Journal of the European Ceramic Society 9(1992) 351–356

Sol–Gel Silica in the Healing of Microcracks in SiC-coated Carbon/Carbon Composites

Tsung-Ming Wu, Wen-Cheng Wei & Shu-En Hsu

Institute of Materials Science and Engineering, National Taiwan University,
Taipei, Taiwan, Republic of China

(Received 24 April 1991; revised version received 20 September 1991; accepted 25 September 1991)

Abstract

A sol–gel silica derived from TEOS is used to heal microcracks in a SiC film, where the film is used as a shielding for the oxidation resistance of C/C. The effect of the sol–gel healing is positive in elevating the oxidation resistance of C/C. The oxidation rate of the impregnated sample is influenced by the time of gelation before the sol–gel is applied to the SiC film. An analysis of the activation energy for oxidation revealed the mechanism of the healing, and a variation of the size of microcrack is found. A model is developed to describe the oxidation of the sol–gel-impregnated SiC-coated C/C.

Aus TEOS und mittels Sol–Gel-Verfahren hergestelltes Siliziumdioxid wurde verwendet, um Mikrorisse in einem Schutzfilm gegen Oxidation aus SiC auf C/C auszuheilen. Das Sol–Gel-Ausheilen wirkt sich positiv auf die Oxidationsbeständigkeit von C/C aus. Die Oxidationsgeschwindigkeit einer imprägnierten Probe hängt von der Gelierzeit vor dem Auftragen des Sol–Gels auf den Film ab. Die Analyse der Aktivierungsenergie der Oxidation gibt Aufschluß über den Mechanismus des Ausheilprozesses. Es wurde eine Veränderung der Mikrorißgröße festgestellt. Zur Beschreibung der Oxidation des mit Sol–Gel-imprägnierten SiC-beschichteten C/C wurde ein Modell entwickelt.

On a utilisé de la silice sol–gel issue du TEOS dans le but de remédier à la microfissuration d'une couche mince de SiC, utilisée comme protection contre l'oxydation de C/C. L'effet du traitement sol–gel permet d'augmenter la résistance à l'oxydation de C/C. La vitesse d'oxydation de l'échantillon imprégné est dépendante du temps de gélation antérieur à l'application du sol–gel sur le SiC. Une analyse de l'énergie d'activation de la réaction d'oxydation permet de mettre en évidence le mécanisme de traitement des microfissures et une variation de la taille des microfissures est trouvée. On a développé un modèle décrivant l'oxydation du C/C recouvert de SiC et imprégné de sol–gel.

1 Introduction

The sol–gel process is attractive because of the excellent homogeneity of the products and the lower processing temperature required. Although the gels crack easily during drying, careful control of the solution content and the drying atmosphere is successful in producing a crack-free monolithic body.[1,2] The sol–gel silica is well studied in its processing characteristics[3–6] and applications,[7] and multicomponent materials have also been developed recently.[8,9] Fabes & Uhlmann[10] report an effective elevation in the strength of the silica bulk by crack healing. The oxidation resistance of SiC-coated carbon/carbon composites (C/C) suffer from microcracking of the SiC film when the coated sample is cooled down from the processing temperature (1600°C). The present study uses the sol–gel silica derived from tetraethylorthosilicate (TEOS) as a microcrack sealant in the SiC film, which in turn acts as an anti-oxidation coating for carbon/carbon composites. The use of sol–gel-derived silica as a sealing material for SiC coating is based on its thermal stability, to as high as 1500°C,[11] and better comparison of its mechanical properties with those of SiC.[12,13] The sol–gel silica impregnation in the SiC film is appropriate in sealing a microcrack at room temperature when the microcrack is open.

