CHAPTER VI

STUDIES ON NITRIDATION OF SILICA GELS
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6.0 INTRODUCTION

Preparation of Nitrogen containing silica glasses is one of the most important task in glass science. The softening temperature, density, refractive index, elastic modulus and hardness are increased and the thermal expansion coefficient is decreased by replacing part of the oxygen atoms in the glass structure by nitrogen atoms [171-174]. It is extremely difficult to obtain N- containing glasses by melting the mixture of powdered SiO₂ and Si₃N₄. Mulfinger [175] first reported the introduction of nitrogen into an oxide glass network by bubbling the glass melts with nitrogen or ammonia. Silicon nitride and Aluminium Nitride have been reported as raw materials for Nitrogen incorporation [171-173]. For that purpose mixtures of nitrides and oxides have been melted in graphite or boron nitride crucibles under an inert atmosphere. For melting, a higher temperature is usually required. Sometimes a too high temperature for melting causes the decomposition of nitrides.

For incorporating nitrogen at lower temperature Brinker et. al. [176-177] reported that sol - gel method can be used by heating silica gels in flow of NH₃ at temperatures below 1000°C. However, when monolithic gel is ammonolyzed it is difficult to obtain the nitrogen content larger than few weight percent. Much more nitrogen can be introduced into the porous structures. Pantano and coworkers [178] reported that 40 mol % of nitrogen was successfully incorporated by ammonolysis of sol - gel derived porous silica films. Fine silica powders were also nitrided to Si₃N₄ powders by heating in flowing ammonia [179]. Fink and coworkers [180] have introduced upto 25 wt % of nitrogen in the SiO₂ by reaction of aerosil with a flowing NH₃ at 1373 K. Silicon oxynitride glass fibers with high nitrogen content upto 32.1 wt % were prepared by ammonolysis of porous silica gel fibers [181]. Silicon nitride is a technologically important material in the
production of high performance integrated circuits because of its strong oxidation resistance, barrier against diffusion of impurities and chemical stability.

Constant efforts of 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. Keeping these important aspects in mind, the present studies of ceramic matrix development through sol-gel route was extended to development of nitrogen containing silicon ceramics through nitridation of silica gels. The studies made and results obtained are reported in this chapter. The glasses obtained were investigated by IR, XRD, Thermal analysis system and optical microscopy. Their oxidation resistance and chemical durability were also analyzed.

Literature survey [182] suggests sol-gel derived silicon di oxide appears to be an effective precursor material for the development of Silicon oxy nitride thin films by high temperature reaction with ammonia. Advantages is that significant amounts of nitrogen could be incorporated at lower temperatures and in shorter times than was generally required for nitridation of dense, thermally grown Silicon dioxide films. Additionally the nitrogen distribution was expected to be more uniform because of their initial interconnected micro porosity. Here the work has been extended to thick dried gels of about 1-2 mm in thickness.

6.1 PHYSICAL APPEARANCE OF THE SAMPLES DURING NITRIDATION

The gel was prepared by the hydrolysis of organometallic compound e.g. Tetraethyl orthosilicate under the conditions optimized in chapter III. The gel was casted and allowed to dry at room temperature. When this gel is dried and pyrolyzed, a sequence of changes in colour of the sample is observed which is due to chemical changes taking place in the material. Each colour is characteristic of the chemical composition of that material. Therefore, during nitridation, the change in colour was followed systematically.
The samples were heated to various temperatures in presence of ammonia and nitrogen gas mixture for predetermined time. The results are compiled in Table 6.1. It shows the physical appearance of the samples heated to different nitridation temperature with heating rate of 3°C/hr. and holding at the final nitridation temperature for 6 hr..

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>State</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>light brown</td>
</tr>
<tr>
<td>550</td>
<td>dark blackish brown</td>
</tr>
<tr>
<td>750</td>
<td>dull black</td>
</tr>
<tr>
<td>800</td>
<td>completely black</td>
</tr>
<tr>
<td>850</td>
<td>completely black</td>
</tr>
<tr>
<td>900</td>
<td>partly black &amp; white</td>
</tr>
<tr>
<td>950</td>
<td>Increasingly white</td>
</tr>
</tbody>
</table>

The samples nitrided at 750°C, 800°C and 850°C were completely black and the samples nitrided at 900°C were partly black and partly white and those nitrided at 950°C were more white.

Table 6.2 below shows the physical appearance of the samples nitrided at different temperature with a slower heating rate of 2°C/hr with hold time during reaction of 2 hours at 250°C, 550°C and a held for 4 hours at 750°C and a held for 4 hours at final nitridation temperature. The nitrogen enters the gel structure as Si-NH₂ at lower temperature by the reaction of silanol groups and ammonia vapours and remains upto around 600°C. Therefore isothermal stops at lower temperatures were selected for chemical equilibrium. As seen from the comparison of Table 6.1 and Table 6.2, with change in heating rate during nitridation reaction the final physical appearance of samples is different. Linear high heating rate without isothermal stops at various temperature results in partly black and white samples at temperature above 900°C. The isothermal stops at lower temperature of
Nitridation may increase the nitrogen content in the nitrided gels by the chemical reaction of hydroxyl groups on the gels and reaction atmosphere.

