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Investigation of the oxidation of sialons with infrared reflection spectroscopy

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Hot-pressed β-sialons ($Si_{6-z}Al_zO_zN_{8-z}$) formed in the Si_3N_4–Al_2O_3–AlN and Si_3N_4–SiO_2–AlN systems have been investigated using infrared reflection spectroscopy (IRRS). As z increases, the IRRS bands decrease in frequency. The decrease can be explained by the decrease in the force constants of the chemical bondings. IRRS has been applied to the study of the oxidation sialons at 1200 and 1300° C as a function of time. The technique has sensitively detected cristobalite, mullite and glass phases on the oxidized surface. This is considered to be effective for understanding the oxidation kinetics of sialons.

1. Introduction

The high strength of β-sialon at elevated temperatures makes it an excellent candidate for engineering applications such as gas turbine components [1–3]. Sialons are a solid solution between Si_3N_4 and $AlN \cdot Al_2O_3$ [2, 3] or $AlN \cdot SiO_2$ [2, 4]. The composition of sialons is represented by the formula $Si_{6-z}Al_zO_zN_{8-z}$ in which $z = 0$ to 4.2 [1, 3].

Spectroscopic studies have been carried out to elucidate the molecular structure of sialons using the techniques of infrared (IR), transmission [5–7] and Raman scattering [8]. However, there are few studies on sialons using the infrared reflection spectroscopy (IRRS) technique. The IR spectra of solid samples usually are recorded in transmission either by pressing samples into KBr pellets or by grinding samples thoroughly with an inert oil, such as paraffin oil (nujol). Samples whose spectra cannot be obtained in transmission can be recorded using the IRRS technique. This technique is able to measure spectra of bulk samples without sample preparation such as grinding. In addition, the advantage of the technique is its sensitivity to the structural change within 0.5 μm of the surface and its ability to detect changes in chemical bonding in glass phases, in a similar way to the technique of IR transmission [9]. Additionally, whenever there may be an advantage in interpretation, IRRS spectra can be converted to IR transmission spectra [10]. Hence, IRRS has been frequently used in the studies of ceramic oxidation [11, 12] and glass corrosion [10, 13].

Hot pressed sialons exhibit better oxidation resistance than hot pressed silicon nitride which is known to be an excellent candidate for ceramic turbine components [1, 14]. In the high-temperature engineering application of sialons, one of the most important factors affecting the performance is their oxidation behaviour. The oxidation resistance is dependent on the formation of a surface oxide layer [15]. It is known that oxidation results in the formation of cristobalite, mullite and glass phases on the surface of the sialons [15, 16]; the composition of oxidized layer has been chiefly studied using X-ray diffraction [15, 16]. However, this technique is only able to detect the presence of crystalline phases. The IRRS technique, on the other hand, is able to detect the presence of both the crystalline and glassy phases, and is sensitive to the structural changes on the surface, as mentioned above. Thus, IRRS is considered to be an effective technique for the non-destructive analysis of the kinetics of formation of both the crystalline and glassy phases on the surface of oxidized sialons.

The purpose of this paper was to measure the IRRS spectra of sialons in the systems Si_3N_4–Al_2O_3–AlN and Si_3N_4–SiO_2–AlN and to obtain information on their oxidation process through the time dependence of the spectra during high-temperature thermal exposure.

2. Experimental details

Sialons in the systems Si_3N_4–Al_2O_3–AlN and Si_3N_4–SiO_2–AlN were produced by hot pressing under the same conditions as those described earlier [6, 7]. For sialons in both systems, the values of z were taken as 1, 2, 3 and 4 in $Si_{6-z}Al_zO_zN_{8-z}$. The powder samples were the same as those used in previous reports [6, 7]. The surfaces of the sialon specimens were polished using Nos. 800, 1500 and 3000 SiC powders successively, and cleaned in an ultrasonic bath. Oxidation was then performed at 1200 and 1300° C in air. The oxidized specimens were measured in the rapidly cooled condition in an attempt to retain the structure of the surface layer, characteristic of the oxidation temperature.

