

Diffusive Phenomena at Si₃N₄/Glass Interfaces

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Keywords: silicon nitride, glass, diffusion, interfaces

Abstract. The chemistry of glass-ceramic interface was studied in two different diffusion couples, YSiAlO/Si₃N₄ and SiO₂/Si₃N₄. Experiments were performed at 1500°C for 2 hours in argon atmosphere. The couples were analyzed through SEM and EDS to draw the concentration profiles across the interface. It was observed that aluminosilicate glass infiltrates within the ceramic secondary phase and detaches the silicon nitride grains. The free grains move toward the glass surface either by solution-precipitation or floating. The glass also dissolves silicon nitride grains and the nitrogen is absorbed, forming a broad zone of YSiAlON glass. In the SiO₂/Si₃N₄ couple there was extensive cation diffusion from the silicon nitride grain boundary to the silica glass, forming an aluminosilicate intermediary phase. It was observed crystallization of some yttrium-rich phase at the interface.

Introduction

Diffusion is a very important process for both solid state chemistry and material engineering. Sintering, grain growth, creep and oxidation are some material science field in which diffusion plays a meaningful role. Diffusion in metals has been studied for long time. Therefore, diffusion models and theory are usually based on it [1]. Oxide ceramics are also largely studied due to their electronic applications as ionic conductors [2]. For covalent ceramics specific diffusion experiments have been done mainly in attention to joining with metals [3].

Among the covalent ceramics, silicon nitride has many high temperature applications, such as engine components, gas turbines and refractories. In such cases ceramic/glass interface can occur in two conditions: in the production of complex components by ceramic-ceramic joints and in the final application due to oxidation reactions or slag contact. Therefore, the ceramic/glass interface and the physical-chemical process at its neighborhood becomes an important matter, to improve the silicon nitride-based ceramics performance.

In recent years, several works have been published about silicon nitride/glass interface, contributing to improve knowledge about its structure and chemistry.

Pan [4] was able to show that the Si₃N₄/SiO₂ interface is sharp, with just some tetrahedrons mismatched to ensure the structural relaxation. His work figure out that the intermediary layer often viewed in TEM images could be just an optical distortion due to some microscope parameters instead a Si₂N₂O interfacial product.

In Si₃N₄ whisker-reinforced ceramics Becher et al. [5] observed, by HREM, a very sharp interface between silicon nitride whiskers and a YSiAlO glass film while a broad intermediary nitrogen-rich phase was observed when using YSiAlON glass.

Weldon et al. [6] show that YSiAlO glasses can be successfully used as adhesive to pressureless join of silicon nitride ceramics at 1600°C for 1 hour. Evidences of solution and

reprecipitation of β - Si_3N_4 grains across the joint were observed and the glass was completely absorbed by the grain boundaries. The same microstructure was observed for joints under pressure with nitrogen-containing glass (YSiAlON). For pressureless joints YSiAlON glass did not show any reaction with silicon nitride bodies. On the other hand, Rongjun et al. [7] observed that, for joints prepared at 1600°C for 30 minutes, YSiAlO glass remains as an intermediary layer with some Si_3N_4 grains disperse in it.

Taira et al. [8] show that silicon nitride is etched by contact with aluminosilicious slags. They observed that the etching rate depends on the nitrogen diffusivity through the slag. The nitrogen released by the silicon nitride grains dissolution is absorbed by the slag until a saturation limit, as also determined by Sun et al [9].

During the oxidation of silicon nitride-based ceramics a glass/ceramic interface is produced *in situ*. The cation migration from the ceramic secondary phase to the new oxide scale is very important to the reaction kinetics. Nevertheless, the mechanism involved still misunderstood [10].

In the present work are studied $\text{Si}_3\text{N}_4/\text{SiO}_2$ and $\text{Si}_3\text{N}_4/\text{YSiAlO}$ interfaces focusing the phenomena that take place at their neighborhood, such as diffusion, dissolution and new phase formation.

Experimental Procedure

Raw materials used to prepare the ceramic were Si_3N_4 (LC 12 - HC Stark), Y_2O_3 (PA - Merck), Al_2O_3 (A 16 - Alcoa) and SiO_2 (Quartz - Fluka). Silicon nitride rods were prepared by hot pressing for 1 hour at 1750°C in a 20 mm graphite die. The nominal powder composition was, in wt%, 94 Si_3N_4 - 4 Y_2O_3 - 2 Al_2O_3 . These rods were sliced with a high-speed diamond saw and polished until 1 μm diamond paste. The discs border was cut off to eliminate any either porosity or contamination.

High purity silica glass plates (Balzers) were cut in same diameter of ceramic discs and polished with 1 μm Al_2O_3 slurry. Yttrium aluminosilicate glass (YSiAlO) was prepared melting a 20 Y_2O_3 - 20 Al_2O_3 - 60 SiO_2 (mol%) powder mixture in a Pt-Rh crucible at 1500°C for 1 hour. The melt was cast on a steel plate and crunched.