Journal of the European Ceramic Society 0955-2219/92/$5.00

2 Experimental Procedure

The matrix C/C is manufactured by the Chung-Sun Institute of Science and Technology (CSIST, Taiwan, People's Republic of China) with a density of 1·85 g/cm^3. The SiC coating was made by reaction sintering of silicon powder with a minor amount of boron added as sintering aid, as previously reported.[14]

The sol–gel solution was prepared by partially hydrolyzing TEOS to derive silica after polymerization. TEOS is mixed with ethanol and water in a volume ratio of 5:3:2, where the water is pre-titrated to a pH value of 1·3 by adding 0·5 N HCl. As the water and ethanol are added to the TEOS the solution separates into two layers, due to the limited solubility of TEOS in water. However, it develops homogeneous transparency after 0·5–1·0 h holding, depending on the temperature of the water bath. The acidic solution forms linear polymeric-type oligomers.[10,15]

In order to obtain a coatable solution to heal the microcrack of the SiC film, the solution is held in an isothermal water bath not exceeding 75°C, in order for it to have a suitable degree of polymerization before application to the samples.[5] The SiC-coated C/C sample is immersed into the solution for 3 min, while the solution wetted the microcrack and provided a healing effect to eliminate the exposed surface of the C/C matrix. Different gelation times of the solution are employed to examine the effect of gelation in healing the microcrack of SiC film.

After impregnation in the sol–gel solution, the sample is placed in a tube furnace to be dried at 200°C for 2 h and then sintered at 1000°C for another 2 h in Ar atmosphere. Thermal gravimetric analysis (TGA) is used to evaluate the effect of the sol–gel healing in elevating the oxidation resistance of SiC-coated C/C. The oxidation rate of the treated sample is measured in a fixed air flow rate, 8 cm/min in linear velocity. The data of weight loss from the TGA recorder are then converted to oxidation rate data in dimensions of mg/h/cm^2. An Arrhenius plot of the oxidation rate is used to find the activation energy for oxidation, and to derive the mechanism of sol–gel healing in elevating the oxidation resistance of SiC-coated C/C.

BET with a special sample holder, a cell 2 cm in diameter and 3 cm in height, was used to measure the surface area of the dried gel. A Philips 515 SEM operating at 25 kV was used for morphological observation on the coated sample. The microhardness of the gel after drying was detected using an Akashi hardness tester with a loading of 200 gf, and is expressed in units of HV, which are equivalent to kg force per square millimeter.

3 Results and Discussion

3.1 Characteristics of the sol–gel

The gelation behavior of the solution is characterized by measuring its time-to-gel, at which time the viscosity of the solution increases rapidly until it becomes rigid. The solution is kept in an isothermal water bath and monitored every 15 min. The time-to-gel is greatly dependent on the temperature provided. A higher temperature results in a faster rate of gelation. An Arrhenius plot of the time-to-gel is shown in Fig. 1. All of the data lie in a straight line and correspond to an activation energy of −13·2 kcal/mol. It means that the gelation of TEOS between 30 and 75°C in this study has the same mechanism. The selection of an optimum processing temperature is then determined mainly by the ease of processing sample coating. Low gelation temperature will delay gelation for as long as six days, and a high processing temperature will cause the coating operation to become messy. A processing temperature of 65°C is selected, corresponding to a time-to-gel of 18 h, which is suitable for studying the relationship between the gelation and the effect in healing the microcrack of SiC film.

The drying of the gel bulk is also monitored by a TGA in a controlled atmosphere, with a fixed flow rate of 100 cm^3/min compressed air. The drying rate with respect to time is well fitted to the parabolic law, as shown in Fig. 2. The evaporation rate of the unreacted solvent in the gel is inversely proportional to time squared. It is due to the increase in diffusion

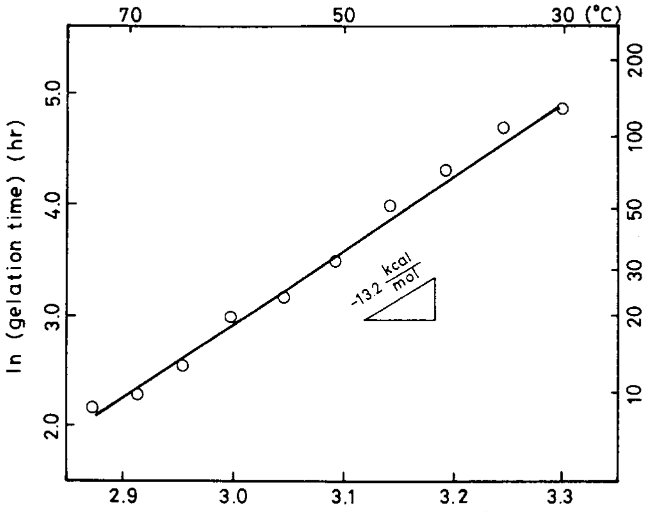

Fig. 1. The Arrhenius plot of the time-to-gel of acidic silica solution.