IRRS spectra were obtained in this study using a Digilab FTS-20c/d FT-IR spectrometer operated in a single reflecting mode. The spectrometer was equipped with a Digilab IR-reflectance accessory in which the incidence angle was fixed at 15°. An aluminium mirror was used to obtain the reference file for the purpose of compensation for air scattering.

3. Results and discussion

3.1. IRRS spectra of sialons

Fig. 1 shows the IRRS spectra of as-machined sialons

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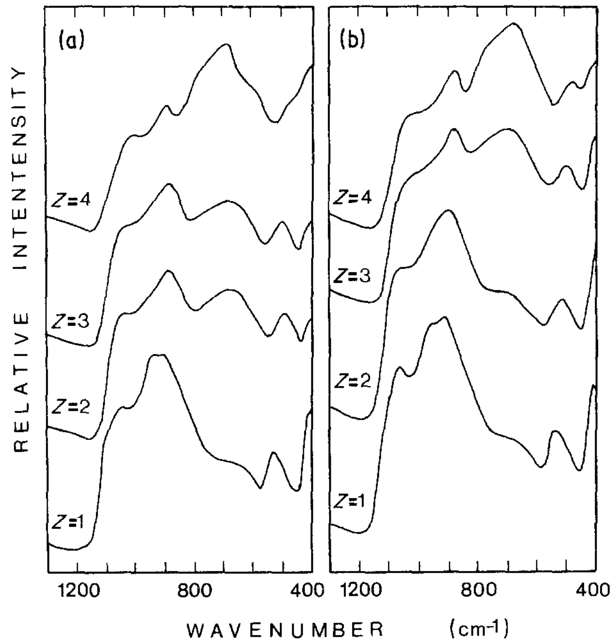

Figure 1 IRRS spectra of sialons in the systems Si_3N_4–Al_2O_3–AlN (a) and Si_3N_4–SiO_2–AlN (b).

in the systems Si_3N_4–Al_2O_3–AlN (a) and Si_3N_4–SiO_2–AlN (b). There is no large difference between the corresponding spectra of sialons in both systems. The powder transmission spectrum of sialon with $z = 1$ in the system Si_3N_4–Al_2O_3–AlN and the IRRS spectrum of that sialon for comparison, are shown in Fig. 2. The overall contour of the spectra, except frequencies of bands and band contrast, differ between the techniques. Usually, maxima in the IRRS spectra do not coincide with transmission minima [17, 18]. However, there is a one-to-one correlation between reflection maxima and transmission minima, as shown in Fig. 2. Such a correlation has been observed in β-Si_3N_4 [19], in which the molecular structure is the same as that of sialon [1]. The IRRS bands may be assigned to the same vibrational modes as those of the corresponding transmission bands. The bands in the 850 to 1100 cm^{-1} spectral range can be assigned to the Si–N stretching vibrations in the β-Si_3N_4 network and those in the 400 to 600 cm^{-1} spectral range to the Si–N–Si and N–Si–N bending vibrations [6, 7, 11].

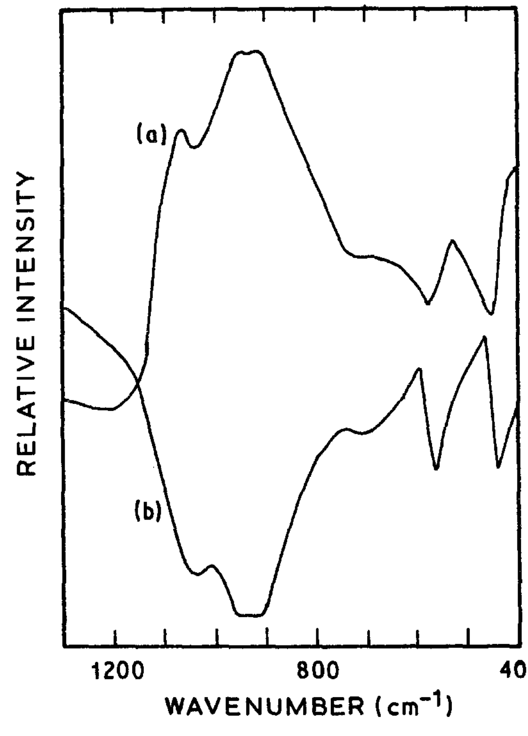

Figure 2 Powder IR transmission and IRRS spectra of sialon with $z = 1$ in the system Si_3N_4–Al_2O_3–AlN.

