are used for components and materials for the aerospace vehicles requiring ultrahigh temperature properties or semiconductor processing equipments requiring high purity and high temperature properties [1-2]. However, the carbon composites are oxidized and degraded rapidly just above 400 °C in air and thus need oxidation resistive coating films [2-3]. Silicon carbide material is one of the best candidates due to its excellent high temperature properties gained by forming silicon oxide film on the surface by limited surface oxidation at high temperatures. Since carbon composites are used at high temperatures of 1500 ~ 2000 °C, their oxidation resistive coating films must have excellent high temperature mechanical properties, low oxygen/carbon permeability, high adhesion and compatibility to their substrates. Required properties are so versatile, and not satisfied with a single layer coating film but with multilayer coating films.

Studies of oxidation resistive multilayer coating films of various materials and structures were reported. Based on silicon carbide materials, $MoSi_2$ [4], $MoSi_2$-SiC [5-6], $MoSi_2$-$CrSi_2$-SiC [7], $MoSi_2$-ZrB_2 [8], yttrium silicate [9-14], silicon oxycarbide [15-16], mullite [17], cordierite-mullite [18], mullite-alumina [19], zirconium silicate [20] were used for the multilayers. Also glass films of borosilicate glass, or glass ceramics [21-23] were coated on the above mentioned multilayer coating films. All the reported multilayer coating films were designed and used at relatively low temperature applications at 1500~1600 °C. But ultrahigh temperature oxidation resistive multilayer films for aerospace application like re-entry vehicle requiring ultrahigh temperatures property above 1700 °C were barely reported.

In this study, multilayer coating films were prepared to protect carbon composite at temperatures of 1700 °C or above having oxidation resistive property. The coating must have excellent thermal and mechanical properties at room temperature. Three layer coating films were prepared with silicon carbide and silicon oxycarbide layers having self-healing capabilities. Oxidation tests were conducted in low or high oxygen partial pressure environment at 1700 °C. Also additional yttria protective film was deposited in order to protect the silicon carbide film. Oxidation tests were performed with the low or high oxygen partial pressure enviromnent at 1900 °C.

Experimental Procedures

Multilayer coating films consisting of silicon carbide, silicon oxycarbide, and silicon carbide layers were prepared on a carbon-carbon composite specimen of a size of $20 \times 20 \times 2\ mm^3$. Silicon carbide film was prepared by chemical vapor deposition (CVD) process using a source gas of methyltrichlorosilane (MTS) at 1150 °C. Silicon oxycarbide film was prepared by a dip

*Corresponding author:
Tel : +82-10-4595-3593
Fax: +82-55-248-5033
E-mail: jdyun@kyungnam.ac.kr

coating and heat treatment of polymer film at 1150 °C in argon. Yttrium oxide protective layer was prepared by electron beam evaporation method. Yttrium oxide granules of 2-5 mm diameter was irradiated and heated by electron beam up to thousand degrees. Yttrrium oxide was evaporated and deposited at a rate of two nm/sec on a substrate maintained at 200 °C. Detailed condition is in elsewhere [15-16].

The 1700 °C oxidation test under a low oxygen partial pressure (13Pa) was performed at a heating rate of 20 °C/min in a vacuum furnace (ThermVac Co., Korea). The 1700 °C oxidation test under a high oxygen partial pressure (2×10^4 Pa) was performed in a box furnace (ThermVac Co., Korea). The 1900 °C oxidation test under a low oxygen partial pressure was performed in the same way as 1700 °C in a vacuum furnace. The 1900 °C oxidation test under a high oxygen partial pressure was performed in a laser beam furnace. The sample was heated by intermittent irradiation of laser beam for 30-240 seconds each time, totaling 1,230 seconds. Heating rate was tremendously fast as 20,000 °C/min and thus high thermal shock was applied to the specimen. The reference sample of sintered silicon carbide (MacTech Co., Korea) with a purity of 99% and density of 99% was used for a comparison. Microstructure and chemical composition change were examined for the samples before and after the oxidation test using scanning electron microscopy (SEM) and an electron probe microanalysis (EPMA).

