

Effect of additives on the thermal nitridation of sol–gel derived silica gel

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Silica gels derived by the sol–gel technique with and without additives such as hexamethylene tetramine, carbon fibre, glucose, etc., were nitrided at different temperatures employing a mixture of nitrogen gas and liquid ammonia. The gels and the nitrided products are characterized by infrared, X-ray diffraction, differential scanning calorimetry, thermogravimetry and surface area studies to investigate the extent of nitrogen incorporation and the effect caused by the nitrogen introduction on the physico-chemical properties of the gel. The gel sintered in air is also investigated for comparison purposes. It is shown that gels synthesized with additives incorporate more nitrogen compared to the gels without additives. It is also shown that nitrided products are thermally stable, tend to have a crystalline structure depending upon the processing conditions, and that the surface area of the gels decreases upon nitridation, the extent of which is influenced by the nitrogen content and nitridation temperature.

1. Introduction

High-temperature oxidation-resistant materials have gained significant importance in recent years as they can be employed as protective coatings on materials such as carbon–carbon composites to inhibit oxidation at elevated temperatures [1]. Constant efforts of the various material scientists have revealed that incorporation of nitrogen or carbon into the silica network leads to the synthesis of a class of compounds called oxycarbide and oxynitride, with excellent mechanical, physical and chemical properties [2–5]. In particular, mention may be made of silicon oxynitride which possesses resistance to thermal shock, corrosion, creep and oxidation and it also has a coefficient of thermal expansion matching that of carbon–carbon composites.

The synthesis of nitrogen-containing glasses is generally accomplished by the melting method in which silica and silicon nitride are melted at high temperatures in a nitrogen atmosphere or by bubbling ammonia through the molten glasses or by chemical vapour deposition. Recently, it has been shown by many authors that nitride glasses can be synthesized by employing the sol–gel technique. It is also learnt from the literature that the various attempts to prepare the nitrided silica by the sol–gel process led to products with varying nitrogen content ranging from 0.1%–5%. This led to the present investigation in which we have tried to incorporate more nitrogen into the silica gel by preparing the gels with compounds containing nitrogen and carbon, and by heating the gels in a mixture of nitrogen gas and ammonia vapours. We have employed liquid ammonia and nitrogen gas mixture instead of dry ammonia gas,

and were able to incorporate nitrogen ranging from 0.18%–1.8% into the silica network by this method.

2. Experimental procedure

2.1. Preparation of gels

All chemicals used were of analytical grade.

2.1.1. Preparation of gel without additives

20 ml tetraethoxy silane (TEOS, Fluka, 98% pure) was mixed with 65 ml distilled water, 20 ml ethanol (99.9% pure), 2.5 ml concentrated nitric acid and 10 ml dimethyl formamide. The mixture was stirred well for 4 h at 40 °C using a magnetic stirrer, cast into a Petri dish and kept in an oven at 60 °C for about 7 days for gelling. The gel obtained was kept in an oven at 60 °C for ageing and drying for about 10 days. The dried gel was labelled P-G.

2.1.2. Preparation of gels with additives

25 ml TEOS, 65 ml distilled water, 20 ml ethanol, 2.5 ml concentrated nitric acid, 10 ml dimethyl formamide were stirred for about 2 h at 60 °C to obtain the sol to which was added 2.5 g of the additive required. The glucose and hexamine were added as such, whereas carbon fibres and pan fibres were chopped well and then added. The mixture was stirred well for 2 h at 60 °C, gelled and dried as described above. The gels obtained were termed P-C (silica gel with carbon fibres), P-P (silica gel with pan fibres), P-GL (silica gel with glucose) and P-H (silica gel with hexamine).