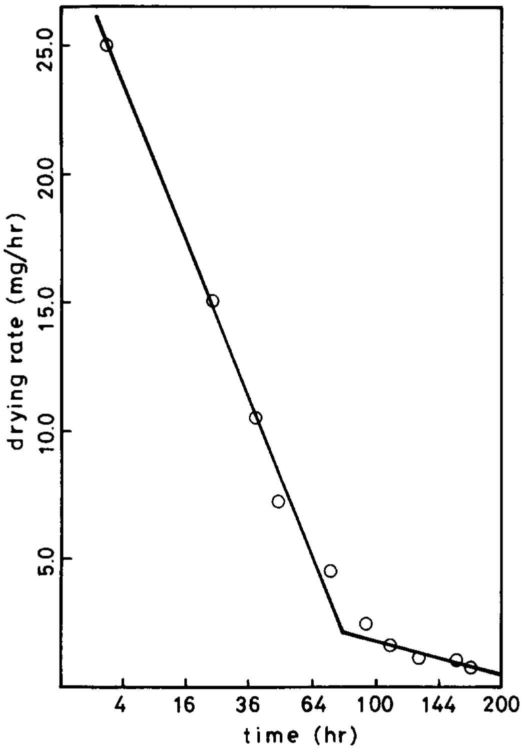

Fig. 2. The drying rate of the 65°C aging gel.

distance in the gel body.[1] The drying rate can be divided into two segments, implying that the evaporation mechanism of solvent from the gel is not a unique process. It is explained by the fact that the different mechanism is due to the higher vapor pressure of ethanol than that of the water. In the beginning of evaporation the ethanol evaporates faster than the water does. But the evaporation rate is slowed down when the ethanol in the gel is in equilibrium with water at the azeotropic point, where the composition of solvent has no difference between the liquid phase inside the gel body and the evaporated vapor phase.

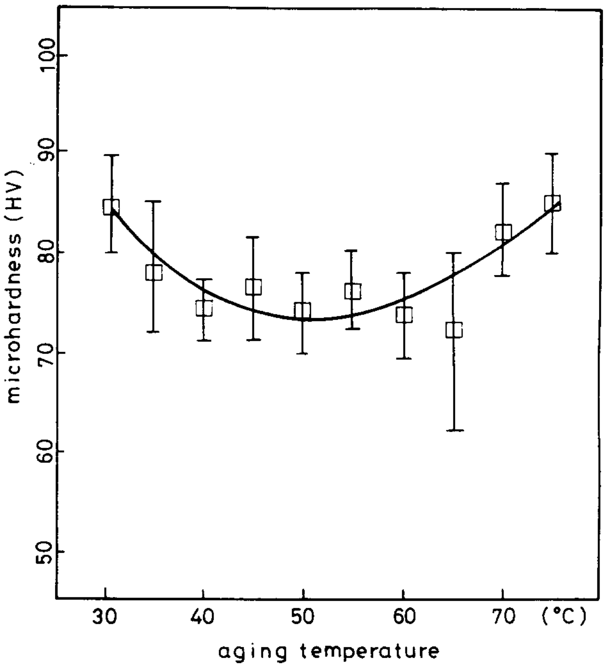

Fig. 3. The microhardness of the gels at various aging temperatures.

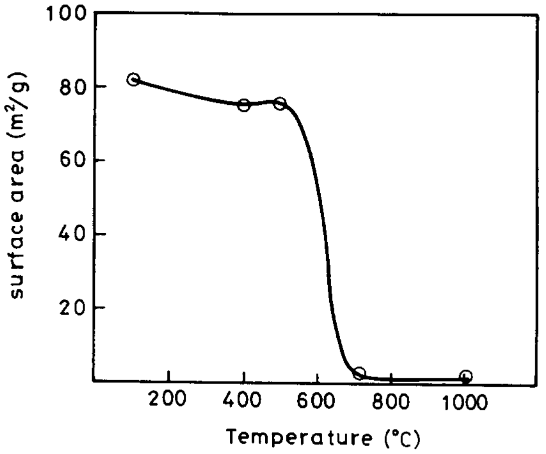

Fig. 4. Surface area of 65°C aging silica gel after heat treatment for 2 h at various temperature.