Finally, the diffusion couples were assembled placing either one disc of silica glass (couple S) or one piece of YSiAlO glass (couple Y) on the silicon nitride discs. Annealing was performed in a vertical graphite furnace (Astro) at 1500°C for 2 hours within argon atmosphere. Afterwards couples were transversally cut and polished. The microstructure around interface was observed by SEM and concentration profiles were obtained by EDS.

Results and Discussion

Fig. 1a shows the SEM image of the S couple. One can see that the interface is sharp with some yttrium-rich sites at the silica portion. The silicon nitride portion is composed by two distinct phases. The major phase is discontinuous, consisting of silicon nitride grains with very low diffusion coefficient. The secondary phase is a continuous yttrium aluminosilicate amorphous film.

This glassy phase, located at the grain boundaries, creates a low energy diffusion path. Hence, in couple S both yttrium and aluminum atoms move from ceramic to glass uniquely through silicon nitride grain boundaries. The interface, from the silica portion viewpoint, acts as a discontinuous cation source as sketched in Figure 1b. This fact can explain the isolated yttrium-rich sites observed. Such sites are probably $\text{Y}_2\text{Si}_2\text{O}_7$ produced according to Eq. 1, when the Y^{3+} concentration at the silica portion attains saturation. A continuous layer at the ceramic/glass interface is expected for longer heat treatments [11].



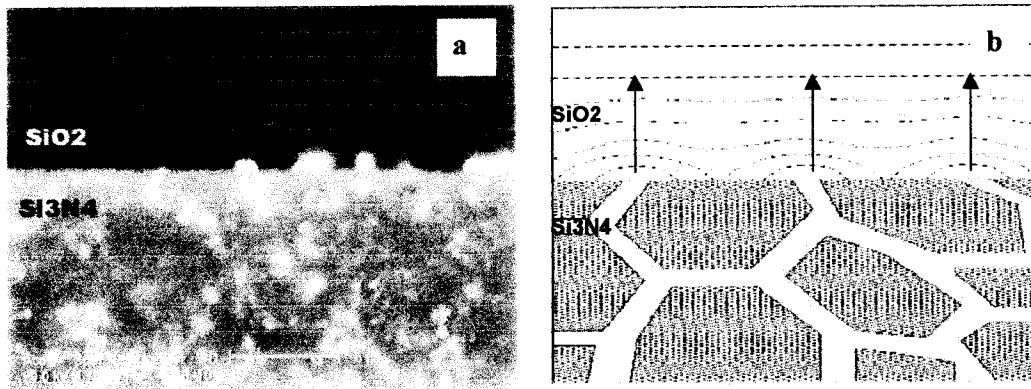


Fig. 1: a) SEM image of couple S interface.
b) Model of cation diffusion from grain boundaries to silica.

In this kind of reaction the driving force is the free energy change of surface. The reaction rate depends on the atomic transport across the interface propelling by chemical gradient between the two portions of the couple. Then the interface should act as an atomic source/sink in order to maintain the equilibrium between the two portions.

Two situations are possible depending on the nature of the interface [12]. In the first one the transport across the interface is fast enough to held the equilibrium at neighborhood. The transport rate depends on the atomic mobility in the bulk of each couple portion. Such condition is called "ideal" and the process kinetics is "diffusion controlled". On the other hand, when the transport across the interface is slower than the mobility through the bulk, the equilibrium near the interface can not be held and the kinetics is "interface controlled". In practice, however, actual interfaces have a mixed behavior.

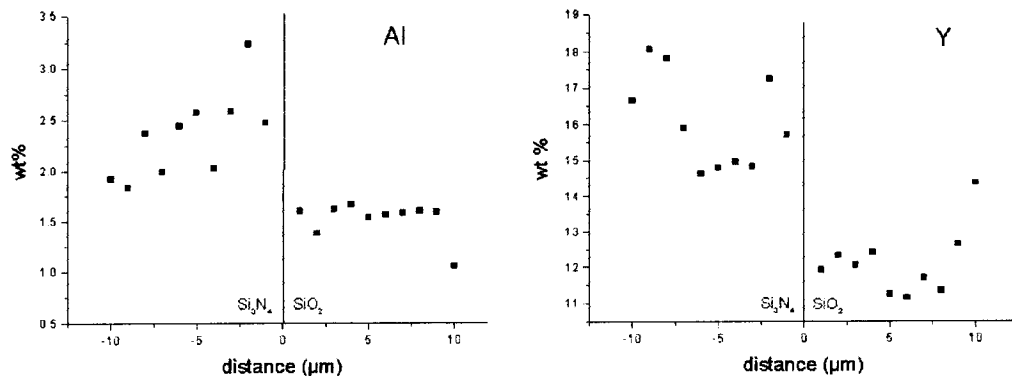


Fig. 2: Concentration profiles for couple S

The concentration profiles (Fig. 2) show that couple S interface has a non-ideal behavior. Both yttrium and aluminum atoms move from ceramic to silica glass due to the chemical gradient. The concentration profiles shows a hoarding zone in the ceramic portion and a depletion zone in the silica glass portion. It denotes that transport across the interface is slower than mobility in bulk phases.

