Fabrication of radiative cooling materials based on Si$_2$N$_2$O particles by the nitridation of mixtures of silicon and silicon dioxide powders

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Silicon oxynitride particles intended for use as radiative cooling materials were synthesized via the nitridation of mixtures of Si and SiO$_2$ powders. The optimal heat-treatment conditions for the formation of silicon oxynitride were determined to consist of a temperature of 1450°C applied for one hour. Specimens formed in this manner from mixtures of Si and SiO$_2$ in 2:1 or 3:1 molar ratios under a nitrogen atmosphere were composed almost exclusively of a single Si$_2$N$_2$O phase. The resulting Si$_2$N$_2$O powders exhibited significant absorption in the so-called atmospheric window IR region between 8–13 μm and had only limited absorption outside of that range.

Key-words : Silicon oxynitride, Radiative cooling material, Nitridation

1. Introduction

It has long been known that the clear night sky acts as a passive heat sink, able to lower the temperature of the Earth’s atmosphere. This phenomenon is referred to as radiative cooling and has been widely studied since the 19th century.¹,²,³ The sky allows heat to escape since infrared (IR) radiation in the wavelength range from 8 to 13 μm is not absorbed by atmospheric gases, and hence this wavelength region is known as the atmospheric window.⁴ Materials on the Earth’s surface that can emit IR radiation in this window also have the ability to lose heat via radiative cooling. A rule that can assist in the selection and design of such materials is that compounds will emit IR radiation in approximately the same wavelength range over which they absorb.⁵ Thus, in order to design radiative cooling materials, we must select compounds with high absorption in the 8 to 13 μm wavelength range and low absorption elsewhere.

Silicon monoxide, silicon oxynitride and PVC are all well-known radiative cooling materials, with significant capacity for cooling.²⁵,³³ In previous studies, Granqvist et al. designed radiative cooling materials using SiO and SiO$_2$N$_2$ films, based on their radiative cooling abilities.²⁵,³³ These materials, in the form of powders, could potentially be embedded in asphalt or concrete roads and concrete buildings, for the purpose of lowering temperatures in urban heat islands. The aim of our work was to build upon this concept by fabricating silicon oxynitride powders with significant absorption in the atmospheric window wavelength range, for potential application as radiative cooling materials.

In prior studies, Suzuki et al. have reported the fabrication of Si$_2$N$_2$O by the direct nitridation of mixtures of silicon and silicon dioxide powders at a Si/SiO$_2$ molar ratio of 3:1,⁶⁵ in which the nitridation reaction proceeds as in Eq. (1) below.

$$3\text{Si} + \text{SiO}_2 + 2\text{N}_2 \rightarrow 2\text{Si}_2\text{N}_2\text{O}$$ (1)

This reaction takes place in two steps. In the first, silicon and silicon dioxide react to produce gaseous silicon suboxide which, in the second step, reacts with nitrogen gas to form Si$_2$N$_2$O.⁵ Furthermore, IR absorption property of Si$_2$O$_2$N was carried out,⁷ but an evaluation of the Si$_2$O$_2$N as a radiative cooling material have not been carried out.

In this investigation, silicon oxynitride powders were fabricated by the direct nitridation of mixed Si and SiO$_2$ powders via this same reaction, and a formation process of Si$_2$N$_2$O was evaluated by observation of the microstructures of the resulting powders. The IR absorption properties of the resulting silicon oxynitride particles were then assessed for a radiative cooling material.

2. Experimental procedures

Silicon powder (5 μm, Kojundo, Saitama, Japan) and SiO$_2$ powder (quartz, 4 μm, Kojundo, Saitama, Japan) were used as raw ingredients, and Si$_3$N$_4$ powder (5 μm, Wako, Osaka, Japan) was used as a standard materials for IR absorption. Quantities of both materials were combined in Si to SiO$_2$ molar ratios ranging from 1:1 to 4:1 and were thoroughly mixed in an agate mortar. Each mixture was subsequently placed into a 10 mm diameter mold and die-pressed using uniaxial force at a pressure of 15 MPa. The resulting pellets were heat-treated at 1450°C for 1 h under a nitrogen atmosphere with a flow rate of 50 sccm.

