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Influence of Water Vapour on High-temperature Oxidation of Al_2O_3–MgO-doped Hot-pressed Silicon Nitride

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Abstract

Silicon nitride is particularly sensitive to high-temperature oxidation. The intensity of oxidation is influenced by the chemical composition of the amorphous phases present at the grain boundaries and consequently by the sintering additives responsible for their formation. The presence of water vapour increases Si_3N_4 oxidation also in intermediate temperature conditions. In this study the influence of water vapour pressure at high temperature (1200°C) on the corrosion of hot-pressed silicon nitride (HPSN) doped with Al_2O_3–MgO was evaluated. The water vapour has a great influence on the devitrification of the amorphous oxide upper layer, due to the formation of crystalline oxides (primarily cristobalite and tridymite). This process increases the oxidation rate, consequently increasing the porosity of the exposed surface. The microstructural evolution of HPSN in the presence of water vapour at 1200°C was analysed by SEM and XRD.

Siliziumnitrid ist bei hohen Temperaturen sehr oxidationsempfindlich. Die Intensität des Korrosionsangriffes hängt von den Eigenschaften der in den Korngrenzen vorhandenen amorphen Phasen und damit von den Sinterzusätzen ab, die für ihre Bildung verantwortlich sind. Die Anwesenheit von Wasserdampf beschleunigt auch bereits bei geringen Temperaturen die Oxidation von Si_3N_4. In dieser Arbeit wird der Einfluß der Partialdruckerhöhung des Wasserdampfes auf die Oxidation bei hohen Temperaturen (1200°C) für heiß-gepreßtes Siliziumnitrid beschrieben, welches mit Al_2O_3–MgO dotiert wurde. Wasserdampf zeigt einen großen Einfluß auf das Auskristallisieren der amorphen Oxid-Schicht, wobei Siliziumoxid in Cristobalit und Tridymit umgewandelt wird. Dieser Vorgang führt zu einem Anstieg der Porosität und bedingt damit eine Erhöhung der Oxidationsgeschwindigkeit. Die Gefügeentwicklung der untersuchten Proben wurden mittels SEM und XRD studiert.

Le nitrure de silicium est très sensible aux milieux oxydants à haute température. L'intensité de la corrosion dépend des caracteristiques de la phase vitreuse et donc des additifs utilisés dans le processus de frittage. La présence de vapeur d'eau accélère l'oxydation du nitrure de silicium, même pour des températures non élevées. On décrit ici l'influence de l'augmentation de la pression partielle de vapeur d'eau sur l'oxydation à 1200°C d'échantillons HPSN dopés par Al_2O_3–MgO. La vapeur d'eau a une grande influence sur la devitrification de la couche amorphe d'oxyde, avec la cristallisation de l'oxyde de silicium en cristobalite et tridymite. Ce processus augmente la vitesse d'oxydation à la suite de l'augmentation de porosité qui en dérive. L'évolution microstructurale des échantillons testés a été suivie au SEM et par XRD.

1 Introduction

The use of silicon nitride components in advanced technology is dictated by their oxidation resistance. MgO-doped silicon nitride was the first HPSN example to be studied and its behaviour in various

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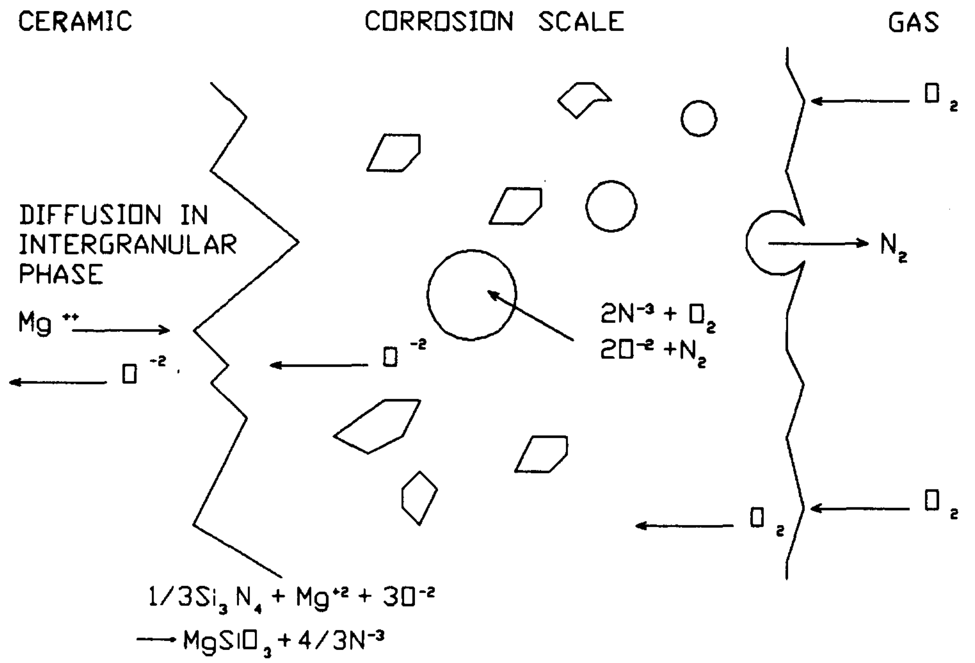