As z increases, the IRRS bands become broadened and difficult to resolve separately. These bands appear to decrease linearly in frequency with increasing z, as shown in Fig. 1. Unit cell dimensions were calculated from X-ray powder diffraction peaks of the sialons in order to obtain a relationship between the cell dimensions and the frequencies of the IRRS bands. The cell dimensions are the same as those obtained in previous studies [6, 7].

Fig. 3 shows the relationship between these frequencies and the cell dimensions. The values of z are also indicated in Fig. 3. There is an apparent linear relationship between the frequencies and the cell dimensions. A similar relation has been observed in the studies of IR transmission [5–7]. In sialons, silicon and nitrogen atoms of the β-Si_3N_4 network are widely substituted by aluminium and oxygen atoms, respectively [1]. As z increases, the substitution increases, resulting in an increase in the degree of structural disorder of the β-Si_3N_4 network. Consequently, this gives rise to a decrease in the force constants of the chemical bonds in the β-Si_3N_4 network. Thus, the decrease in frequencies of IRRS bands with increasing z can be explained by a decrease in the force constants of chemical bonding in analogy with that of the IR transmission bands [5–7].

New bands appear near 700 cm^{-1} in sialons with $z = 2, 3$ and 4 and the relative intensity of these bands increase with increasing z. Their frequency also increases with z, as shown in Fig. 3. Such bands have been observed in IR transmission spectra [5, 6]. They have been assigned to Al–O and Al–N stretching vibrational modes in the β-Si_3N_4 network which is largely substituted [6]. The appearance of new bands suggests that structural changes are occurring in sialons with large z. However, this remains a subject for future investigation.

3.2. Analysis of the oxidation of sialons with IRRS

The properties of the surface of the oxidized layer formed during the oxidation of sialons have been studied by various methods [14–16, 20]. The determination of chemical composition of the layer has been chiefly studied by the technique of X-ray spectroscopy [15, 16]. The study has shown that cristobalite and mullite first appear on the surface [16]. As z increases, the formation of cristobalite decreases and that of mullite increases. In particular, cristobalite has not been detected on the oxidized surface of sialon with $z = 4$ [16]. Thereafter a glassy phase was formed on the surface which increased with increasing oxidation time. It was suggested that a part of the cristobalite changes to the glassy phase through migration of impurities present in grain boundary layers to the oxidized surface [15, 16].