Results and Discussion

Preparation and characterization of the multilayer coating film

Prepared multilayer coating was found to have, as shown in Fig. 1, silicon carbide layer of 50 μm on top of the carbon-carbon composite substrate, silicon oxycarbide layer of 2-3 μm, and silicon carbide film of 20 μm thickness. Oxidation test for carbon-carbon composites with the multilayer coating films at 1700 showed that weight loss (Fig. 2) was as low as 0.04% after 120 minutes exposure to the low oxygen partial pressure atmosphere, while silicon carbide reference sample lost 0.03% of its weight. Carbon-carbon composite with multilayer coating films showed a weight loss of 0.11% after 120 minutes of exposure to the high oxygen partial pressure (air) atmosphere, which was better result compared to that of reference sample with a weight loss of 0.28%.

Surface of the sample before the test was rough having faceted grains (Fig. 3) but changed to a flat one after the oxidation test at 1700 °C in air. This is because amorphous silica glass was formed on the surface due to oxidation of silicon carbide. Silicon carbide reference samples (Fig. 4) showed also glassy surface but with many crater-like dimples, implying that multilayer film coated samples have better high temperature stability.

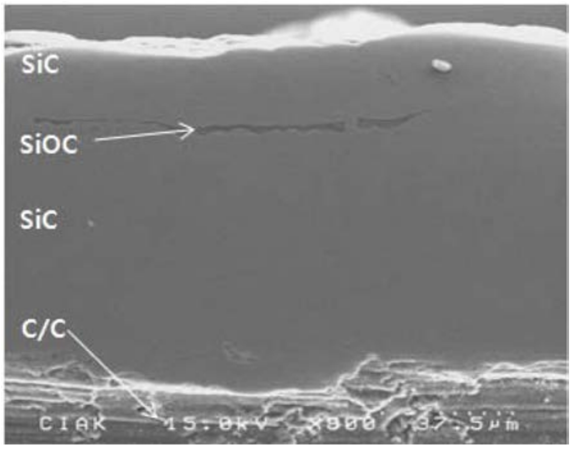


Fig. 1. Cross sectional microstructure of carbon-carbon composite with multilayer coating.

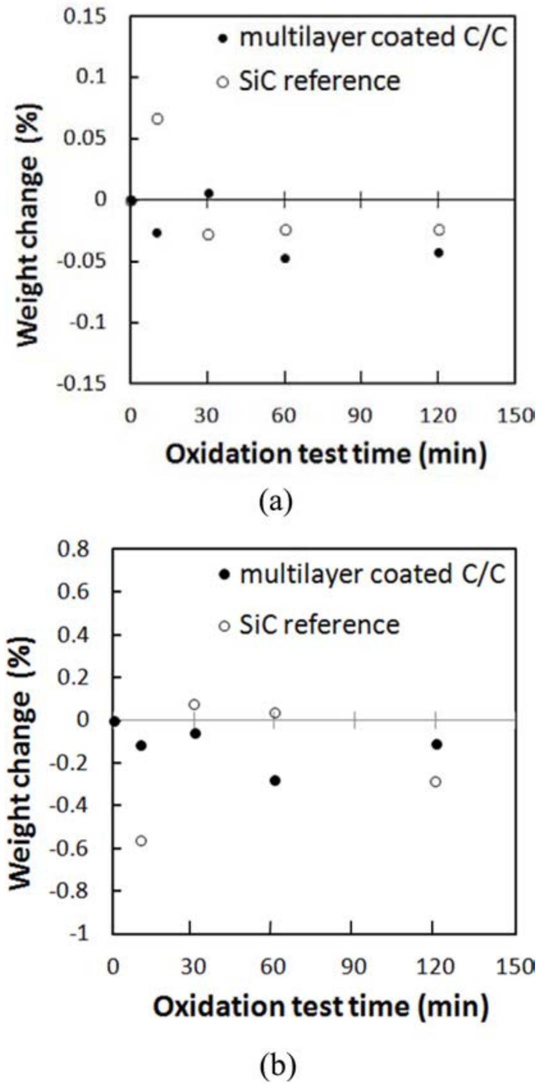
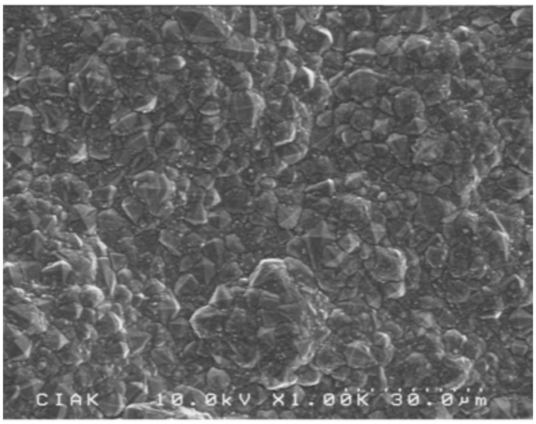
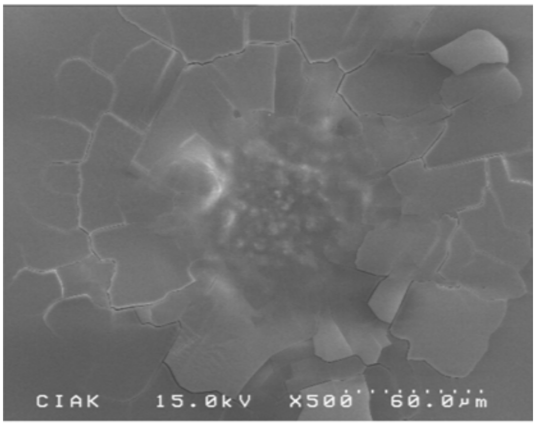