2.2. Nitridation of the gels

The gels were kept in quartz crucibles and heated to 1000 °C in a quartz tube furnace in a mixture of nitrogen gas and ammonia vapours (Fig. 1) according to the schedule given in Fig. 2. The flow rate of nitrogen was kept at 0.5 l min⁻¹ throughout the experiment. A mixture of nitrogen gas and ammonia vapour was also passed through the sample during the cooling cycle. The samples thus obtained were heated to 600 °C to remove all organic residues and labelled P-G nitrided, P-P nitrided, P-C nitrided and P-GL nitrided, depending upon the precursor used for nitridation.

The silica gel without additive was heated in air using the same heating schedule (Fig. 2) to obtain silica which was also characterized for purposes of comparison.

2.3. Characterization

The decomposition behaviour of the gels and of the nitrided samples was investigated using a thermogravimetric analyser (Mettler TA-3000) and a differ-

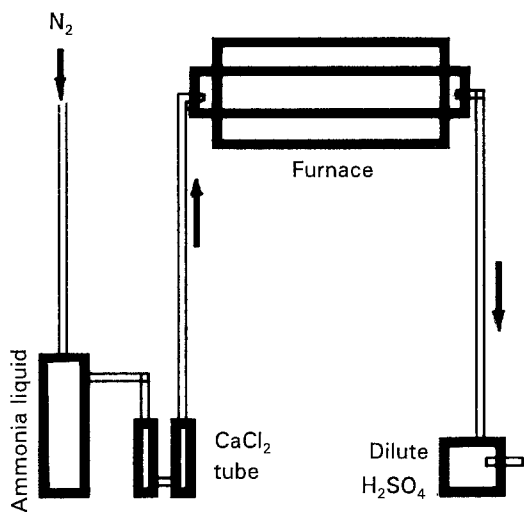


Figure 1 Nitridation of the gel.

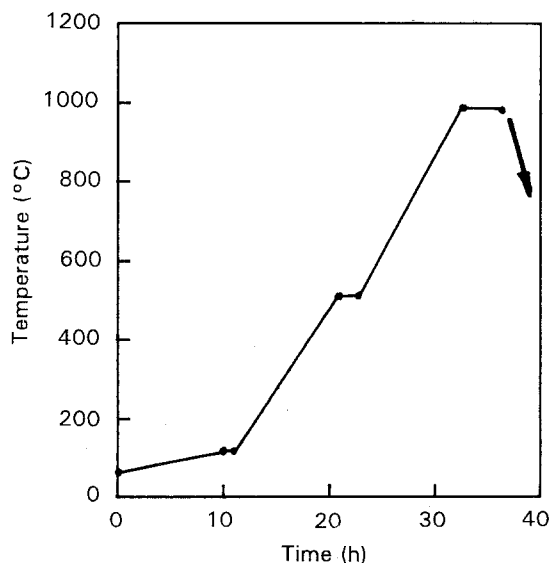


Figure 2 Heating schedule for nitridation.

ential scanning calorimeter (Mettler DSC-20). X-ray diffraction data were recorded using an X-ray diffractometer (Siemens D-500). Infrared spectra were obtained by the KBr method using a Fourier transformed infrared (Nicolet) spectrometer. Surface-area measurements were made by the BET method.

The nitrogen content was determined using Kjeldahl's method: 0.5 g sample was dissolved in a mixture of concentrated sulphuric acid and hydrofluoric acid and later distilled with sodium hydroxide. The ammonia evolved during distillation was absorbed in excess hydrochloric acid and back-titrated with sodium hydroxide.

3. Results and discussion

3.1. Structural characterization

The infrared spectra of the gel sintered in air, in a mixture of nitrogen and ammonia and of the gel nitrided at different temperatures, are given in Figs 3 and 4.

