# INFILTRATION OF POROUS ZIRCON PREFORMS WITH ALUMINA PRECURSOR

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**Abstract** A process is described which involves infiltration of aluminum nitrate into partially sintered (porous) zircon bodies. Infiltration kinetics were studied using infiltration curves with two distinct regions. The final infiltrated samples were sintered at 1600 °C for 2 h and yielded specimens containing the tetragonal zirconia. The experimental results show that in spite of the similar porosity of the infiltrated preform and of pure zircon sintered at 1600 °C, the former has a higher flexural strength and fracture toughness due to the incorporation of the $ZrO_2$ particles and the elongated mullite grains resulting from the infiltration and subsequent heating of the preform.

**Key Words** Infiltration; $Al_2O_3$ precursor; zircon; mullite; mechanical properties

چکیده کار حاضر در مورد نفوذ محلول نیترات آلمینیوم به داخل بدنه متخلخل زیرکونی بحث می‌کند. کینتیک‌های نفوذ با مطالعه منحنیهای نفوذ مورد بررسی قرار گرفت و دو ناحیه تشخیص داده شد. پس از آخرین عمل نفوذ، بدنه‌ها در دمای ۱۶۰۰ درجه سانتیگراد به مدت ۲ ساعت حرارت دهی شدند و فاز زیرکونیای تتراگونال تشکیل شد. نتایج آزمایشها نشان داد که با وجود مقدار تخلخل مشابه بین بدنه نفوذ داده شده و بدنه زیرکونیای خالص ، بدنه نفوذ داده شده استحکام مکانیکی و چقرمگی بیشتری به دلیل وجود ذارت زیرکونیا و ذرات کشیده مولایت نسبت به بدنه زیرکونیای خالص به دست می‌دهد.

## 1. INTRODUCTION

Infiltration of a liquid into a porous medium can be used for producing ceramic matrix composites [1-4]. The infiltration technique may yield a second phase which improves the mechanical properties. Infiltration techniques consist of an impregnation of an organic precursor or a sol-gel system into a porous powder compact. Several impregnations are required because of the shrinkages that occur upon thermal decomposition and consolidation of the infiltrants. The intruded liquid is converted to an inorganic powder during a low-temperature heat treatment and the pores within the preform are partially occupied. The present work investigates the incorporation of $Al_2O_3$ by infiltration of aluminium nitrate into the porous zircon. It was found that both the flexural strength and toughness were increased due to the significant effect of $ZrO_2$ on improving the toughness of the ceramic matrix composite. It is felt that this system offers several advantages; first, the $SiO_2$ necessary for forming mullite is already present in zircon and secondly; the $ZrO_2$ particles needed for toughening the compact are simultaneously produced by dissociation of zircon.

## 2. EXPERIMENTAL PROCEDURE

In this work, a partially-sintered zircon (Zircosil 5; Cookson Matthey Ceramics & Materials) was repeatedly infiltrated with an aqueous solution of

aluminum nitrate ($Al(NO_3)_3.9H_2O$, Merck). Zircon powder was compacted in a 50 x 50 mm steel die at a pressure of 4 MPa. These preforms had a well defined geometry for the bars needed for measuring the four and three point bend strength. The pressed zircon powder was fired at 1100 °C for 2h in order to obtain a sufficient strength for the subsequent infiltration process. The preforms were infiltrated at room temperature with aluminum nitrate solution by fully immersing them. The process of infiltration was repeated 16 times and after each cycle of infiltration and removal of nitrate solution adhering to the specimen surfaces, the infiltrant was thermally decomposed to alumina by heating it at 600 °C (10 °C /min. 2 h). Following the last infiltration, a final sintering step was carried out at 1400 and 1600 °C (2 h). The extent of infiltration was studied by measuring the weight change of the immersed preform suspended with a wire from an electronic balance (± 0.0001 g). The extent of infiltration was calculated as $\Delta V / V_i$, where $\Delta V$ is defined as $\Delta W / D_{Solution}$, where $\Delta W$ is the weight change in a given period corresponding to the amount of intruded liquid and $D_{Solution}$ is the density of the alumina precursor solution (1.23 g/cm$^3$). $V_i$, the total volume of residual pores in the specimen after the ith infiltration cycle can be expressed as