Fig. 1. Mechanism of oxidation of MgO-doped Si_3N_4.[2]

environments is well known. However its oxidation resistance is influenced both by its MgO concentration[1] and by the impurities or other additives present.

Its oxidation rate follows the parabolic law, and can be expressed by the equation:

$$W^2 = kt + c$$

where W is the weight increase, t the oxidation time, k the parabolic rate constant, and c is a constant that takes into account the reaction which has already developed.

The oxidation of MgO-doped Si_3N_4 is controlled by the diffusion rate of Mg^{++} ions through the corrosion scale, in fair agreement with the process described by Cubicciotti & Lau[2] and shown in Fig. 1. Cubicciotti & Lau explain the influence of the MgO additive on the oxidation process making the following considerations: the silicon nitride probably dissolves in the corrosion scale, which is a silicate phase, and the dissolved nitride reacts with molecular oxygen which has penetrated into the scale. As magnesium diffuses out of the bulk of the material into the corrosion scale, it reacts locally with silicon nitride to dissolve it. This process increases the nitride concentration in the melt and, subsequently, the oxidation rate. The migration of magnesium towards the corrosion scale corresponds to a variation in chemical composition from the bulk to the surface of the ceramic material, involving a shift of phase equilibrium in different compatibility triangles of the Si_3N_4–MgO–SiO_2 system,[3] each one

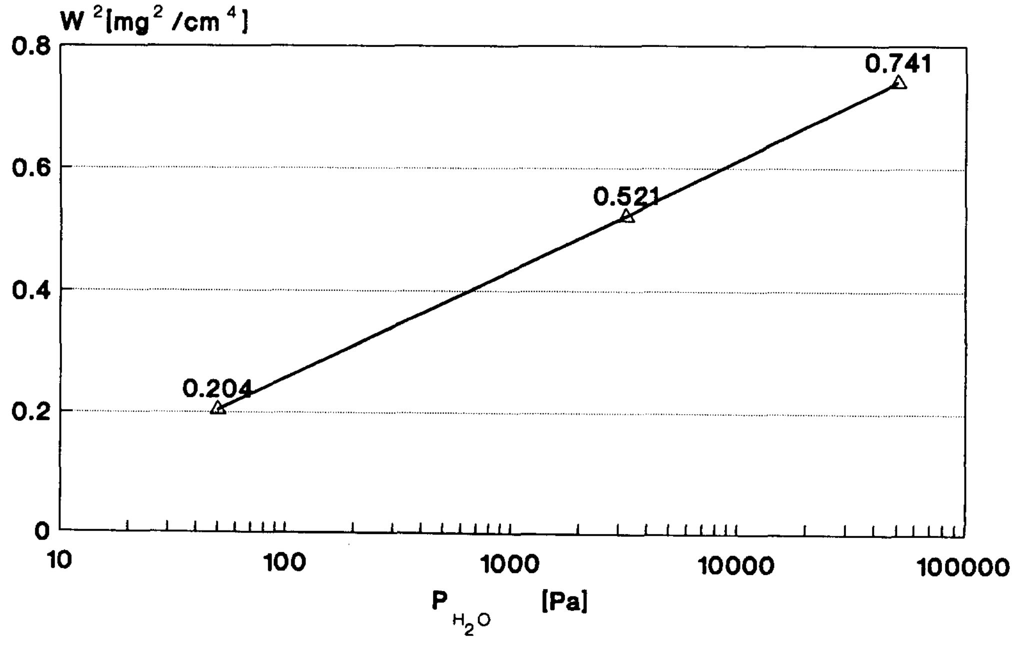

Fig. 2. Weight gain of the samples after the tests.