For quantitative comparison of the gel strength the dried gel is measured by Vickers indentation. At least 10 samples are indented for each processing temperature. It shows that the strength of the gel is not heavily influenced by the processing temperature, with maximum deviation less than 20%, as shown in Fig. 3.

The gel is then sintered at various temperatures in Ar atmosphere and the surface area is measured by BET. A maximum sintering temperature of 1050°C is used in this study, as referred to by Scherer.[1] The variation of specific surface area with respect to the sintering temperature is illustrated in Fig. 4. A small surface area is desired in order to prohibit the penetration of air/oxygen when applied to heal the microcrack of SiC film.

3.2 Oxidation resistance

The SiC coating on the surface of C/C shields almost all of the C/C surface, but it leaves the microcrack as a diffusion path for air/oxygen. If the sol–gel impregnation is suitable for sealing the microcrack of the SiC film, the oxidation resistance will be elevated. The cross-section of SiC-coated C/C is shown in Fig. 5. The coating layer is identified by XRD as a composite of β-phase SiC and unreacted residual Si. Leaving some residual Si in the coating layer is useful in sealing the microcrack after the temperature exceeds the melting point. The measurement of oxidation rate is made in order to explore the effectiveness of the sol–gel in healing the microcrack of SiC film. Figure 6 shows the elevation of oxidation resistance by sol–gel impregnation. The

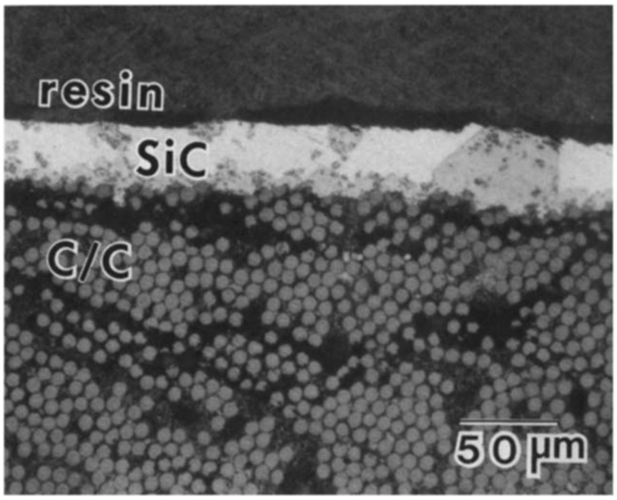

Fig. 5. Micrograph of the cross-section of SiC-coated C/C.

figure indicates two points: firstly, the usefulness of the sol–gel in the enhancing of oxidation resistance is confirmed; secondly, the influence of gelation time in elevating the oxidation resistance is apparent. This is stated in the Fabes' model about the strengthening of monolithic silica rods by microcrack healing. The oligomer size of the sol–gel is increased in the polymerization, and the optimum size of the oligomer in healing the microcrack has the same order of width as the microcrack. The sol–gel is used to heal the microcrack of SiC coating in the present study, and it is reasonable to suggest that the size of the oligomer influences the effectiveness of SiC coating in healing the microcrack. The measurement on the oxidation resistance in Fig. 6 reveals that a longer gelation results in a weaker effect in elevating the oxidation resistance of C/C. It also reveals an unusual variation in the oxidation rate around the range of 750 to 1050°C. The oxidation rate of uncoated C/C matrix is monotonically increased as the temperature is elevated in spite of the fact that the oxidation mechanism has been shifted from reaction control to oxygen diffusion control as temperature is raised.[16,17] The abnormal decreasing of the oxidation rate around 750 to 1050°C will be discussed further.