$$Vi = W_0 (1/ D_0 - 1/ D_{zircon}) - (W_i - W_0)/ D_{alumina}$$

Where $W_0$ and $W_i$ are the dry weight before infiltration and after the ith infiltration, respectively. $D_{zircon}$, $D_{alumina}$ are the theoretical densities of zircon (4.67 g/cm$^3$) and γ-alumina (3.47 g/cm$^3$), respectively and $D_0$ is the bulk density of the sample before infiltration.

The viscosity of the aluminum nitrate solution was evaluated with the help of a Brookfiled digital rheometer (Model DV-III). Density and porosity were determined according to ASTM-C373. The four-point flexural tests were conducted with a support span of 40 mm and a load span of 20 mm on testing bars with dimensions of 48 X 5 X 3 mm. The fracture toughness was tested on the bar samples according using SENB method in three point loading. Scanning electron microscopy (SEM) was performed on polished and thermally etched samples and the different phases were distinguished by using energy-dispersive spectroscopy (EDS) and backscattered electron images.

## 3. RESULTS AND DISCUSSION

The infiltration extent of the preforms during the

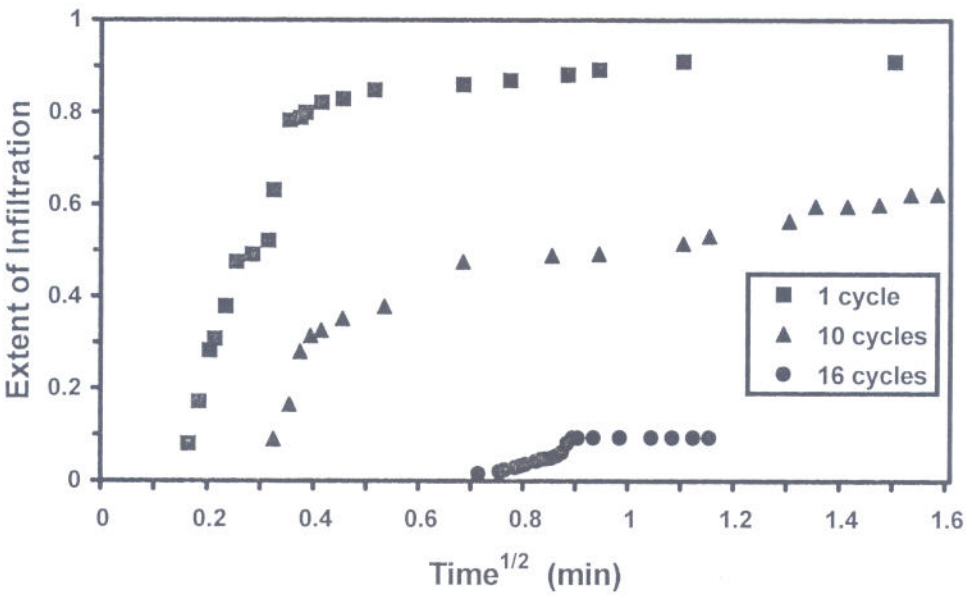


**Figure 1**. Infiltration cycles as a function of (time)$^{1/2}$ for aluminum nitrate solution into the porous zircon.

first, tenth and sixteenth infiltration cycles is shown in Figure 1. One reason for the high intrusion rate especially for the first cycle can be attributed to the low viscosity (1.1 poise) of the liquid precursor [5]. From the form of the infiltration curves (Fig. 1), two distinct regions are distinguishable. In the first region, a large amount of liquid precursor penetrates into the pores of preform due to the capillary pressure and the second region reveals the gradual fill of the pores by the extraction of the entrapped air. Further consideration on Figure 1 reveals that by increasing the number of infiltration cycles, the extent of infiltration reduces. This can be explained by considering two phenomena. First, as expected, in each infiltration cycle, the alumina precursor is precipitated in the zircon pores and hence the free space of the pores decreases, as the porosity measurements confirm (Fig. 2). Second, during the heat treatment of the infiltrated sample the amount of the formed gel [$Al(OH)_3$] increases from the interior to the surface by migration of precursor molecules. This leads to a decreasing of the free space of the pores in the surface of preform [6]. Figure 3 shows the amount of alumina in zircon preform calculated from the weights of the specimens before and after infiltration, and subsequent calcination. As expected, by increasing the infiltration cycle, the cumulative amount of alumina introduced into the porous zircon increases. However, after sixteenth infiltration no considerable weight increase was observed in subsequent infiltration cycles.

