

## Development of multielement nanostructured ceramics through solution route

Satish M Manocha

Department of Materials Science, Sardar Patel University,  
Vallabh Vidyanagar-388 120, Gujarat, India

E-mail : sm\_manocha@rediffmail.com

**Abstract** : The silicon and transition metal alkoxides are very important as an area of sol-gel science and technology because of their simple processing and well-known hydrolysis/condensation reactions. Especially methyltriethoxysilane (MTES) is typical precursor. Hybrid gel prepared from silane after heat treatment and pyrolysis leads to Si-C-O nanoceramics hybrid gel. These are expected as good anti oxidation materials. Mixed carbides of Si, Zr and Ta have been developed in our laboratory using sol-gel method. Metalalkoxides of these metals have been cohydrolysed with addition of a carbonaceous source in appropriate ratios. These modified gels have been heated to 1000–1700°C. The transformations taking place during heat treatments have been studied by FTIR, NMR and XRD. These nanostructured ceramics have been characterized for thermal stability in oxygen environment and are found to possess superior oxidation resistant properties.

**Keywords** Sol-gel, intercarbides, heat treatment, silicon oxycarbide, zirconium carbide

**PACS Nos.** 81.20.Fw, 81.07.-1, 33.20.Ea, 81.05.Je

### 1. Introduction

Multielements nanostructured ceramics with improved mechanical and thermal properties themselves as well as in composites form will have potential application as high temperature structural material. Oxide ceramics with carbon atoms incorporated into the network exhibit improved mechanical and thermal properties as compared to parent monoliths or carbon itself. Therefore, over past decade, there has been great interest in developing these ceramics, the so called oxycarbides (1–3). Silicon based oxycarbides are generally prepared from alkyl-substituted silicon alkoxides  $R_nSi(OR^-)_{4-n}$  with an aim to introduce Si-C bonds into siloxane network. Pantano *et al* [4–6] tried to increase the carbon content of Si-O-C ceramics synthesized by sol-gel method with alkyl-substituted silicon alkoxides as precursors and water as hydrolysing agent. However, the carbon content in the final products was found to be much lower than the expected.

Present authors in their earlier work [7,8], developed these materials through sol-gel route and have demonstrated the effectiveness of butanediol (BD) to form Si-C bonding in Si-O-C ceramics at low temperature and lower O/Si ratio. However, Si-C bonding in pyrolyzed products was still low. Further, these materials exhibited glassy structures at low normal heat treatment temperatures. With interest in nanostructured materials, especially in carbon nanofibers and nanotubes, nanostructured

ceramics have also attracted the attention of the Scientists worldwide. More so, since carbon has the drawback of getting oxidized at low temperatures (above 500°C). Though these materials can be synthesized by many conventional routes such as CVD *etc.*, solution route synthesis through organic-inorganic hybrid gel gives the flexibility of introducing more than one elements in the structure. Not only this, the materials with tailored nanocrystalline structures can also be synthesized from trifunctional silane, transition metal alkoxide as well as salts of refractory metals. In this paper we report development of multielement ceramics of carbon, silicon, tantalum, zirconium and oxygen with part nanostructures through hydrolysis and gelation of silanes, tantalum and zirconium salts and pyrolysis of the hydrolyzed gel at temperature 1000–1700°C.

### 2. Experimental

Silicon oxycarbide ceramics were prepared through hydrolysis of methyl triethoxysilane (MTES) with butanediol (BD). MTES and BD were mixed in  $CCl_4$  with a molar ratio of MTES : BD :  $CCl_4$  = 1 : 3 : 2. The mixture was stirred at 40°C until the solution became transparent. Then the sol was gelled at 60°C. The gel was dried at 180°C followed by pyrolysis in the temperature range 1000–1450°C in nitrogen.

TEOS sol was prepared by hydrolysing TEOS with water in presence of ethyl alcohol with HCl as catalyst. Tantalum added

tetraethyl orthosilicate sol was prepared by adding tantalum pentaethoxide directly to the hydrolyzed TEOS sol. Stirring was continued till the viscosity of the sol increased. The percentage of the tantalum pentaethoxide in the TEOS sol was 10%. The sol was gelled at 60°C and further heat treated to temperatures between 1000–1700°C.

A mixed carbide of zirconium and silicon was prepared by first making zircon sol followed by addition of carbon source. Zircon sol was prepared by mixing hydrolyzed tetraethyl orthosilicate and hydrolyzed zirconium nitrate. Once it started gelling, a carbon source in the form of aromatic pitch was added to it and the complete system was heat treated to temperatures from 1000–1700°C in presence of nitrogen.