The characteristic band due to Si-O-Si is observed around 1150 cm⁻¹ in the gel and in the gel sintered in air (silica), whereas in the nitrided sample, the band is shifted to a lower wavelength region and is located at 1100 cm⁻¹. The absorption peaks which appear around 1500-1300 cm⁻¹ due to residual ethoxy

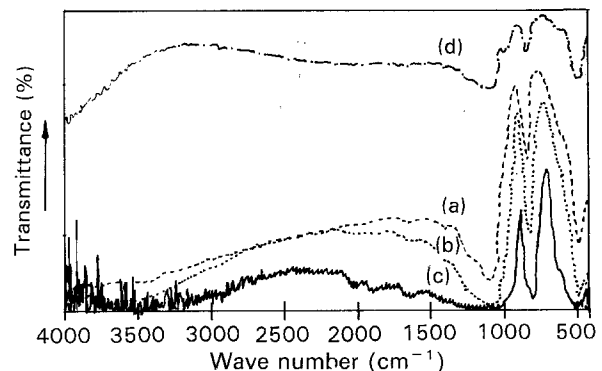


Figure 3 Infrared spectra of silica and nitrided products. (a) P-P nitrided, (b) P-H nitrided, (c) P-C nitrided, (d) P-G sintered in air.

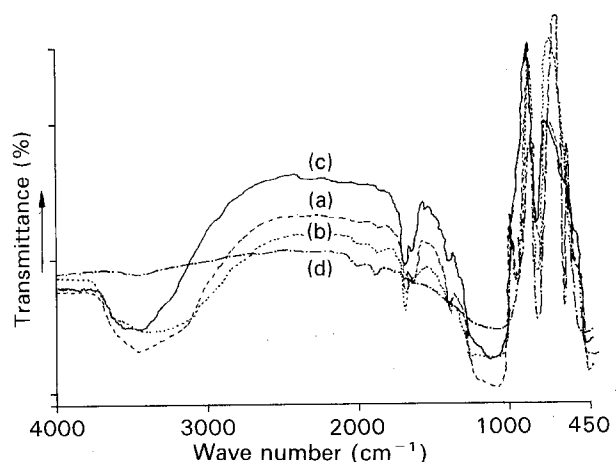


Figure 4 Infrared spectra of gel and nitrided products at different temperatures. (a) P-G, (b) P-G nitrided at 400 °C, (c) P-G nitrided at 600 °C, (d) P-G nitrided at 1000 °C.

groups are absent in the gel samples, indicating complete hydrolysis [6]. This is expected because the TEOS: H₂O ratio employed in the present investigation is greater than 10. The stretching vibration of non-bridging Si-OH is observed at 950 cm⁻¹ and symmetric bending and symmetric stretching vibrations of O-Si-O and Si-O-Si are observed at 450 and 780 cm⁻¹, respectively [6]. The spectrum of the gel also shows characteristic bands of silanol groups and adsorbed water around 1600 and 3400 cm. The gel sintered in air (silica) shows absorptions at 1150, 780 and 450 cm⁻¹ attributable to Si-O-Si and O-Si-O linkages. The gel nitrated at 1000 °C shows broadening of the band around 1000 cm⁻¹, which is due to the incorporation of nitrogen into the gel network. It is generally observed that nitrogen incorporation in the silica gel network shifts the band around 1100 cm⁻¹ to the lower wavelength region [7]. The nitrated products obtained from gel precursors with additives clearly show the broadening of the band around 1000 cm⁻¹ which is due to Si-N in addition to the Si-O bond [8]. The bands due to Si-N are also observed at 800 and 500 cm⁻¹ [4]. The gels nitrated at 400 and 600 °C show bands around the 3400 and 3500 cm⁻¹ region (Fig. 2) which are assigned to Si-NH₂ group [9] and these bands are absent in the gel samples nitrated at 1000 °C and also in silica.