The structures of the powders thus produced were characterized by X-ray diffraction (XRD) using a Rigaku Miniflex II with Cu Kα radiation. IR absorption spectra of these materials in KBr pellets were measured using a Fourier transform infrared spectrometer (Jasco FT-IR 660 plus). Prior to both XRD and IR analyses, the pelletized sample materials were ground back into powders using an agate mortar. The microstructures of the raw materials and the resulting pellets were observed by scanning electron microscopy (SEM) using a Hitachi S-2100.
Acquired for various specimens. In this ratio ranging from 1:1 to 4:1.

Obtained at both lower and higher molar ratios. The specimen in Fig. 1(d), with a Si to SiO₂ molar ratio of 3:1 should be optimal, Si₂N₂O was produced silicon suboxide gas which reacted with nitrogen to form very fine Si₂N₂O particles which agrees with our own observations. The polished pellet surfaces for the 2:1 and 3:1 materials, however, shows numerous voids indicating the formation of gas pockets. We know that gaseous substances, including silicon suboxide, are formed during the reaction process, and it appears that a greater quantity of gas evolves in the 3:1 mixture as opposed to the 2:1, leading to the voids. The cross-sectional images of specimens made using Si/SiO₂ ratios of 2:1 and 3:1 are shown in Figs. 3(c) and 3(f). These SEM images of the pellet interiors indicate that specimens produced from both 2:1 and 3:1 ratios were sufficiently sintered, with adequate grain growth under the applied heat-treatment conditions. These results confirm that, for

**3. Results and discussion**

As noted above, silicon oxynitride powders were fabricated by the nitridation of Si and SiO₂ at 1450°C under a N₂ atmosphere over a period of 1 h, from a mixture of Si and SiO₂ powders combined at Si/SiO₂ molar ratios ranging from 1:1 to 4:1. **Figure 1** shows the XRD patterns obtained from materials synthesized using Si/SiO₂ molar ratios of (a) 1:1, (b) 2:1, (c) 3:1 and (d) 4:1. XRD peaks with no markers are assigned to Si₃N₄.

![XRD patterns obtained from materials synthesized using Si/SiO₂ molar ratios](image)

**Figure 1.** XRD patterns obtained from materials synthesized using Si/SiO₂ molar ratios of (a) 1:1, (b) 2:1, (c) 3:1 and (d) 4:1. XRD peaks with no markers are assigned to Si₃N₄.

Results suggest that the optimal conditions for the synthesis of Si₂N₂O are at 1450°C for 1 h. IR absorption spectra were acquired for the synthesized specimens, as well as for pure SiO₂ and Si₃N₄ reference materials. **Figure 2** provides the IR spectra obtained for these powders. In each spectra, the atmospheric window region is indicated by dashed lines. Figure 2(a) presents the spectrum of SiO₂ powder. Based on a previous report, peaks for this compound were expected at 9.13, 12.5, 12.8, 14.3, 19.2 and 21.6 μm, all of which were observed in the sample. The absorption peaks for Si₃N₄ powder [Fig. 2(b)] were also confirmed at values expected based on a previous report, at 10.5, 11.7, 14.5, 20.1 and 21.6 μm. The heat-treated specimens, all of which include Si₂N₂O (as confirmed by XRD measurements), exhibit the Si₂N₂O absorption peaks that have been reported previously. Based on their IR absorption spectra, we evaluated the radiative cooling abilities of these materials. Both SiO₂ and Si₃N₄ showed absorption in the atmospheric window region, but their absorption ranges were rather narrow compared to the width of the window. All the fabricated specimens, however, exhibited wide absorption bands which filled most of the atmospheric window, as a result of the absorption properties of Si₂N₂O. The specimen with a Si/SiO₂ ratio of 1:1 [Fig. 2(c)] also showed undesirably strong additional absorption within the wavelength range of 20 to 23 μm, which we attribute to the presence of SiO₂ in this sample. The remaining specimens with Si to SiO₂ ratios from 2:1 to 4:1 had somewhat less absorption outside of the atmospheric window region. Of these, the specimen with a Si/SiO₂ ratio of 4:1 [Fig. 2(f)] exhibited the most narrow absorption band within the atmospheric region. Part of this sample’s absorption in the window region is the result of Si₃N₄, observed in this specimen during XRD analysis, which contributes some absorption in the wavelength range of 8 to 9 μm. If we subtract the contribution of Si₃N₄, therefore, the IR absorption of the 4:1 specimen within the atmospheric window is less than that of the 2:1 and 3:1 materials. These results suggest that powders produced at Si/SiO₂ molar ratios of 2:1 and 3:1 are the most suitable candidates for radiative cooling materials.