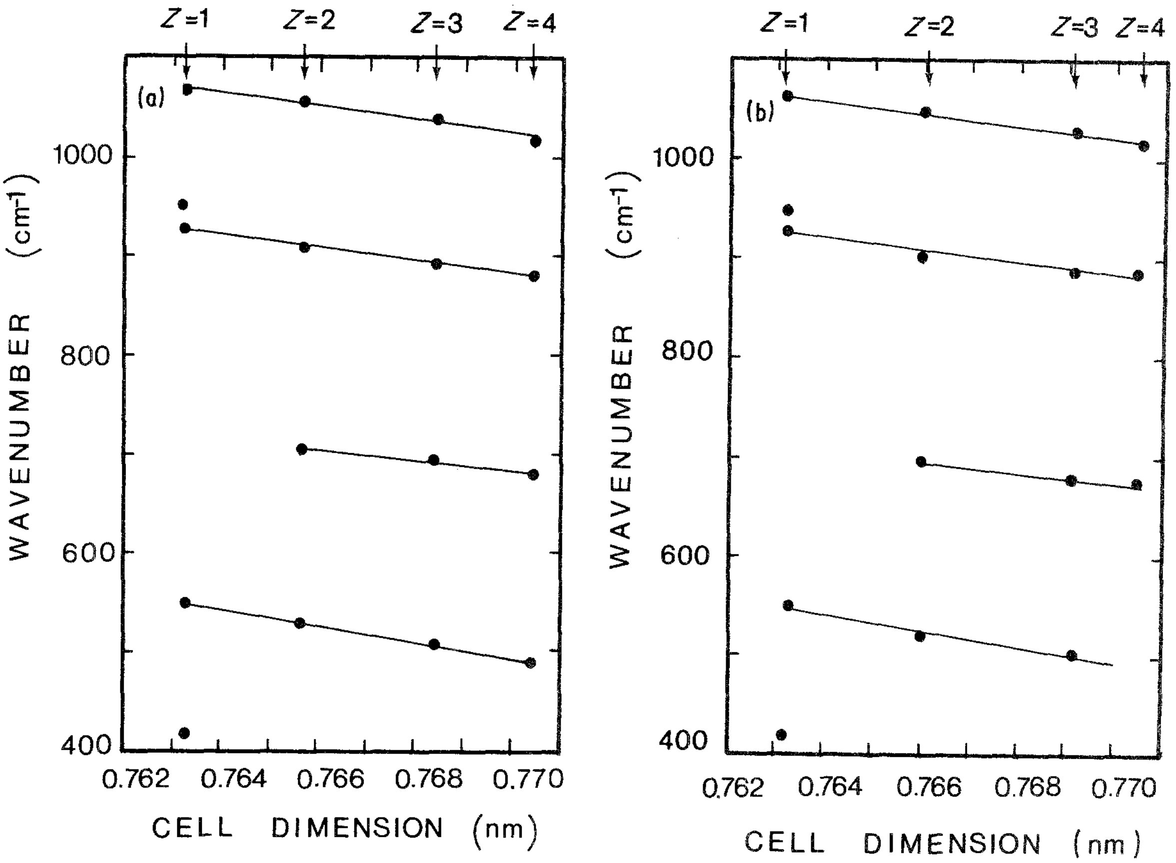

Figure 3 Plots of frequencies of IRRS bands against cell dimensions for sialons in the systems (a) Si_3N_4–SiO_2–AlN and (b) Si_3N_4–Al_2O_3–AlN.

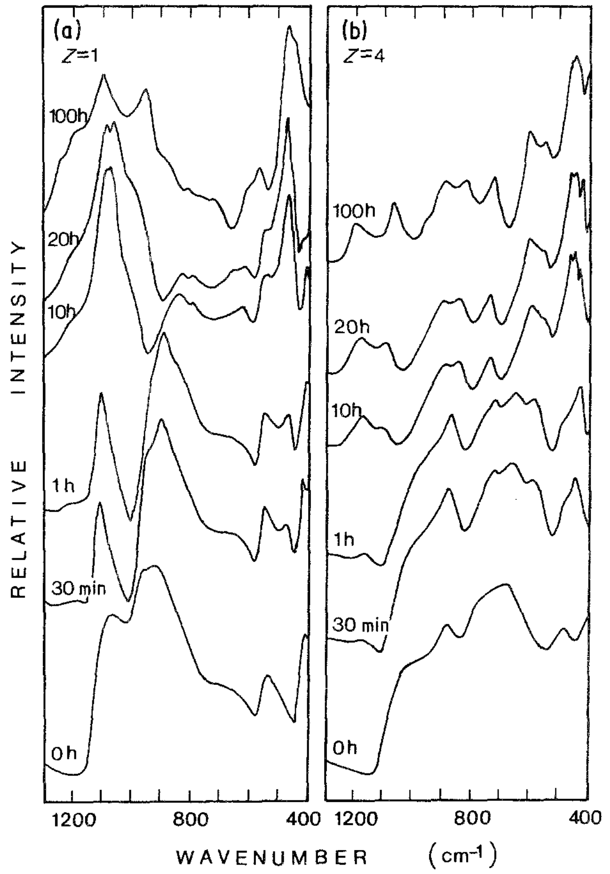

Figure 4 IRRS spectra of sialons in the system Si_3N_4–Al_2O_3–AlN before and after oxidation for various times at 1300° C: (a) $z = 1$ (b) $z = 4$.