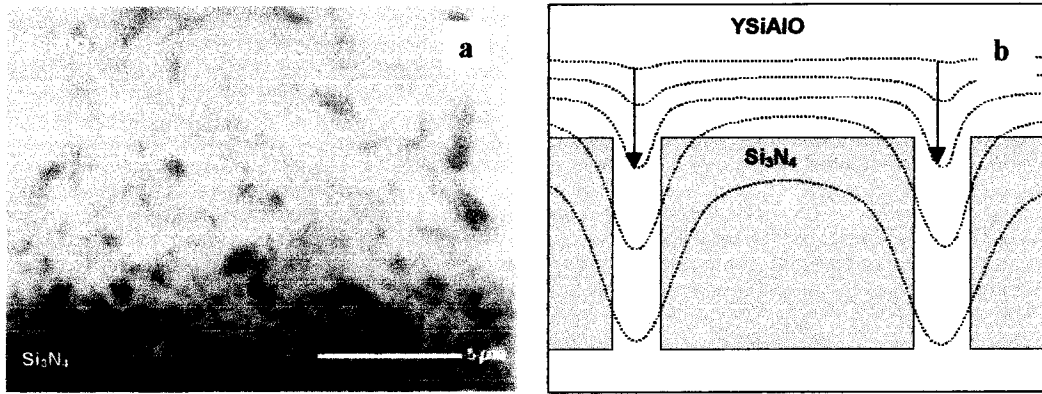


Fig. 3: a) SEM image of couple Y interface.
b) Glass infiltration through the boundaries and grain dissolution

Fig. 3a shows the SEM image of couple Y interface. One can see that the interface is very diffuse and do not correspond to the original interface position. The presence of silicon nitride grains in the glass portion is remarkable. In this couple the microstructure of ceramic is the same as in couple S. The grains are detached from the ceramic portion due the glass infiltration into the secondary phase of ceramic, as sketched in Figure 3b. Some features of the grain boundary, such as amorphous structure, non-equilibrium state and high concentration of defects enhance this process.

Fig. 4 shows the concentration profiles for couple Y. Besides corrode the ceramic secondary phase YSiAlO glass dissolves the silicon nitride grains as can be seen by the nitrogen profile. Comparing SEM image and nitrogen concentration profile it is remarkable that the ceramic dissolution is faster than the glass infiltration. Nitrogen has a high mobility in the glass, forming a broad range of YSiAlON glass. The nitrogen dissolved into the glass can be incorporated in the network substituting oxygen atoms in the SiO_4 tetraedra [6,8].

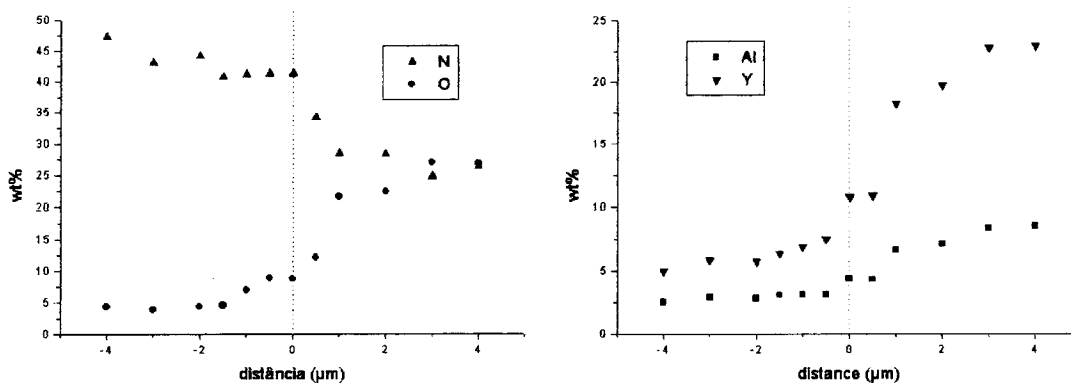


Fig. 4 : Concentration profiles for couple Y

Murakami and Yamamoto [13] have shown that the maximum solubility of Si_3N_4 within a YSiAlO glass is about 6 mol% at 1550°C. The incorporation of nitrogen by YSiAlO glass changes both the glass transition temperature and the softening temperature, from 884°C to 945°C and from 934°C to 1015°C, respectively [6,14]. Hence, the rate of corrosion should