Fourier transform infrared spectroscopic analysis (FT-IR) was carried out using SHIMADZU FTIR Magic angle spinning nuclear magnetic resonance (MAS NMR). Spectra of  $^{13}\text{C}$  and  $^{29}\text{Si}$  were obtained using JEOL JNM-EXCALIBUR-270. The X-ray diffraction (XRD) analysis was made on powder samples using RIGAKU RINT2000. Thermogravimetric analysis was carried out using Mettler Thermal Analyser TA 400.

### 3. Results and discussion

#### 3.1. Silicon oxycarbides :

##### 3.1.1. Hydrolysis behavior

Figure 1 shows FT-IR spectrum of dry gel. Absence of peaks of ethoxy group bonded to Si atoms suggests complete hydrolysis of ethoxy groups in MTEOS. Presence of peaks at 1120 and 780  $\text{cm}^{-1}$  due to Si-C vibrations indicates that methyl groups connected to Si atom do not get hydrolysed. These observations are further confirmed by NMR spectra of the gels. Figure 2 shows  $^{13}\text{C}$ -NMR spectrum of dry gel. The sharp peak at -3 ppm due to  $\equiv\text{Si-CH}_3$  confirms that hydrolysis of methyl groups do not take place. The other peaks at 30 ppm and 63 ppm are due to  $\alpha$  and  $\beta$  sites  $\equiv\text{Si-O-}\alpha\text{CH}_2\text{-}\beta\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-O-Si}\equiv$ .

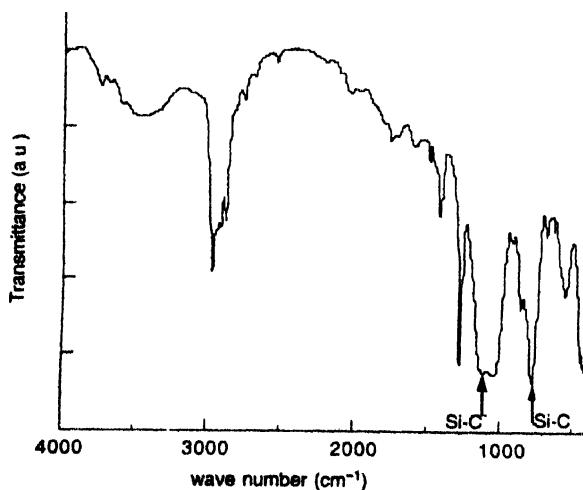


Figure 1. FTIR spectrum of dried gel made from MTEOS and butanediol.

NMR spectrum also suggests almost complete hydrolysis because no peaks due to ethoxy groups of MTEOS are observed.

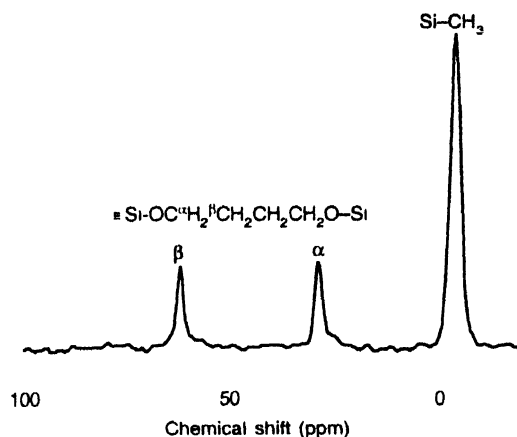


Figure 2.  $^{13}\text{C}$  NMR spectrum of dried gel made from MTEOS and butanediol

##### 3.1.2. Pyrolysis of gels

Figure 3 shows FT-IR spectra of gel pyrolyzed at various temperatures (A : 1000°C B : 1300°C and C : 1500°C). The broad peak around 1000–1200  $\text{cm}^{-1}$  in Figure 3-A consists of two peaks at 1120  $\text{cm}^{-1}$  for Si-C vibration and at 1050  $\text{cm}^{-1}$  for Si-O. The peaks at 1500  $\text{cm}^{-1}$  and 1900  $\text{cm}^{-1}$  assigned to carbonaceous matter indicate the cleavage of hydrocarbon in BD and some methyl groups. The intensity of these peaks is found to decrease with the increased temperature. No peak at 550  $\text{cm}^{-1}$  for siloxane vibration is detected in the heat treated material. It suggests that siloxane is reduced by carbonaceous matter to form SiC tetrahedron.