Fig. 4 typically shows the changes of IRRS spectra of oxidized sialons with $z = 1$ and 4 in the system Si_3N_4–Al_2O_3–AlN as a function of oxidation time at 1300° C. For comparison, the IRRS spectra of initial sialons before oxidation (indicated by 0 h) are also shown in Fig. 4. After exposure for 30 min the IRRS spectrum of the oxidized sialon with $z = 1$ has been considerably changed in its overall contour compared with the initial spectrum, as shown in Fig. 4a; 30 min. Of particular interest are the bands at 1111 and 478 cm^{-1} which newly appear after exposure for 30 min. These bands can be observed even after 5 min oxidation. As oxidation time increases, these increase in intensity and show a slight shift (about 10 cm^{-1}) to lower frequencies (Fig. 4a).

X-ray diffraction analysis has shown that cristobalite is produced on the surface of sialon after exposure for 1 day [16]. In this study, X-ray analysis could not detect the presence of cristobalite on the surface after exposure for 30 min. However, when silicon nitride is oxidized at temperatures between 1200 and 1400° C, a rapid weight gain was observed between 15 and 60 min [21]. The oxidation product is cristobalite. Fig. 5 shows the IRRS spectra of cristobalite (a), silicate glass (b) and mullite (c) (these materials were kindly supplied by Mr Tsunematsu of this Institute). The spectra of cristobalite and silicate glass are in good agreement with those presented earlier [22]. The bands at 1111 and 471 cm^{-1} of oxidized sialon with $z = 1$ show considerable

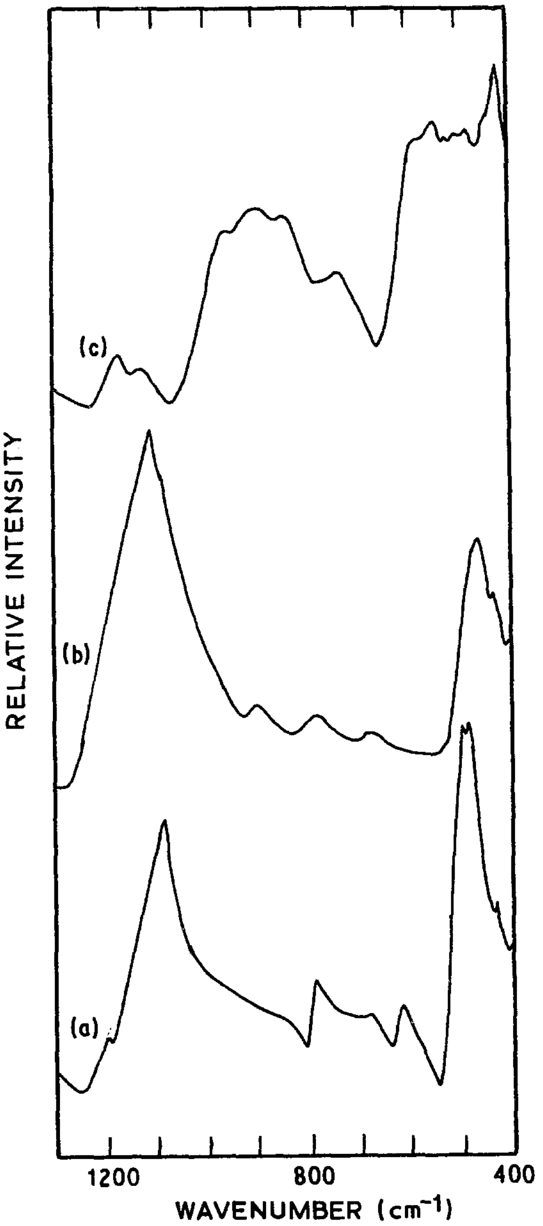

Figure 5 IRRS spectra of cristobalite (a), silicate glass (b) and mullite (c).