The infrared spectra of samples nitrated at different temperatures indicate that nitrogen incorporation into the gel network proceeds in steps. The absorptions at 3400 and 3500 cm⁻¹, which are due to Si-NH₂, are seen only in samples nitrated at 400 and 600 °C. This is because nitrogen enters the gel structure as Si-NH₂ at 400 °C and remains as Si-NH₂ up to 600 °C. At a temperature as high as 1000 °C, Si-N linkage is established which, in turn, causes the broadening of the band at 1000 cm⁻¹. The idea of nitrogen entering the silica network in steps is supported by the surface-area measurements (Table I). The BET surface area of the samples shows (Table II) that nitrogen

TABLE I Effect of sintering temperature and atmosphere on surface area of the gel

Temperature (°C)	Surface area (m ² g ⁻¹)	
	Sample sintered in air	Sample sintered in nitrogen + ammonia
400	809	800
800	677	585
1000	402	245

TABLE II Effect of nitrogen incorporation on the surface area of the nitrated gel samples

Sample	Surface area (m ² g ⁻¹)	Nitrogen content (wt %)
P-G nitrated	245	0.15
P-C nitrated	240	0.34
P-GL nitrated	189	0.70
P-P nitrated	160	0.98
P-H nitrated	90	1.82

incorporation involving the removal of OH groups in the silica network leads to densification and this causes a decrease in surface area. It is also evident that nitrogen incorporated at 1000 °C reduces the surface area considerably when compared to the nitrogen introduced at 400 and 600 °C, and the decrease in surface area is very much dependent on the nitrogen content (Table II).

3.2. X-ray studies

The X-ray powder patterns of the gel and gel sintered in air are amorphous (Fig. 5) whereas nitrated gels tend to become crystalline, the extent of which depends upon the processing conditions. It is evident from Fig. 5 that nitrogen incorporated at 1000 °C introduces crystallinity into the products. The XRD patterns also support the observation that nitrogen in the silica network takes place in stages. Gels nitrated at 400 and 600 °C reveal very little crystalline structure when compared to those nitrated at 1000 °C. The X-ray studies in conjunction with infrared and BET studies show that nitrogen incorporated in steps into the silica network changes the properties of the gels. It is important to mention here that nitrated products prepared with a gel precursor containing hexamine reveals a highly crystalline structure and needs further investigation.

3.3. Thermal stability

The TGA and DSC curves are presented in Figs 6 and 7. The TGA of gels shows weight loss up to 100 °C due to evaporation of water and alcohol. The weight loss from 150–400 °C is assigned to the evaporation of OH groups, dimethyl formamide and to the decomposition of the additives. It is observed that gel sintered in air shows weight loss attributable to the loss of water which is absorbed by the sample. It is evident from the TGA studies that nitrated silica gels show negligible weight loss, which is dependent on the nitrogen content. The TGA studies of the gels and the nitrated samples show that nitrogen incorporation into the gel network enhances the thermal stability of the gel. The

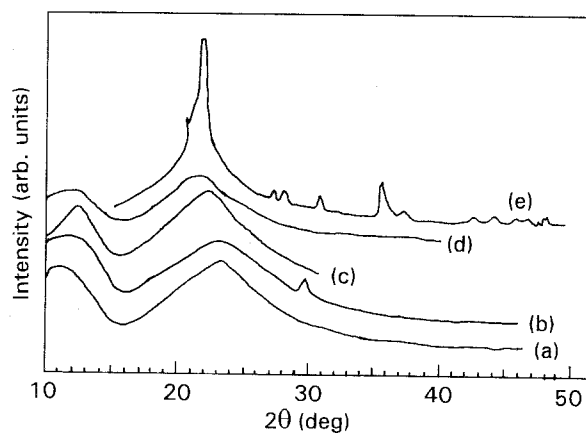


Figure 5 X-ray diffraction patterns. (a) P-G, (b) P-G nitrated at 400 °C, (c) P-G nitrated at 600 °C, (d) P-G sintered in air at 1000 °C, (e) P-G nitrated at 1000 °C.