Fig. 2. Results of 1700 °C oxidation test under (a) low and (b) high oxygen partial pressure atmosphere for the multilayer coated carbon-carbon(C/C) composites and silicon carbide reference sample.

After the oxidation test in a low oxygen partial pressure atmosphere at 1700 °C, the sample with



(a)



(b)

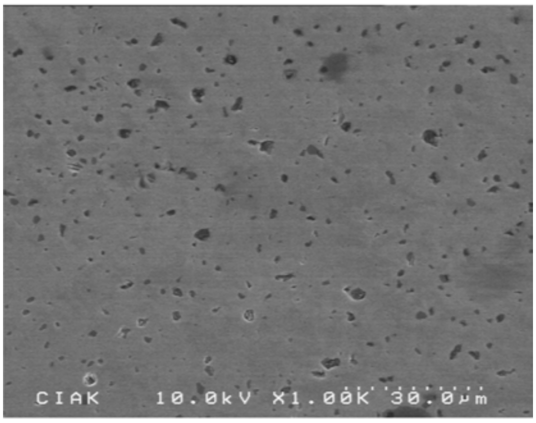
Fig. 3. Surface microstructures of carbon-carbon composites with multilayer coating (a) before and (b) after oxidation test at 1700 °C for 120 minutes in air.

multilayer coating showed bare change (Fig. 5), but silicon carbide reference sample showed considerable amount of erosion (Fig. 6) on the surface.

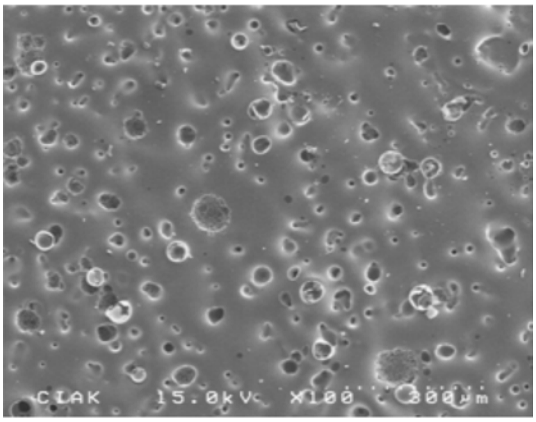
After the oxidation test at 1700 °C in a high oxygen partial pressure atmosphere, a layer with a few micrometer thickness was formed on the surface of multilayer coating film and also on the silicon carbide reference sample, while in a low oxygen partial pressure atmosphere surface oxide film was not formed. The EDS analysis showed that silicon and oxygen was detected from the surface layer formed.

Preparation and characterization of multilayer coating film with a protective coating

Sekigawa et. al. [27] reported that oxidation behavior of the silicon carbide changes from a passive to an active one when oxygen partial pressure is low and temperature is high. When the temperature is high above 1700 °C and oxygen partial pressure is low, the silicon carbide is eroded because of active oxidation. Thus additional layer of yttrium oxide was designed and prepared by electron beam evaporation to protect



(a)



(b)

Fig. 4. Surface microstructures of silicon carbide reference sample (a) before and (b) after oxidation test at 1700 °C for 120 minutes in air.