characterized by an eutectic with its own chemical composition and melting temperature. This process can promote the formation of liquid phases at intermediate temperatures. The melting point of these eutectic phases can be further lowered by the presence of impurities. The presence of liquid increases the ionic mobility and, consequently, the oxidation rate. Further work by Clarke[4] substantially agrees with the above model.

2 Wet Oxidation

Few data are available on the influence of water vapour on silicon nitride oxidation. However Contet *et al.*[5] demonstrated that at temperatures higher than 300°C in the presence of high humidity, the oxidation of Si_3N_4 increases as water vapour pressure increases. Singhal[6] pointed out that the oxidation of silicon nitride and carbide is promoted by the presence of water vapour, which acts as a catalyst for the devitrification of the SiO_2 layer formed during the oxidation process. A higher oxidation rate may result, according to Singhal, from a reduction of viscosity of the surface oxide, and therefore from an increased diffusion rate of additives through this layer. The oxidation reaction can be described by the following equation:

$$Si_3N_4(s) + 6H_2O(g) = 3SiO_2(s) + 4NH_3(g)$$

or, better, at temperatures above 800°C:

$$Si_3N_4(s) + 6H_2O(g) = 3SiO_2(s) + 2N_2(g) + 6H_2(g)$$

Sato *et al.*[7] propose that the oxidation rate is independent of water vapour at pressures higher than 1·5 kPa; this would demonstrate that the diffusion rate of water vapour as OH^- and O^{2-} ions through the oxide layer is not the rate-determining step in the oxidation process.

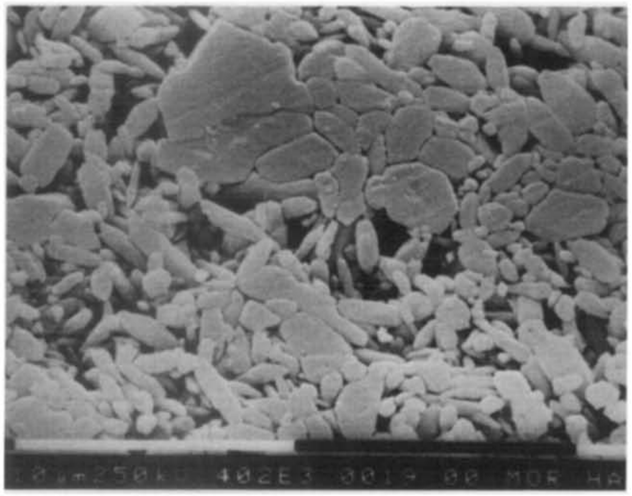

Fig. 3. Silicon nitride before oxidation. Secondary electron image show the microstructure and grain size.

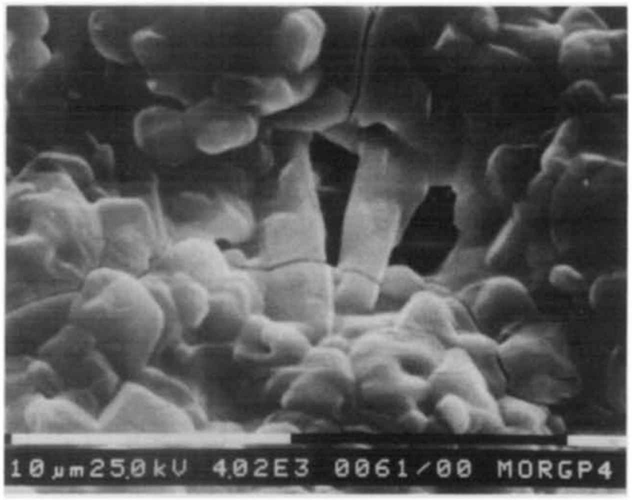

Fig. 4. Silicon nitride oxidized at 1200°C. Partial pressure of water vapour in the air flow equal to 50 Pa.