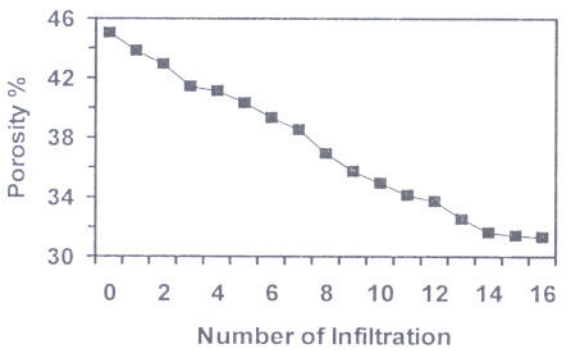


**Figure 2** . Porosity of zircon preform as a function of infiltration number.

The x-ray patterns of pure zircon (Z) and the infiltrated (MZ) samples are shown in Figure 4 after sintering at 1600 °C for 2 h. Mullite peaks are distinguishable in infiltrated sample due to the reaction between introduced alumina precursor and $SiO_2$ of the zircon. As Figure 4a reveals, monoclinic zirconia peaks appear due to the dissociation of zircon at 1600 °C. These peaks sharpen in the MZ sample at 1600 °C due to the incorporation of the alumina precursor and the enhanced dissociation of zircon by the reaction with $SiO_2$. Figure 5 shows the effect of the heating conditions on the density of the Z and MZ samples. The zircon preform fired at 1100 °C and infiltrated with precursor solution has a higher density than that of pure zircon due to the incorporation of the alumina particles. By increasing the sintering temperature to 1600 °C, the difference between densities of Z and MZ samples increases due to the more dissociation of zircon and consuming of alumina powders (Fig. 5).

Table 1 exhibits the flexural strength of the samples at different sintering temperatures. By introducing the alumina particles into the porous zircon sample, the flexural strength improves. By sintering the samples at 1400 °C, the Z sample showed higher strength than the MZ sample due to the lower porosity of the former sample (Table 1). A higher strength was observed by increasing the sintering temperature to 1600 °C for both samples. In this case, the MZ sample displayed higher strength than the Z sample, while the concentration of porosity is nearly the same in the two samples (Table 1). The improved strength of the MZ sample can be related to the $ZrO_2$ and mullite particles resulting from the reaction between the alumina precursor and the $SiO_2$ of the zircon. The microstructure of MZ sample sintered at 1600 °C (Figure. 6) confirms the existence of zircon, mullite and zirconia grains. The acicular shape of mullite grains can increase the fracture toughness of the MZ sample, since as previously reported [7-9] the presence of elongated grains in ceramic alloys deflects the direction of propagation cracks and increase the fracture toughness. The role of $ZrO_2$ particles especially tetragonal zirconia in increasing the fracture toughness is well known [10-11].