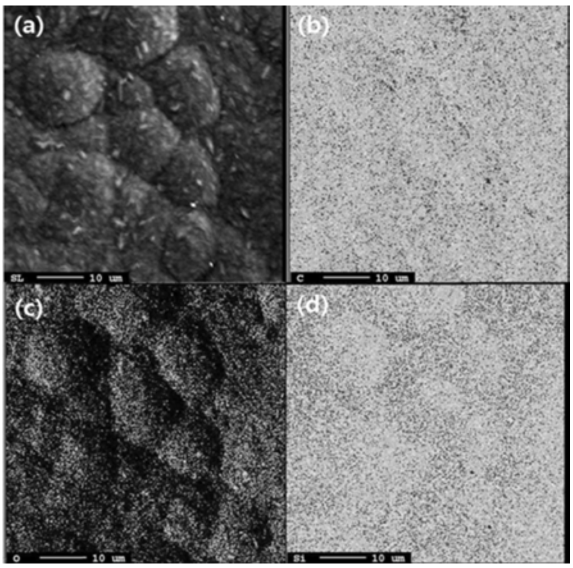


Fig. 5. (a) secondary electron image and X-ray maps of (b) carbon, (c) oxygen, and (d) silicon obtained from EPMA for the multilayer coated sample after the oxidation test at 1700 °C for 120 minutes in a low oxygen partial pressure atmosphere.

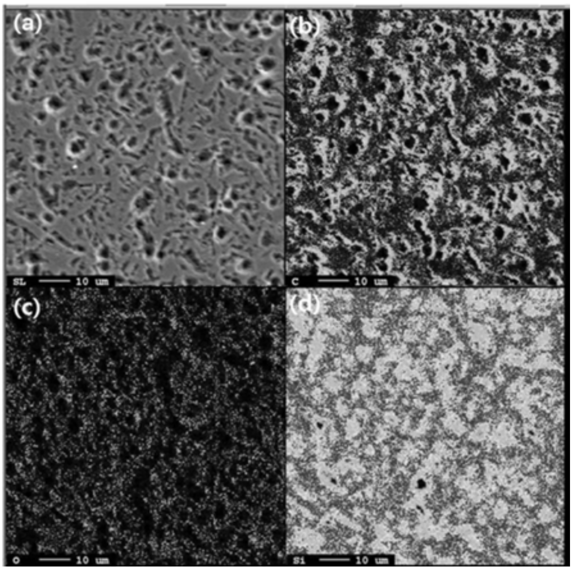


Fig. 6. (a) secondary electron image and x-ray maps of (b) carbon, (c) oxygen, and (d) silicon obtained from EPMA for the silicon carbide reference sample after the oxidation test at 1700 °C for 120 minutes in a high oxygen partial pressure atmosphere.

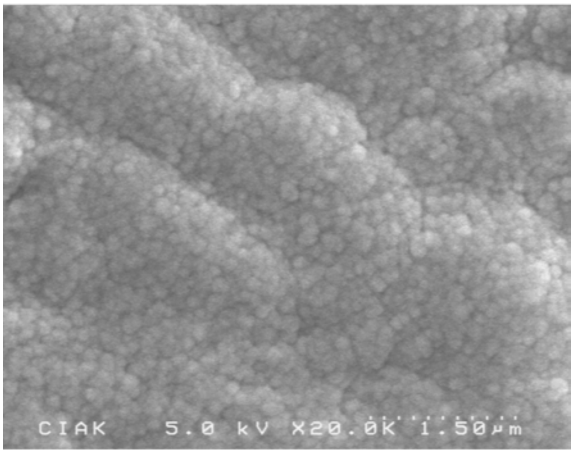


Fig. 7. Surface of yttrium oxide protective layer prepared by electron beam evaporation.

silicon carbide film. Oxidation test was performed with the protective film under low or high oxygen partial pressure. Yttria protective layer of 3 μm thickness was found very dense and uniform made of nanoparticles of 100 ~ 200 nm (Fig. 7)

Multilayer coating films with additional yttria layer after oxidation tests at 1900 °C in a low oxygen partial pressure of 13Pa showed weight loss after 600 seconds of 0.1% compared with 0.3% of silicon carbide reference sample (Fig. 8). With additional yttrium oxide protective layer the weight loss was reduced by about 1/3. It was found that loss rate was 0.5 g/m^2 per minute considering surface area. It corresponds to the rate of removal of 0.1 micron thickness for every minute. The rate may not be so fast given that the condition is very severe.