similarity in frequencies of those of cristobalite. It is reasonable to conclude that the bands can be assigned to the vibrational modes of cristobalite. The 1111 cm^{-1} band is ascribed to the Si–O stretching vibrational mode and the 471 cm^{-1} band to the Si–O rocking vibrational mode. Thus, the presence of cristobalite at an early stage can be detected by the technique of IRRS, but not by the X-ray technique. This shows that the IRRS technique is sensitive to the surface changes of sialon caused by oxidation.

The band at 1065 cm^{-1} from the initial sialon, which is assigned to a Si–N stretching mode of the Si_3N_4 network [6], cannot be observed after 30 min exposure, as shown in Fig. 4a, 30 min. The bands at 941 and 926 cm^{-1}, from the initial sialon, which are also assigned to Si–N stretching mode [6], shift to 879 and 846 cm^{-1}, respectively. The behaviour of these bands cannot be definitely explained at present, but may be explained by the selective absorption of IRRS from the cristobalite layer formed on the sialon surface. As oxidation proceeds, the 879 and 846 cm^{-1} bands decrease in intensity and slightly shift to lower frequencies. After exposure for 10 h these become weak in intensity. The band at 549 cm^{-1}, which is assigned to the Si–N rocking mode [11], appears to be little changed in frequency, but has been buried in the band at 463 cm^{-1} after a long exposure time. The oxidized layer increases in thickness with time. This prevents detection of the signal from the sialon surface. Therefore, those bands may decrease in intensity with oxidation time.

The 1111 and 471 cm^{-1} bands shift to 1088 and 463 cm^{-1}, respectively, after 10 h oxidation as noted above. The slight shift may be explained by the effect of intermixing of impurities from the sialon bulk into the oxidized layer (cristobalite) [16]. The intermixing produces an increasing degree of structure disorder in crystobalite which brings about a decrease in force constants of Si–O bondings. Thus, the slight shift can be explained by the decrease in force constants. After exposure for 30 h, the 1088 cm^{-1} band appears to be a doublet at 1096 and 1057 cm^{-1}. As oxidation time increases further, the band at 463 cm^{-1} increases in intensity but does not shift. The band at 1096 cm^{-1} slightly shifts to a higher frequency (1103 cm^{-1}) after exposure for 100 h. Silicate glass shows intense bands at 1103 and 463 cm^{-1}, as shown in Fig. 5b.

It is known that a glassy phase is formed on the surface layer after long oxidation times, as mentioned above. Thus, the bands at 1103 and 463 cm^{-1} for 100 h oxidized sialon can be ascribed to the vibrational modes of silicate glass, while the band at 1057 cm^{-1} is in fair agreement with the frequency of the IRRS band of ordinary window glass in which various impurities are contained. Window glass shows the band at 463 cm^{-1}, which is of identical frequency to that of oxidized sialon. These bands may be ascribed to the presence of a glass phase. The 1057 cm^{-1} band appears to shift to 949 cm^{-1} after exposure for 100 h, as shown in Fig. 4a. The intense band at 949 cm^{-1} cannot be explained at the present stage. It is known that metallic impurities diffuse into the surface SiO_2 layer from grain boundaries of sialons [15, 16]. This results in the formation of an impurity-rich glassy phase [15].

In an IR transmission study of $Na_2O \cdot xSiO_2$ glass ($x = 2$, 3, 4 and 5), the band ascribed to the Si–O stretching vibration has been observed at 1038 cm^{-1} for $x = 3$ [23]. The band has split into two at 1066 and 964 cm^{-1} for $x = 2$. This decrease in frequency for the 964 cm^{-1} band has been explained by a decrease in the force constant due to the interaction of the non-bridging O atom of the –Si–O– with the Na^+ ion to form an ionic bond. Such a phenomenon has been observed in silicate glasses containing oxides [9, 17]. The behaviour of the 949 cm^{-1} band of oxidized sialon can be explained in a similar manner to those of silicate glasses, that is, the impurities decrease the order of the silicate glass network, resulting in the decreased force constant of the Si–O bond. Accordingly, the band shifts to lower frequency.