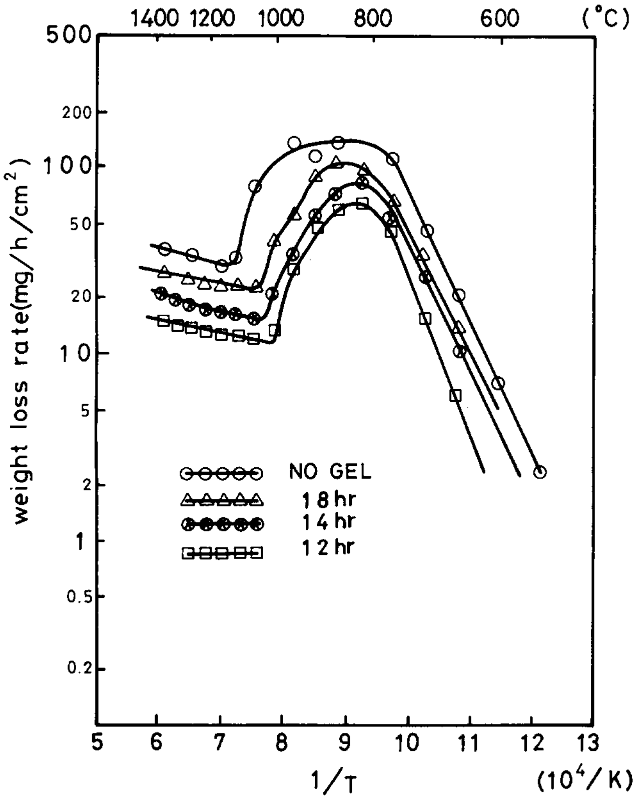

Fig. 6. The oxidation rate of SiC-coated C/C after impregnation with silica sol.

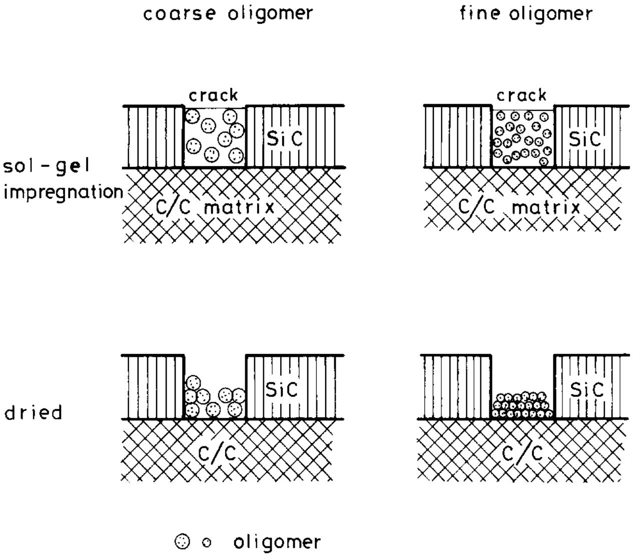

Fig. 7. Scheme of the effect of aging in healing the microcrack of SiC film.

The longer gelation of the solution does not help in improving the oxidation resistance of SiC-coated C/C. It is a result showing the difficulty of a larger oligomer in penetrating the microcracks of SiC film, and the coarse size of oligomer also results in a loose packing after the solvent has evaporated,[18] as described in Fig. 7.

3.3 Activation energy analysis

The oxidation rate below 750°C shows a straight line in the Arrhenius plot and corresponds to an activation energy for oxidation of about 14 kcal/mol, for both samples with or without sol–gel impregnation, whereas an activation energy of about 1·3 kcal/mol is found for those above 1050°C, as shown in Table 1 and Fig. 6. That the discrepancy of oxidation rate decreases around 750 to 1050°C is believed to be the result of microcrack closing due to the different coefficient of thermal expansion between C/C and SiC film. In examining the oxidation activation energy the authors find the

Table 1. Activation energy for the oxidation of SiC-coated carbon/carbon composites after silica sol–gel impregnation