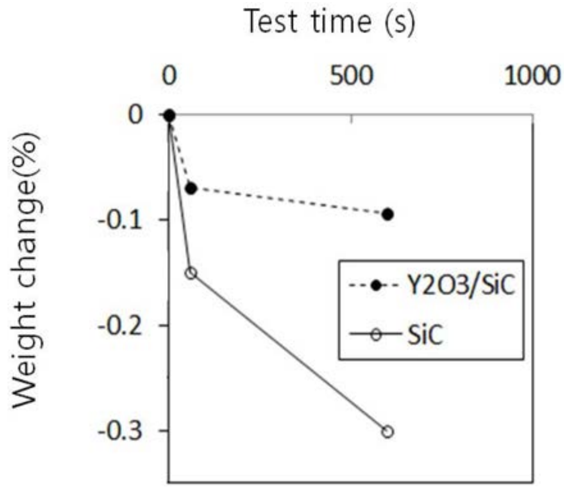


Fig. 8. Weight change of multilayer sample with yttria coating and reference sample after a oxidation test at 1900 °C in a low oxygen partial pressure of 13 Pa.

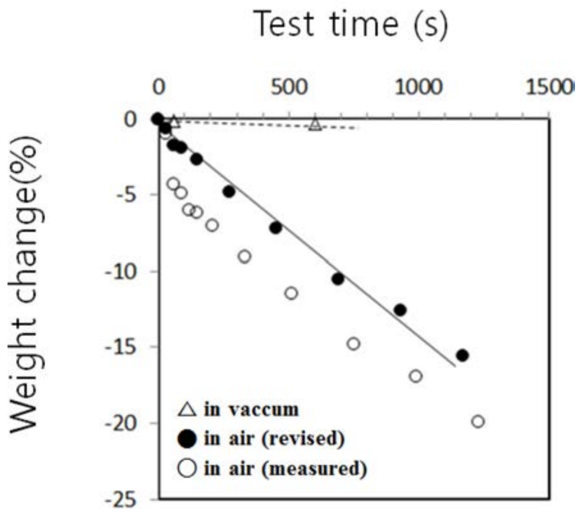


Fig. 9. Weight change of carbon-carbon composites with multilayer coatings after a test at 1900 °C in air or vacuum.

Oxidation test by laser beam irradiation at 1900 °C in air showed that there was 4% loss of weight during the initial period of 60 seconds (Fig. 9). It would be the surface layer preferentially evaporated. Once oxidation was stabilized and the rate was reduced to 0.9% for every minute. Weight loss was less than 5% for the five minutes. The coating film may be used for an applications requiring short term stability in highly severe conditions, such as surface tiles of reentry vehicle.

Conclusions

A multilayer coating films consisting of three layers were prepared. In order to protect the silicon carbide coating film an additional yttria coating was applied. After the oxidation test for 120 minutes at 1700 in air, weight loss was 0.11% for the multilayer coating and

0.28% for the silicon carbide reference sample. It is then 0.04% for the multilayer coating, and 0.03% for the reference sample under low oxygen partial pressure atmosphere. Surface of multilayer coating film was almost unchanged after oxidation test. It appeared to be stable compared to the reference sample where the surface erosion was progressed.

With an additional yttria protective film of 3 μm thickness, weight loss was 0.1% at 1900 °C under a low oxygen partial pressure after 10 minutes. This corresponds to an erosion rate of 0.1 μm/min. Yttria protective layer was shown to inhibit the oxidation of silicon carbide at high temperature. It showed a weight loss of 5% or less at 1900 °C under high oxygen partial pressure for 5 minutes. It can be used for the application requiring stability for a short period of time under severe condition.

Acknowledgments

This work was supported by Kyungnam University Foundation Grant, 2009. Authors are grateful to Dr. Guhyeon Yi (KIMS), Dr. Wontae Bae (Gyeongsang University), Mr. Jongseong Yun (TCK) and Dr. Yoonsuk Oh (KICET) for their technical assistances.