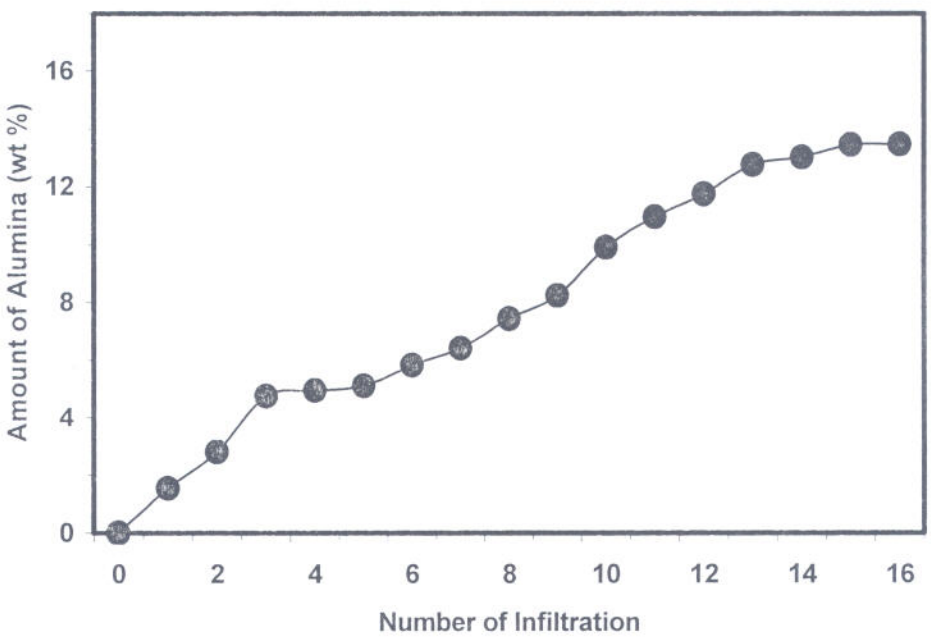


**Figure 3.** Amount of alumina incorporated into the zircon preform

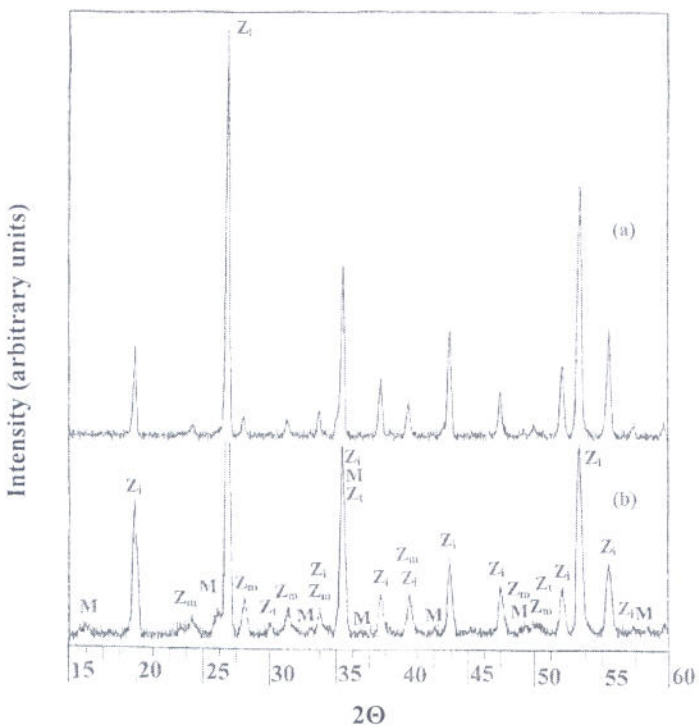


**Figure 4**. X-ray diffraction patterns of Z (a) and MZ (b) samples sintered at1600 °C for 2 h. M: mullite, $Z_i$: zircon, $Z_t$: tetragonal zirconia, $Z_m$: monoclinic irconia.