Sample	*Gelation time (h)*	*Activation energy (kcal/mol)*	
		<750°C	*>1050°C*
1	No impregnation	14·3	1·38
2	12	15·0	1·33
3	14	14·6	1·35
4	18	14·0	1·31

value does not correspond to that of the oxidation of carbon as reported by McKee,[17] with values of 42, 20·8 and 5 kcal/mol, corresponding to an oxidation controlling regime of chemical reaction, matrix diffusion and boundary layer diffusion, respectively. The lowering of the oxidation rate in a coated sample is a result of the reduction in the surface area for oxidation, in which the surface of C/C is covered by SiC coating except at the site of microcrack. Whenever the oxidation happens in the C/C matrix the activation energy for oxidation should be similar to that of the reported data. In addition, the value of the activation energy in the present case does not correspond to that of the oxygen diffusion through the silica, which has an activation energy of 28·0 kcal/mol as reported by Costello & Tressler.[19] The oxidation behavior in the present experiments corresponds to neither the case of carbon oxidation in an uncoated surface (the site of microcrack) nor an oxygen diffusion through silica (microcracks healed by sol–gel). The oxidation should be a combined process, different from the simple controlling mechanism of oxygen diffusion through microcracks or SiC coating.

The existence of microcracks in the SiC coating can also be deduced from the fact that the sol–gel is effective in decreasing the oxidation rate. The occurrence of microcracks is due to the thermal mismatch between the SiC and the C/C matrix when it cools down from the 1600°C sintering temperature. Theoretically, the microcrack should be re-healed when the sample is heated to the sintering temperature. The fact that oxidation above 1050°C shows an activation energy of about 1·3 kcal/mol can also be explained as a combined effect of oxygen boundary diffusion, with an activation energy of 5 kcal/mol,[17] and the reduction of the size of microcrack from thermal expansion.

The oxidation rate at 750–1050°C is suggested to be a result of microcrack closing as temperature is elevated. The overall oxidation rate is determined by two factors: firstly, the microcrack closing decreases the flux of oxygen diffusion to the surface of C/C as temperature rises; secondly, the diffusion rate of oxygen in the matrix is increased as temperature is elevated. The dominant step will determine whether the oxidation rate is elevated or lowered when the temperature rises. The reduction of the oxidation rate in the range 750–1050 with respect to temperature is a result of microcrack closing, whereas the activation energy is positive in the other two regions (<750 and >1050°C), which is believed to be the result of the dominance of the oxidation controlling mechanism.

3.4 Modeling

The variation of the oxidation rate is explained as a combined process of the sol–gel sealing and the microcrack closing due to thermal expansion. From the kinetics point of view, the factors which influence the oxidation resistance can be taken as elements of 'resistor'. The higher the resistance of the elements, the lower the overall oxidation rate. The present case is described in Fig. 8. The overall oxidation resistance R(overall) is expressed in eqn (1):

$$R(\text{overall}) = R1 + 1/((1/R2) + (R3)) + R4 + R5 \quad (1)$$

The overall resistance of the whole combination is determined by the largest step, by taking $R2$ and $R3$ as a block. At the lower temperature the chemical reaction is the slowest step, with a largest resistance for oxidation, and the overall oxidation rate in this region is determined by $R5$. In contrast, the boundary layer diffusion controls the overall process in the elevated temperature region, resulting in a maximum $R1$. In the medium temperature region the overall oxidation resistance is controlled by the diffusion of oxygen through the matrix, an $R3$ maximum. But the aforementioned criteria are affected by the closing to the microcrack in the present case, represented by a variation of $R4$. As $R4$ is a weak function with respect to R(overall), the controlling mechanism of oxidation is easily identified by inspecting the activation energy in each temperature interval. In other words, a dominant $R4$, greatly dependent on the working temperature, will influence the R(overall) and the resulting controlling mechanism does not correspond to a single step. The SiC-coated sample without sol–gel

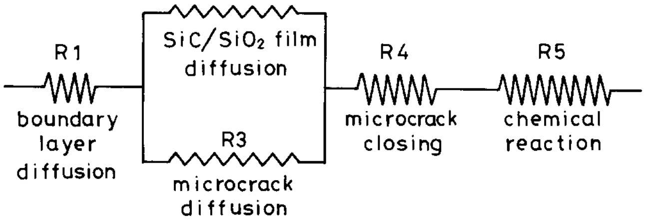

Fig. 8. Modeling of the oxidation resistance of SiC/silica-protected C/C.

impregnation exhibits oxidation resistance to some extent. It is consistent with the fact that *R*4 is a strong function in the present study, and so greatly alters the behavior of the oxidation resistance of C/C.