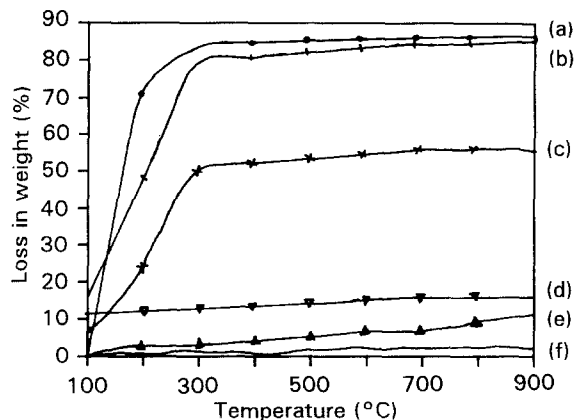


Figure 6 TGA curves of gels, silica and nitrated products. (a) P-H, (b) P-GL, (c) P-G, (d) P-G sintered in air, (e) P-G nitrated, (f) P-P nitrated.

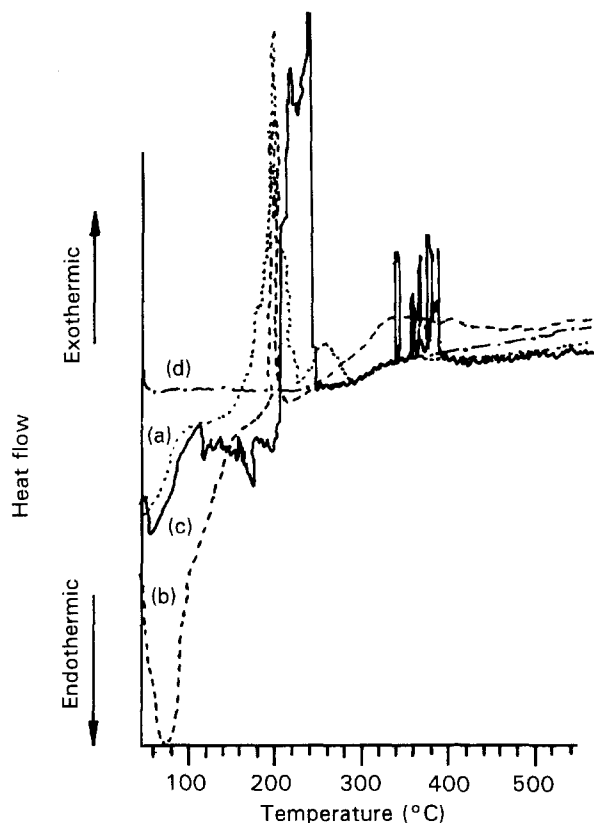


Figure 7 DSC curves of gels and nitrated products. (a) P-G, (b) P-GL, (c) P-H, (d) P-G nitrated.

above observations are supported by the DSC studies which show endothermic peaks assignable to the evaporation of water, alcohol, dimethyl formamide and hydroxyl groups, and exothermic peaks, which are attributable to the decomposition of the additives in gel samples. The negligible weight loss shown by the nitrated species in TGA studies is supported by the absence of peaks in DSC curves. This is expected because nitrogen introduction into the gel structure increases the thermal stability of the resultant product.

3.4. Nitrogen content

The nitrogen content of the products obtained on ammonalysis was found to vary from 0.1%–1.8% in the present method (Table II). It was noticed that gels synthesized with carbonaceous materials or nitrogen contain compounds as additives incorporated more nitrogen into the gel structure. This is due to the fact that gels prepared by the sol-gel technique accommodate the additives in the gel network, and these additives embedded in the gels are released depending upon the reaction conditions [10]. In the present investigation, carbonaceous materials added during synthesis probably help in carbothermic reactions leading to the formation of nitrated silica [11]. Carbonaceous compounds such as carbon fibre and pan fibre, contain carbon and nitrogen as constituents which help in the carbothermic reactions of silica initially and on prolonged heating leading to the formation of nitrated silica. The nitrogen-containing compounds added as additives in the gels evolve ammonia during sintering, which perhaps is linked to the silicon atom as Si-NH₂ by replacing the OH groups in the silica network. On further heating in ammonia and nitrogen atmosphere at high temperature (1000 °C), the Si-N bond is established, leading to the formation of nitrated silica. The formation of silicon oxycarbide is ruled out, because the final product is not a black glass and does not leave residual carbon on treatment with hydrofluoric acid.

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