Table 6.2
State of sample with nitriding temperature

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>State</th>
</tr>
</thead>
<tbody>
<tr>
<td>750</td>
<td>Brownish black</td>
</tr>
<tr>
<td>800</td>
<td>black</td>
</tr>
<tr>
<td>850</td>
<td>black</td>
</tr>
<tr>
<td>950</td>
<td>black</td>
</tr>
</tbody>
</table>

Weight loss of samples when heated in different environment were correlated for reaction products. Gels prepared with hydrolyzed TEOS as described in chapter III when heated in air at 800°C are white opaque and showed a little higher weight loss of 25.3% compared to the weight loss of 24.7% for same sample when heated in nitridation atmosphere of ammonia and nitrogen gas mixture.

6.2 INFRARED STUDIES OF NITRIDED GELS

The silica sol obtained by hydrolysis of Tetraethylorthosilicate (TEOS) with water to TEOS in the molar ratio of 8 : 1 was gelled as described in chapter II. The dried gels in the temperature range of 60-70°C were heated to 100°C in nitrogen atmosphere. At 100°C ammonia was introduced along with nitrogen in the reaction chamber. The temperature of final heat treatment in presence of ammonia and nitrogen gas mixture was varied from 750°C to 1300°C.

Figure 6.1 show the Infrared spectra of the nitrided samples prepared at 750°C. For comparison the infrared spectra of the material sintered in nitrogen at the same temperature is also included. Curve (a) shows spectra for the sample heated in nitrogen atmosphere and
Figure 6.1 Infrared spectra of sample heated
(a) in Nitrogen at 750°C and (b) in Ammonia atmosphere at 750°C
curve (b) shows spectra for the sample heated in ammonia and nitrogen gas mixture. Curve (a) shows the characteristic band due to Si-O-Si stretching vibration at around 1000-1200 cm\(^{-1}\). Also a sharp peak at 800 cm\(^{-1}\) due to SiO\(_4\) tetrahedron is observed. In curve (b) for samples nitrided at 750°C more broad band located at 1100 cm\(^{-1}\) is observed. The nitrided product obtained from gel precursors clearly show the broadening of the band around 1100 cm\(^{-1}\) which is due to Si-N in addition to Si-O bond. The symmetric stretching vibrations of O-Si-O at 470 cm\(^{-1}\) is also observed in nitrided as well as in samples heated in nitrogen.

Infrared spectra recorded over the wave number 400 cm\(^{-1}\) to 4000 cm\(^{-1}\) of the silica gels nitrided at different temperatures are shown in Figure 6.2. The comparison of spectra with nitridation temperature clearly shows with increasing nitriding temperature the broadening of the band at around 1100 cm\(^{-1}\) which may be due to Si-N in addition to the Si-O bonds takes place. Spectra show a small broad peak at 1600 cm\(^{-1}\) and broad band at 3400-3600 cm\(^{-1}\). The nitrogen enters the gel structure as Si-NH\(_2\) at lower temperature and remains up to around 600°C. At a temperature as high as 900°C, Si-N linkage is established which, in turn, causes the broadening of the band at 1000 cm\(^{-1}\).

Figure 6.3 shows the infrared spectra for the samples nitrided at 1200°C and 1300°C in ammonia atmosphere. It is seen from figure that both the spectras almost overlap each other showing not much effect of higher nitriding temperature.

6.3 THERMAL STABILITY OF NITRIDED CERAMICS

Thermal stability of the nitrided materials was studied using TGA. The samples were heated to 1000°C in air and the weight loss was recorded. Figure 6.4 shows the TGA plot of the sample nitrided at 900°C. As seen from the figure, there is negligible weight loss in the sample at 1000°C in air. Therefore, the oxidation studies of the nitrided sample shows that nitrogen incorporation into the gel network enhances the thermal stability of the samples.
Figure 6.2 Infrared spectra of sample Nitrided at (a) 800°C (b) 850°C (c) 950°C temperature
Figure 6.3 Infrared spectra of sample Nitrided at (a) 1300°C and (b) 1200°C temperature
Figure 6.4 TGA scan of sample Nitrided at 900°C in air
6.4 X-RAY DIFFRACTION STUDIES ON NITRIDE GELS

XRD scans of samples nitrided at different temperature were recorded. Figure 6.5 shows the XRD scan of sample nitrided at 1200°C and 1300°C in ammonia atmosphere. The powder x-ray diffraction pattern for sample nitrided at 1200°C gives a broad pattern at around 2θ = 21° (d = 3.5-4.5 Å) a characteristic of an amorphous silicate structure. With increase in nitriding temperature not much change in the pattern is observed. This is also confirmed by infrared spectra.

6.5 MICROSTRUCTURE OF THE NITRIDE SAMPLES BY OPTICAL MICROSCOPY

The nitrided samples were embedded in polymeric moulds, polished and examined under optical microscope. Figure 6.6 (a) and (b) are the optical micrographs of the nitrided (80% white) samples. A comparison of nitrided samples well recognize the difference in the structure of these samples as compared to non nitrided sample is quite apparent from Figure 6.6 (c). The nitrided samples show more glass type shinning fine structure. The completely nitrided (white) samples exhibit very bright shinning fine structure (figure 6.6 (d) and (e)).

These studies on nitridation of the matrix show that nitrogen can be incorporated into the silica network relatively at lower temperature by heating the silica gels at around 900°C in presence of ammonia. Such materials are promising materials to be used as matrix material for ceramic matrix composites as well as for oxidation resistant carbon/carbon composites.
Figure 6.5 XRD scan of samples Nitrided at 1200°C and 1300°C in ammonia atmosphere
Figure 6.6 Optical micrographs of Nitrided samples
Figure 6.6 Optical micrograph of non nitrided sample
Figure 6.6 Optical micrographs of completely Nitrided samples