**Table 1.** Porosity and mechanical properties of samples fired at different temperatures

| Sample | Firing Temperature (°C) | Apparent Porosity % | Fracture Strength (MPa) | Fracture Toughness ($MPa.m^{1/2}$) |
|---|---|---|---|---|
| Z | 1100 | 45 | $17 \pm 5$* | - |
| | 1400 | 20.2 | $98 \pm 6$ | - |
| | 1600 | 2.8 | $179 \pm 13$ | $2.8 \pm 0.3$ |
| MZ | 1100 | 21 | $26 \pm 4$ | - |
| | 1400 | 25 | $55 \pm 15$ | - |
| | 1600 | 2.9 | $216 \pm 14$ | $4.8 \pm 0.1$ |

* Ten bars were used.

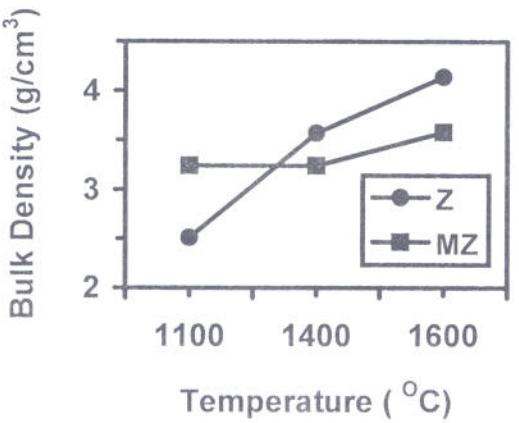


**Figure 5.** Bulk density of Z and MZ samples as a function of sintering temperature

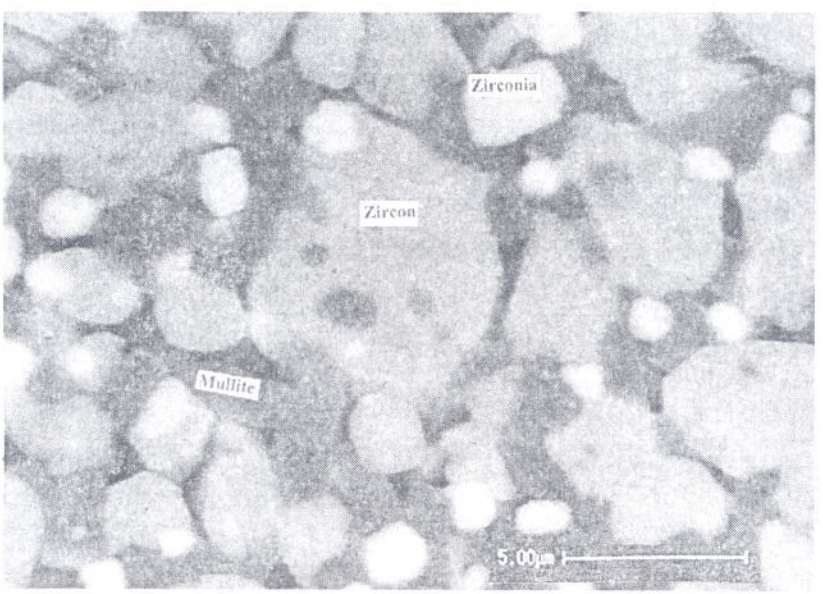


**Figure 6.** SEM micrograph of thermal etched (30 min at 1500 °C) surface of MZ sample sintered at 1600 °C for 2 h (A; Zircon, B; Zirconia and C; Mullite).

## 4. SUMMARY AND CONCLUSIONS

The fabrication of zircon/zirconia/mullite composites througha infiltration processing has been investigated. The alumina contents increase step by step by repeatedly infiltrating the zircon preform. After 16 infiltration cycles, although porosity still remained in the preform, further infiltration process could not lead to any increase in the alumina content. The infiltration curves showed two distinct regions: (a) the penetration of liquid precursor into the pores of the preform, and (b) the gradual fill of the pores. From the mechanical tests, it would be concluded that the flexural strength and fracture toughness of the preformed zircon can be improved by introducing alumina precursor due to the generation of $ZrO_2$ particles and mullite grains by the reaction between the alumina precursor and the zircon at 1600 °C.

## 5. REFERENCES


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