Thus, after exposure for 100 h, the outer surface is wholly enveloped in the glass phase, and cristobalite and mullite phases have not been observed by IRRS, in contrast to X-ray diffraction. This may be related to

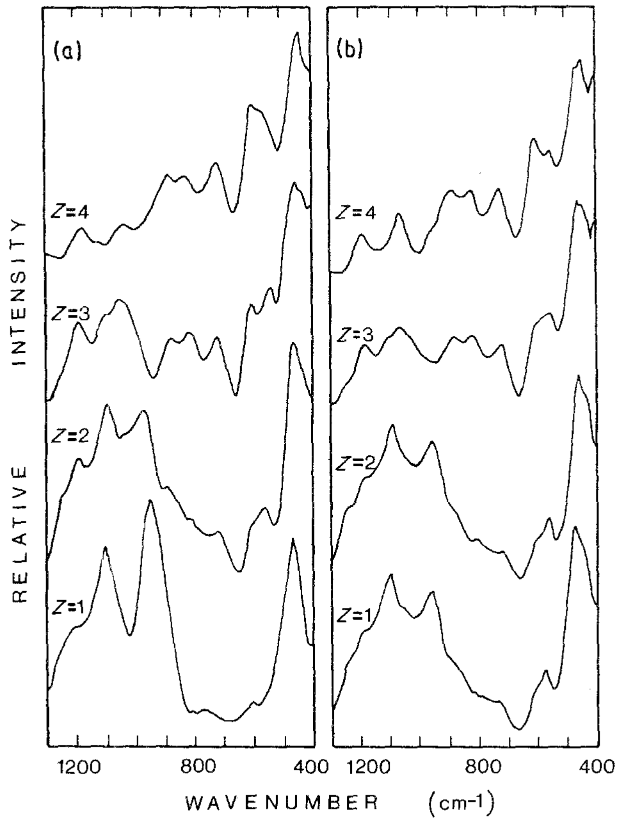

Figure 6 IRRS spectra of sialons oxidized in the systems Si_3N_4–Al_2O_3–AlN (a) and Si_3N_4–SiO_2–AlN (b). Oxidation was conducted for 100 h at 1300° C.

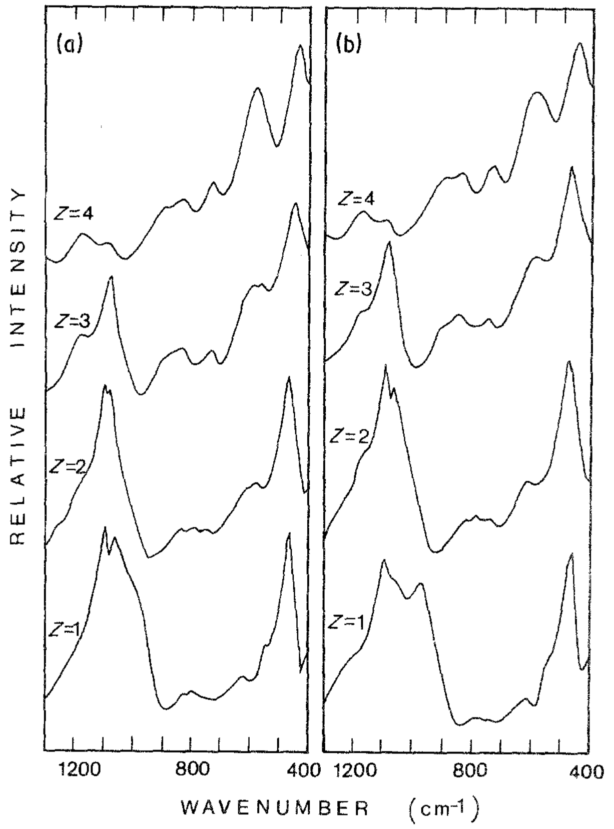

Figure 7 IRRS spectra of sialons oxidized in the systems (a) Si_3N_4–Al_2O_3–AlN and (b) Si_3N_4–SiO_2–AlN. Oxidation was conducted for 100 h at 1200° C.

the limitation of the depth of penetration of light (about 0.5 μm). Therefore, it is considered that the signals from cristobalite and mullite are prevented by the increase of glass layer thickness with time.