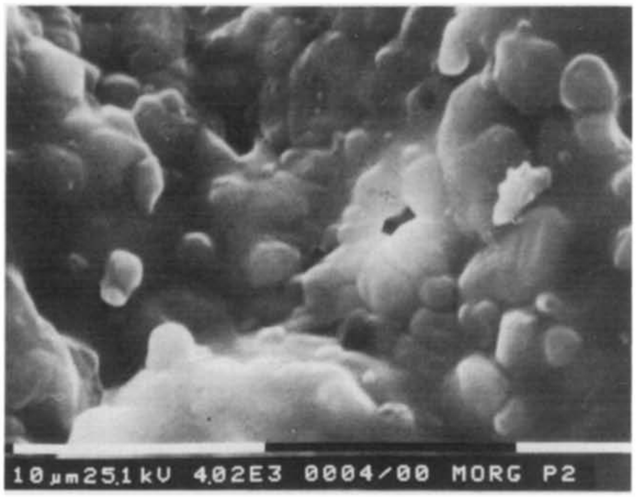

Fig. 5. Silicon nitride oxidized at 1200°C. Partial pressure of water vapour in the air flow equal to 3·2 kPa.

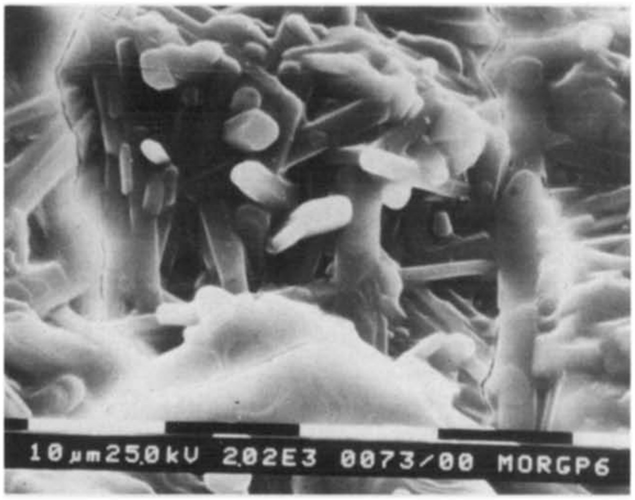

Fig. 6. Silicon nitride oxidized at 1200°C. Partial pressure of water vapour in the air flow equal to 50 kPa.