To further investigate the formation of Si₂N₂O powders by the nitridation of the raw ingredients, the surface and cross-section microstructures of pellets made from Si/SiO₂ ratios of 2:1 and 3:1 were examined. **Figure 3** depicts the SEM images obtained from pellet surfaces with or without polishing as well as cross-sections. For both of the unpolished specimens [Figs. 3(a) and 3(d)], fine particles are observed on the pellet surfaces. In a previous report concerning the formation of Si₂N₂O powders by nitridation of Si and SiO₂, the heat treatment of Si and SiO₂ produced silicon suboxide gas which reacted with nitrogen to form very fine Si₂N₂O particles, which agrees with our own observations. The polished pellet surfaces for the 2:1 and 3:1 samples [Figs. 3(b) and 3(e)] presented dense, flat surfaces. The surface of the pellet from the 3:1 mixture, however, shows numerous voids indicating the formation of gas pockets. We know that gaseous substances, including silicon suboxide, are formed during the reaction process, and it appears that a greater quantity of gas evolves in the 3:1 mixture as opposed to the 2:1, leading to the voids. The cross-sectional images of specimens made using Si/SiO₂ ratios of 2:1 and 3:1 are shown in Figs. 3(c) and 3(f). These SEM images of the pellet interiors indicate that specimens produced from both 2:1 and 3:1 ratios were sufficiently sintered, with adequate grain growth under the applied heat-treatment conditions. These results confirm that, for
Fig. 2. IR spectra obtained for (a) pure SiO₂, (b) pure Si₃N₄, and materials synthesized using Si/SiO₂ molar ratios of (c) 1:1, (d) 2:1, (e) 3:1 and (f) 4:1.

Fig. 3. SEM images of (a and d) unpolished surfaces, (b and e) polished surfaces and (c and f) cross-sections of pelletized specimens synthesized using Si/SiO₂ molar ratios of 2:1 and 3:1 respectively.
both the 2:1 and 3:1 mixtures, Si$_2$N$_2$O powders were formed by the nitridation of gaseous silicon suboxide, and that the subsequent heat-treatment was sufficient to produce larger Si$_2$N$_2$O particles inside the pelletized samples.

4. Conclusion

Silicon oxynitride particles were fabricated by the nitridation of Si and SiO$_2$ powder mixtures. Si$_2$N$_2$O was successfully obtained following heat-treatment at 1450°C in a nitrogen atmosphere. When employing Si to SiO$_2$ molar ratios of 2:1 and 3:1, materials were obtained composed almost entirely of Si$_2$N$_2$O. These materials exhibited significant absorption within the 8 to 13 μm wavelength range and relatively low absorption elsewhere in the IR region of the spectrum, signifying that Si$_2$N$_2$O is well suited for application as a radiative cooling material.

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