In the oxidation of sialon with $z = 4$, X-ray diffraction investigation has shown that the principal component of the oxidized layer is mullite and the cristobalite phase is not observed [16]. The IRRS spectrum of sialon oxidized for 100 h (Fig. 4b) is very similar in overall contour to that of mullite (Fig. 5c). The presence of a glass phase was not detected, because cristobalite was not formed on the oxidized surface of sialon with $z = 4$ [16]. After exposure for 30 min at 1300° C, the bands ascribed to the vibrational modes of mullite were observed in the IRRS spectrum. The bands increase in intensity with increasing oxidation time, as shown in Fig. 4b. The bands ascribed to sialon remain up to 1 h oxidation but cannot be observed after 10 h oxidation. Consequently, the IRRS spectrum shows the presence of the mullite phase alone on the oxide layer after long oxidation times.

Fig. 6 shows the IRRS spectra of the other members of sialon after exposure for 100 h at 1300° C. There is no large difference in the spectra of both systems (Si_3N_4–Al_2O_3–AlN and Si_3N_4–SiO_2–AlN) except that in sialons with $z = 1$ the corresponding bands mutually show a little difference in intensity. However, this is not a substantial difference. In both systems, the spectrum of sialon with $z = 3$ is close to that of sialon with $z = 4$, i.e. mullite, while the spectrum of sialon with $z = 2$ is close to that of sialon with $z = 1$, i.e. glass phase. The spectra of sialons with $z = 2$ and 3 in the course of the oxidation process are similar to those of sialons with $z = 1$ and 4, respectively. When z increases, the mullite phase is observed to increase and the glass phase to decrease.

Fig. 7 shows the IRRS spectra of sialons in both systems after exposure for 100 h at 1200° C. There are no large differences in the spectra with corresponding z-value between the systems, except in the spectra of sialons with $z = 1$. The corresponding band at 972 cm^{-1} of sialon in the Si_3N_4–SiO_2–AlN system has not been clearly observed in sialon in the Si_3N_4–Al_2O_3–AlN system, but is observed as the shoulder band. These spectra are similar to those of corresponding sialons oxidized for 50 h at 1300° C. The rate of weight gain on oxidation is known to increase with increasing temperature [21]. The result of the IRRS study agrees with this fact.

A substantial difference has not been observed in the IRRS spectra oxidized at 1200 and 1300° C, except that at 1300° C the formation of oxidized material is fast.

4. Conclusions

For hot pressed sialons in the Si_3N_4–Al_2O_3–AlN and Si_3N_4–SiO_2–AlN systems, IRRS spectra have been observed in the spectral range 1300 to 400 cm^{-1}. As z increased, the IRRS bands were observed to decrease in frequency in a similar manner to those of IR transmission. The decrease in frequency can be similarly explained by a decrease in the force constant of their vibrational modes.

IRRS was tentatively used to analyse the surface of oxidized sialons. The formation of cristobalite and mullite after a short oxidation time could be sensitively detected using IRRS technique. However, the change in the surface could not be observed in the X-ray diffraction spectrum after short oxidation times. The IRRS shows the presence of silicate glass and impurity-rich glass phases on the surface after 100 h oxidation. Thus, the IRRS technique is found to be a sensitive tool for changes occurring on the sialon surface by oxidation. To obtain information on the whole of the oxidation layer, it is necessary to measure the IRRS spectra as a function of depth, by removing sequential layers of the oxidized surface, because IRRS can provide a composition profile only to depths much less than 0.5 μm.

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