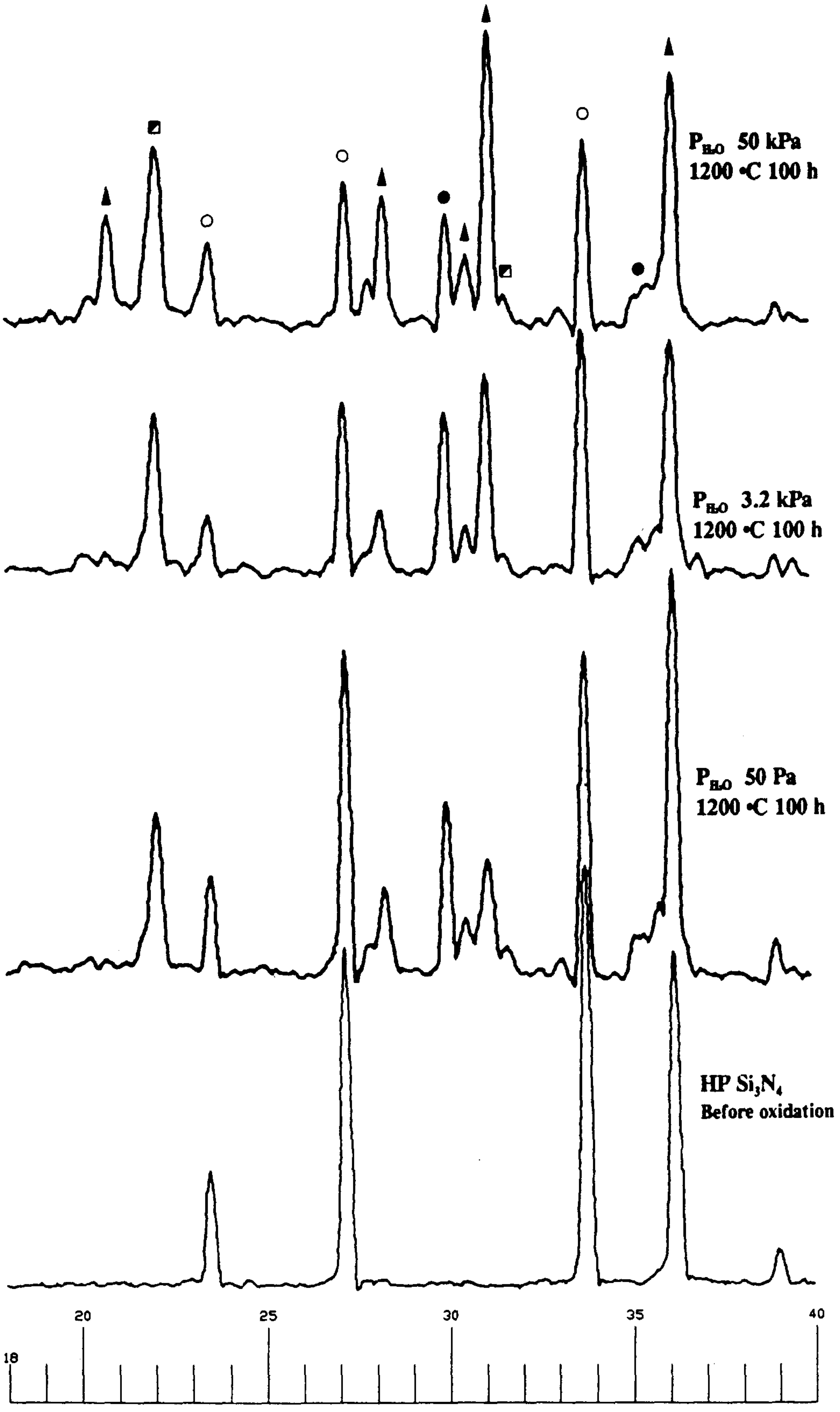

Fig. 7. XRD profiles of oxidized HP-Si_3N_4. (▲) Estatite ($MgSiO_3$), (●) CaO.Al_2O_3, (■) α-cristobalite (SiO_2), (○) β-Si_3N

3 Experimental

Specimens of commercial hot-pressed silicon nitride, with 2·5% wt of Al_2O_3 and 2% wt of MgO (Morgan Matroc Ltd, UK), supplied as small plates with dimensions of 10 × 10 × 4 mm, were used for the oxidation tests. In Table 1 the chemical composition of the samples, from EDS analyses, as well as some structural parameters are reported. Before the oxidation tests, the specimens were surface-polished with SiC sandpaper (800 grit) and synthetic cloths with diamond pastes (6, 3 and 1 μm), and cleaned in an ultrasonic bath in acetone. Before and after each test the samples were weighed by means of a precision balance. In a typical oxidation run, the sample was placed in a platinum holder inside a quartz-tube furnace, at 1200°C for 100 h. The oxidizing atmosphere in the furnace was obtained by means of an air flow of 2 litres/h. The partial pressure of water vapour in the air flow was adjusted to 50 Pa, 3·2 kPa and 50 kPa respectively, by flowing the air through silica gel at 25°C, and by bubbling through distilled water at 25°C and 85°C. After oxidation, the samples were examined by X-ray diffraction (XRD) and by scanning electron microscopy (SEM).

Table 1. Characteristics of the material used in the experimentation

EDS microanalysis (at %)					
Al	*Mg*	*Ca*	*Fe*	*Cr*	*Si*
1·86	1·58	0·18	1·44	0·17	REM
Micro-structural parameters					
Density (g/cm^3)	*Mean grain size (μm)*	*Main crystalline phase*	*Secondary crystalline phase*		
3·19	2·5	β-Si_3N_4	FeSi		