4 Conclusion

The effectiveness of sol–gel impregnation in elevating the oxidation resistance of SiC-coated C/C is confirmed in this study. The enhancement of the oxidation resistance is explained as the result of crack healing by silica gel, resulting in the reduction of the exposed surface of the C/C matrix. The degree of gelation also influences the effect of shielding on the microcrack. The analysis of the activation energy for oxidation reveals that the size of the microcrack on SiC film is changed as temperature rises. A model is established to identify the dominant controlling mechanism in the overall oxidation process.

Acknowledgements

The authors express their great appreciation to the CSIST for their assistance in the preparation of samples and their kind permission to use their research facilities. The financial support from the National Science Council is also acknowledged for the contract No. NSC79-0210-D006-06.

References

1. Scherer, G. W., Drying gel. *J. Non-Cryst. Solids*, **87** (1986) 199–225.
2. Simpkins, P. G., Johnson, Jr D. W. & Fleming, D. A., Drying behavior of colloidal silica gels. *J. Am. Ceram. Soc.*, **72**(10) (1989) 1816–21.
3. Muktherjee, S. P., Cordars, J. F. & Debsikdar, J. C., Pore structures and microstructures of silica gel monoliths at different stages of sintering. *Adv. Ceram. Mat.*, **3**(5) (1988) 463–74.
4. Scherer, G. W., Sintering of low-density glasses. *J. Am. Ceram. Soc.*, **60**(5) (1977) 236–46.
5. Rabinovich, E. M., Johnson, Jr D. W., MacChesney, J. B. & Vogel, E. M., Preparation of transparent high-silica glass articles from colloidal gels. *J. Non-Cryst. Solids*, **47** (1982) 435–9.
6. Yamane, M. & Sakaino, T., Preparation of a gel from metal alkoxide and its properties. *J. Mat. Sci.*, **13** (1978) 865–70.
7. Chu, P. Y. & Clark, D. L., Coating porous substrates by the sol–gel method. *Adv. Ceram. Mat.*, **3**(8) (1988) 249–53.
8. Villegas, M. A. & Navarro, J. M., Characterization of boron oxide–silica glasses prepared via sol–gel. *J. Mat. Sci.*, **23** (1988) 2464–78.
9. Low, M. & McPherson, R., Crystallization of gels in the silica–alumina–zirconia system. *J. Mat. Sci.*, **24** (1989) 1648–52.
10. Fabes, B. D. & Uhlmann, D. R., Strengthening of glass by sol–gel coatings. *J. Am. Ceram. Soc.*, **73**(4) (1990) 978–88.
11. Strife, J. R. & Sheehan, J. S., Ceramic coatings for carbon/carbon composites. *Ceram. Bull.*, **67**(2) (1988) 369–74.
12. Crane, R. L., Non-destructive evaluation method for coated carbon/carbon composites. US Patent 4 661 369, 28 April 1987.
13. Gray, P. E., Oxidation resistance of refractory coated carbon/carbon composites. US Patent 4 894 286, 16 January 1990.
14. Wu, T. M., Wei, W. C. & Hsu, S. E., A study on the oxidation resistance of coated carbon/carbon composite. *Chinese J. Mat. Sci.*, **22**(2) (1990) 70–8.
15. Sakka, S. & Kamiya, K., The sol–gel transition in hydrolysis of metal alkoxides in relation to formation of glass fiber and films. *J. Non-Cryst. Solids*, **48** (1982) 31–46.
16. Chang, H. W. & Rusnak, R. M., Oxidation behavior for carbon/carbon composites. *Carbon*, **17**(4) (1979) 407–10.
17. McKee, D. W., Boron treatment of carbon fibers and carbon/carbon composites for improved oxidation resistance. *Carbon*, **24**(6) (1986) 737–41.
18. Scherer, G. W., Brinker, C. J., Roth, E. P. & Tallant, D. R., In *Science of Ceramic Chemical Processing*, ed. L. L. Hench & D. R. Ulrich. John Wiley, New York, 1986, pp. 37–51.
19. Costello, J. A. & Tressler, R. E., Oxidation kinetics of silicon carbide crystals and ceramics. *J. Am. Ceram. Soc.*, **69**(9) (1986) 674–81.