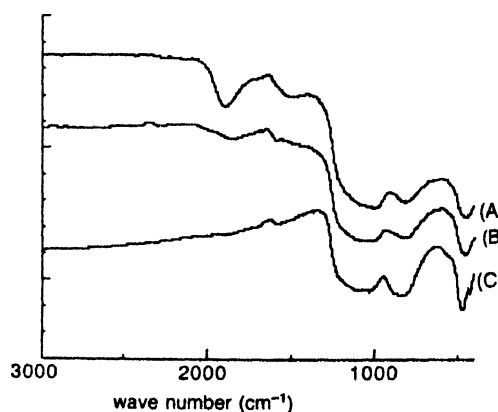


Figure 3. FTIR spectrum of heat treated gel made from MTEOS and butanediol : (A) HTT 1000°C; (B) 1300°C; (C) 1500°C.

The  $^{29}\text{Si}$ -NMR spectra of gel pyrolyzed at various temperatures (A : 1000°C B : 1500°C) are shown in Figure 4. As seen in Figure 4-A, the peak around -21 ppm for  $\text{SiC}_2\text{O}_2$  increases and one around -63 ppm for  $\text{SiCO}_3$  decreases after heat-treatment at 1000°C. In addition, a new peak around -109 ppm for  $\text{SiO}_4$  appears. This indicates that the conversion of  $\text{SiCO}_3$  into  $\text{SiC}_2\text{O}_2$  and  $\text{SiO}_4$  is owing to the exchange rearrangement between carbon and oxygen atoms. The peak around -21 ppm

is doublet; one at  $-21$  ppm for  $\text{SiC}_2\text{O}_2$  and the other at  $-17$  ppm for  $\text{SiC}_4$ . Disappearance of the peak at  $-63$  ppm for  $\text{SiCO}_3$  as shown in Figure 4-B means complete conversion of  $\text{SiCO}_3$  to  $\text{SiC}_4$ ,  $\text{SiC}_2\text{O}_2$  and to  $\text{SiO}_4$ .

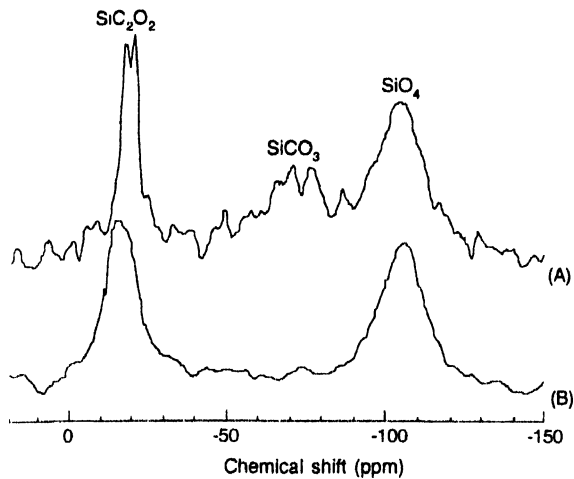


Figure 4.  $^{29}\text{Si}$  NMR spectra of gels heat treated to different temperatures: (A) HTT  $1000^\circ\text{C}$ ; (B) HTT  $1500^\circ\text{C}$

The X-ray diffraction patterns for gel pyrolyzed at various temperatures is shown in Figure 5. In the case of gel pyrolyzed at  $1000^\circ\text{C}$ , only a broad band existed around  $2\theta = 22^\circ$ , which is a characteristic of amorphous silicate and disordered carbon. The peaks assigned to  $\beta$ -SiC appeared after pyrolysis above  $1500^\circ\text{C}$ . On heat treatment to  $1700^\circ\text{C}$ , these peaks became very sharp. On observation under HRSEM, the heat treated material is found to be a nanosize mix of various species, dominantly SiC, C and silica. This was also indicated by EPR spectrum of the material.

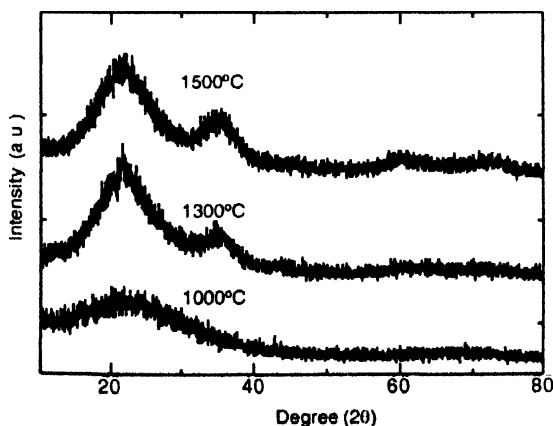


Figure 5. XRD patterns of gels heat treated to different temperatures.