4 Results and Discussion

The weight gain of silicon nitride oxidized during the tests is shown in Fig. 2. Increasing water vapour pressure causes a considerable weight gain, such as to demonstrate a promotion of the oxidation process. A remarkable microstructural variation of the oxidized layer was observed by SEM and XRD analyses. The micrographs of specimen surface before and after the oxidation test are shown in Figs 3–6; the results of XRD analyses are shown in Fig. 7. The most relevant microstructural variations were observed after oxidation tests performed between 3·2 kPa and 50 kPa of water vapour pressure. At high pressure a considerable growth of silicate crystals in the surface oxidized layer was observed. These results appear in fair agreement with previous studied by Maeda *et al.*[8] the water vapour causes or emphasizes the devitrification of surface amorphous mixed oxides. As a consequence of the devitrification process, the porosity of the oxide layers increases. The surface exposed to the wet atmosphere contains many bubbles, blowholes and cracks, so that new Si_3N_4 can be exposed to the oxidizing environment. As a result, the water vapour strongly increases the oxidation intensity. This phenomenon is also seen in XRD analyses (see Fig. 7). Exposition at high temperature (1200°C) is also responsible for the enrichment of impurities in the glassy silica upper layer (as shown in Fig. 8). The crystalline phases of cristobalite, estatite ($MgSiO_3$), clinoestatite ($CaO–Al_2O_3$) and the silicate phases such as kaonite ($(MnMg)_2–SiO_6$) are, however, easily identified. As the water vapour pressure increases (from 50 Pa to 3·2 kPa), the cristobalite peak progressively increases; at 50 kPa, the tridymite is no longer detected, while the cristobalite peaks become more

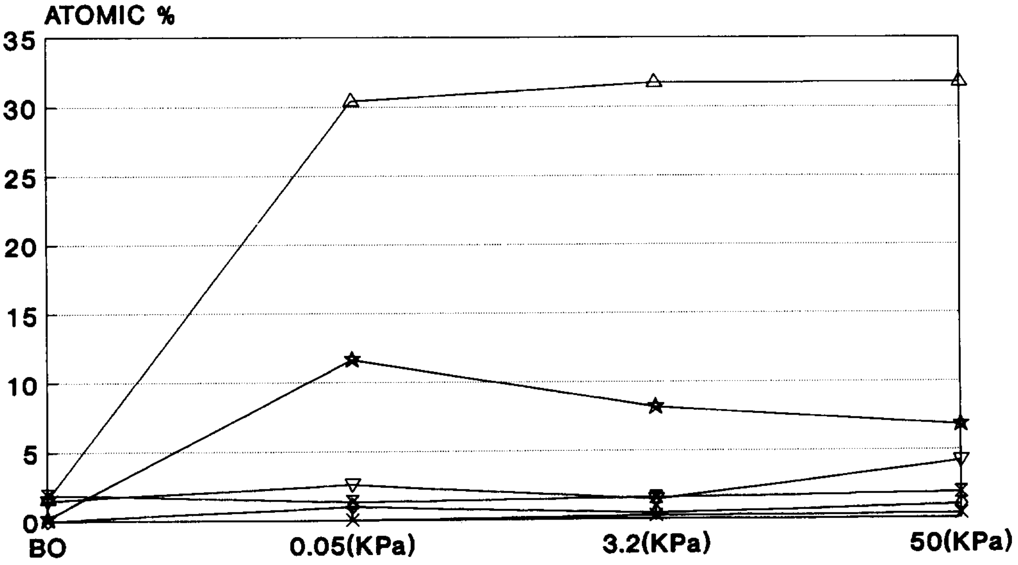

Fig. 8. Average concentration of impurities contained in glassy and crystalline phases of the upper layer (EDS). (△) Mg, (⧗) Al, (▽) Fe, (★) Ca, (×) K, (◇) Mn.

intense. The influence of air humidity on different kinds of HPSN sintered with Y_2O_3 and ZrO_2 was also evaluated. The specific weight gains of these samples are lower than the corresponding values for MgO-doped Si_3N_4; however, increasing values of weight gain were measured at increasing water vapour pressures. The presence of water vapour particularly affects the chemical composition of the surface, by promoting the growth of an oxide layer with a high content of impurities, such as Al, K and Mg.

5 Conclusions

Si_3N_4 sintered with additives is particularly sensitive to oxidizing environments. The amount and the chemical composition of the additives strongly influences the corrosion resistance of HPSN. The presence of water vapour can promote surface oxidation, by affecting the microstructure of the outer layer. The devitrification of surface amorphous silica and the consequent growth of different crystalline phases (cristobalite and tridymite mainly) can induce the origination of micro- and macro-cracks, bubbles and blowholes in the corrosion scale. As a consequence, new Si_3N_4 is exposed to the wet oxidizing atmosphere and the oxidation process is intensified.

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