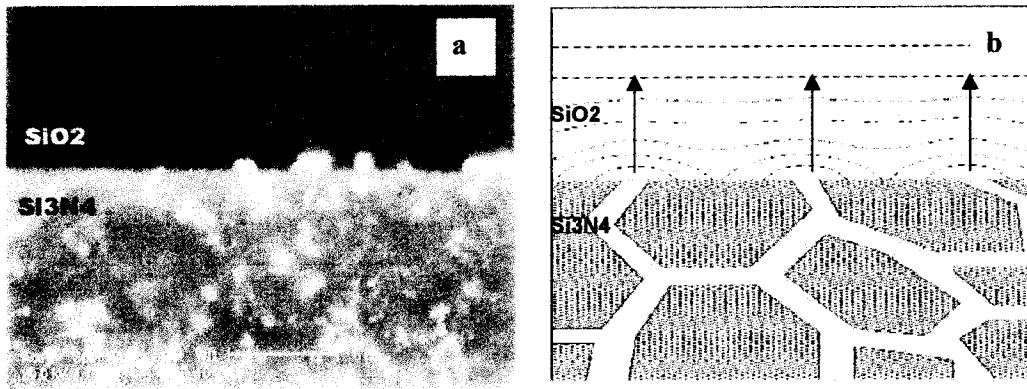


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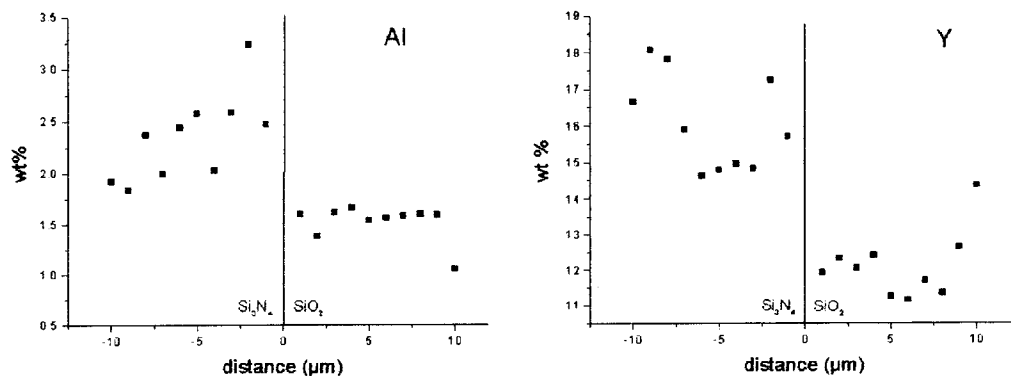


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decrease as the nitrogen saturation is achieved. To minimize this effect, Taira et al. [8] used the rotating specimen method to study the dissolution rate of silicon nitride into molten slags.

At first sight, the glass infiltration within the grain boundaries is faster than the grain dissolution inasmuch as some silicon nitride grains are located far from the interface. Although the interface have been moved due to the glass infiltration, the grain distribution within the glass portion points that, once detached from the ceramic portion, the silicon nitride grains can float toward the glass surface. The silicon nitride density is 3.19 g/cm³ while the density of YSiAlO glass is 3.50 g/cm³ [14] and of YSiAlON glass is 3.78 g/cm³ [6]. Such difference should be enough to promote grain floating. Also the grains present in the glass could come from precipitation of sialon in the nitrogen-rich zone. Evidences of the solution reprecipitation of β -sialon were found at temperatures as lower as 1400°C [6].

Conclusions

The behavior of silicon nitride/glass interface changes according to the glass composition. For high purity silica glass a sharp interface was observed. The cation transport across this interface was slower than the cation diffusivity through the bulk phases. There was an interfacial reaction forming a discontinuous thin layer of a crystalline phase. In a broad extension the glass composition changes to an yttrium aluminosilicate glass. There was no remarkable interface displacement.

For YSiAlO glass a diffuse interface was observed. Glass can infiltrate within the grain boundaries and dissolves the silicon nitride. Grains at the interface are detached and float toward the glass surface due to either hydrostatic force or solution-reprecipitation process.

For long-term experiments one can expects some alteration in the interface behavior. In couple Y the displacement rate of interface should decrease due to the changes in the glass, such as nitrogen saturation and viscosity increase. On the other hand, the behavior of couple S should get the same of couple Y, due to the changes in chemical composition.

Acknowledges

The authors are grateful to CNPq and Fapesp for financial support.

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Advanced Powder Technology III

doi:10.4028/www.scientific.net/MSF.416-418

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doi:10.4028/www.scientific.net/MSF.416-418.603