References

1. Y.A. Kim, Physics & high technology 12[3] (2003) 31-35.
2. I.S. Han, S.Y. Kim, S.G. Woo, J.I. Kim and Y.H. Jeong, J. Kor. Ceram. Soc. 13[6] (2010) 54-63.
3. C.G. Choi, W.J. Lee and C.O. Park, J. Kor. Ceram. Soc. 28[6] (1991) 478-482.
4. J.F. Huang, B. Wang, H.J. Li, M. Liu, L.Y. Cao and C.Y. Yao, Corrosion Sci. 53[2] (2011) 834-839.
5. Q.G. Fu, X. Zou, Y.H. Chu, H.J. Li, J.Z. Zou and C.G. Gu, Vacuum 86[12] (2012) 1960-1963.
6. F.Q. Gang, H.J. Li, Y.J. Wang, K.Z. Li and T. Jun, Surf. Coatings Technol. 204[11] (2010) 1831-1835.
7. Y.J. Chu , Q.G. Fu, C.W. Cao, H.J. Li, K.Z. Li and L. Qin, Surface & Coatings Technology 205[2] (2010) 413-418.
8. W.Z. Zhang, Y. Zeng, L. Gbologah, X. Xiong and B.Y. Huang, Trans. Nonferrous Met. Soc. China. 21[7] (2011) 1538-1544.
9. J.F. Huang, H.J. Li, X.R. Zeng, K.Z. Li, X.B. Xiong, M. Huang, X.L. Zhang and Y.L. Liu, Carbon 42[11] (2008) 2356-2359.
10. J.F. Huang, H.J. Li, X.R. Zeng and K.Z. Li, Surf. Coatings Technol. 200[18-19] (2006) 5379-5385.
11. J.F. Huang, H.J. Li, X.R. Zeng and K.Z. Li, Ceram. Int. 32[4] (2006) 417-421.
12. J.F. Huang, H.J. Li, X.R. Zeng, F. Deng, X.B. Xiong and K.Z. Li, Ceram. Int. 33[5] (2007) 887-890.
13. M. Aparicio and A. Duran, J. Am. Ceram. Soc. 83[6] (2000) 1351-1355.
14. M. Liu, J.F. Huang, Y.T. Zhang, F. Deng, L.Y. Cao and J.P. Wu, J. Coat. Technol. Res. 6[4] (2009) 531-535
15. Y. Choi, H. Lee and J. Yun, J. Ceram. Proc. Res. 10[3] (2009) 340-343.
16. J. Kim, C. Hwang, A. Jeong, H. Lee and J. Yun, J. Adv. Mater. 24 (2012) 41-46.
17. J. Huang and Q. Zhang, J. Surf. Coat. Technol. 205[21] (2011) 5077-5082.
18. F. Lan and Q. Fu, Carbon 45[13] (2007) 2708-2710.
19. J. Huang and K. Li, Appl. Surf. Sci. 252[12] (2006) 4244-4249.
20. J.L. Cao, J. Huang, Y. Xin, W. Yang, J. Fei and C. Yao, Surf. Coat. Tech. 206 (2012) 3270-3274.
21. Q.G. Fu, H.J. Li, X. H. Shi, K.Z. Li, J. Wei and M. Huang, Mater. Lett. 60[3] (2006) 431-434.
22. C. Isola, P. Appendino, F. Bosco, M. Ferraris and M. Salvo, Carbon 36[7-8] (1998) 1213-1218.
23. K.Z. Li, F.T. Lan, H.J. Li, X.T. Shen and Y.G. He, J. Eur. Ceram. Soc. 29[9] (2009) 1803-1807.
24. E. Jeon, H. Kim and J. Yun, J. Ceram. Proc. Res. 13[3] (2012) 239-242.
25. K. Kang and J. Yun, J. Ceram. Proc. Res. 12[5] (2011) 583-587.
26. H. Kim, J. Kim, H. Lee, Y. Ahn and J. Yun, J. Kor. Ceram. Soc. 49[1] (2012) 95-99.
27. T. Sekigawa, K. Oguri, J. Kochiyma and K. Miho, Mater. Trans. 42[5] (2000) 825-828.