### 3.2. $\text{TaO}_2$ -MTES system :

Figure 6 shows XRD pattern of Ta-MTES gel heated to  $1000$ – $1700^\circ\text{C}$ . XRD pattern of gel heated to  $1000^\circ\text{C}$  shows presence of amorphous constituents, predominately, silica and tantalum oxide. On heat treatment to  $1500^\circ\text{C}$ , presence of crystalline phases are observed. The intensities due to these crystalline phases become

sharp on heat treatment at  $1500^\circ\text{C}$  and above. Under high resolution microscopy, nanocrystallites of carbides and oxides of tantalum and silica embedded in silica were observed.

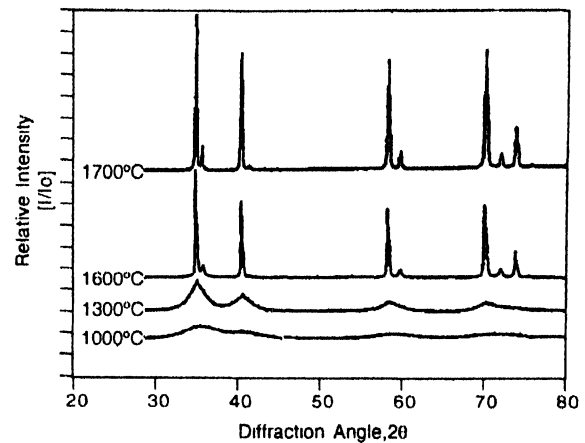


Figure 6. XRD patterns of Ta-MTES gels heat treated to different temperatures

### 3.3. Mixed carbides of zirconium and silicon :

#### 3.3.1. Gel stage

Incorporation of carbon source in the zircon network at gel and heat treated stages was studied by FTIR. Infrared spectra were recorded for the zircon modified pitches heat treated to different temperatures in an inert atmosphere. FTIR spectra of the zircon modified pitch (2 : 3) heated to  $1000^\circ\text{C}$ ,  $1300^\circ\text{C}$  and  $1700^\circ\text{C}$  is shown in Figure 7. FTIR spectra of the sample heated to  $1000^\circ\text{C}$  (Figure 7a) shows the characteristics peaks at  $453.2$ ,  $582.5$ ,  $1062.7$   $\text{cm}^{-1}$  and some other associated peaks. The peak at  $453.2$   $\text{cm}^{-1}$  is assigned to Si-O bond and the peak at  $582.5$   $\text{cm}^{-1}$  is assigned to Zr-O bond. The band at  $1062.7$   $\text{cm}^{-1}$  is assigned to Si-O stretching in Zr-O-Si bond. The FTIR spectrum of the sample heated to  $1300^\circ\text{C}$  (Figure 7b) shows the band at  $459$   $\text{cm}^{-1}$  assigned to Si-O bond. The band at  $669.3$   $\text{cm}^{-1}$  is assigned to Zr-O stretching in Zr-O-Si bond. The band at  $871.8$   $\text{cm}^{-1}$  is assigned to C-Si-C bond. Samples further heat treatment to  $1700^\circ\text{C}$  (Figure 7c),

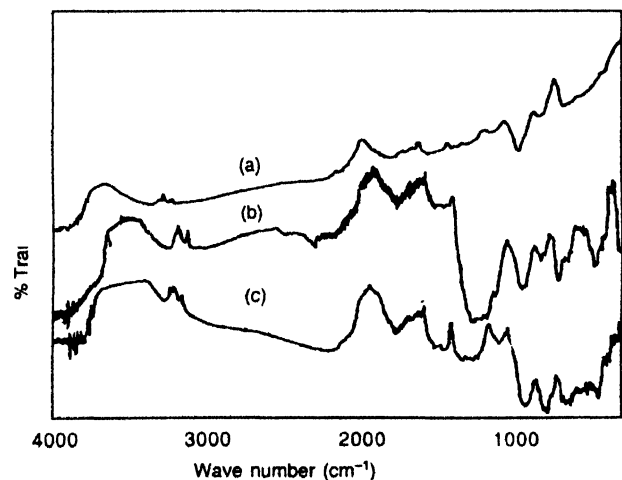


Figure 7. FTIR spectra of heat treated gels made from zircon and pitch : (a)  $100^\circ\text{C}$ , (b)  $130^\circ\text{C}$  and (c)  $1700^\circ\text{C}$ .