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MODELING INFILTRATION KINETICS OF LIQUIDS INTO POROUS ALUMINA PREFORMS

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ABSTRACT

MODELING INFILTRATION KINETICS OF LIQUIDS INTO POROUS ALUMINA PREFORMS. Alpha-alumina preform was infiltrated with different infiltrant and pressure for studying the infiltration kinetic. Effects of pre-sintering temperature, type of infiltrant, pressure and multiple infiltrations on the rate of infiltration into porous alumina preforms were described. The pore radius of alumina preform is calculated based on the preform-water system by using Washburn model. The pore radius from this model, r of 0.0147 μm is good agreement to the average pore radius found by using mercury porosity measurement, r of 0.0170 μm. The pore radius of 0.0147 μm is used to calculate the rate of infiltration, k. The k factors are 64.83 x 10^{-5} $ms^{½}$ and 27.11 x 10^{-5} $ms^{½}$ for water and $TiCl_3$ respectively without involving pressure in the calculation. On the other hand, by using pressure, the k factors are 75.14 x 10^{-5} $ms^{½}$ and 31.40 x 10^{-5} $ms^{½}$ for water and $TiCl_3$ respectively. Other formulas were also included as comparisons. The kinetic of water and titanium trichloride alumina preform system is parabolic in time or linier in square root of time.

Key words : Pre-sintering, infiltrants, pressure, multiple, pore radius

ABSTRAK

PEMODELAN KINETIK INFILTRASI CAIRAN KE DALAM PRABENTUK ALUMINA BERPORI. Telah dilakukan penelitian kinetik infiltrasi terhadap prabentuk alpa-alumina dengan tekanan dan bahan penginfiltrasi yang berbeda. Dalam studi ini ditinjau efek suhu *pre-sintering,* tipe bahan penginfiltrasi, tekanan dan infiltrasi berulang pada laju infiltrasi ke dalam prabentuk alumina berpori. Jari-jari pori prabentuk alumina dihitung berdasarkan sistem air-prabentuk dengan memakai model *Washburn*. Jari-jari pori dengan model ini, r adalah 0,0147 μm, dan bersesuaian baik dengan jari-jari pori rata-rata yang didapat dengan pengukuran porositas air-raksa, r sebesar 0,0170 μm. Jari-jari pori sebesar 0,0147 μm dipakai untuk menghitung laju infiltrasi (k). Faktor k adalah masing-masing 64,83 x 10^{-5} $ms^{½}$ and 27,11 x 10^{-5} $ms^{½}$ untuk air dan $TiCl_3$ tanpa melibatkan tekanan pada perhitungan. Pada sisi lain dengan melibatkan tekanan, didapatkan faktor k sebesar 75,14 x 10^{-5} $ms^{½}$ and 31,40 x 10^{-5} $ms^{½}$ untuk air dan $TiCl_3$. Perumusan-perumusan lain juga disertakan sebagai perbandingan. Kinetik sistem air dan $TiCl_3$ adalah parabolik dengan waktu atau linier dalam akar terhadap waktu.

Kata kunci: *Pre-sintering*, penginfiltrasi, tekanan, berulang, jari-jari pori

INTRODUCTION

Liquid-phase infiltration of preforms has now emerged as an extremely useful method for the processing of composite materials. The process involves the use of a low viscosity liquid such as sols, metals- or polymers-melts. Using this infiltration process, it is possible to design new materials with unique microstructures (eg. graded, multiphase, microporous) and unique thermomechanical properties (graded functions, designed residual strains, thermal shock).

Liquid infiltrating into dry porous can be done according to the capillary phenomenon. The bodies mechanism of infiltration of liquids into porous bodies has been studied by many researches in the fields of soil physics, chemistry, powder technology and powder metallurgy. However, the processes and kinetics of liquid infiltration into a powdered preform are rather complex and have not been completely understood. Based on the Darcy's fundamental principle and the Kozeny-Carman equation [1], Semlak and Rhines [2] and Yokota *et al.* [3] have developed infiltration rate equations for porous glass and metal bodies. However, it remains to be verified whether these rate equations can be successfully used to describe the kinetics of liquid infiltration in porous ceramics preforms.

In this paper, the effects of pre-sintering temperature, types of infiltrant, vacuum and multiple infiltrations on the rate of infiltration into porous alumina preforms are described. Initial attempts to model the observed infiltration kinetics using various rate equations are also described. The deficiencies of the existing models to describe the infiltration kinetics in this study are discussed.

METHOD

A powder of reactive aluminas (AES-11C, Mandoval, United Kingdom, 99.9 % and mean particle size of 0.4 μm) was used for fabrication of alumina porous preform. The powder was uniaxially pressed at a pressure of 50 MPa to form bars dimensions (0.5 x 1.2 x 6) cm^3. Green compacts were presintered at 1000°C, 2 h. For studying the effect of pre-sintering, it was also heated to 900°C and 1100°C. After sintering, 1 cm of preform was immersed to infiltrants (water with colour indicator and $TiCl_3$ from BDH Limited Poole England with 30 % w/v of titanium chloride). Remnant of 5 cm was scaled in mm for the purpose of kinetic study. The height of arising liquid was recorded as function of time. The experiment was also conducted with and without vacuum. Other experiment is ran in three cycles with $TiCl_3$ under vacuum where cycle 2 is recurrence of cycle 1 and cycle 3 is recurrence of cycle 2 after sample was dried at room temperature for 24 hours. SEM photo of alumina preform was taken from a Phillips XL30 in the Department of Applied Physics at Curtin University of Technology, Perth. The photo was taken 2 mm from the surface. It meant that the photo represent the pore structure inside sample.

The viscosity of water and $TiCl_3$ were measured with Oswald viscometer in the Department of Applied Chemistry at Curtin University of Technology, Perth. The measurement is based on the driving liquid through the capillary which is proportional to density. By comparing the flow time of two liquids where one is used as a standard, the viscosity can be calculated. Methanol and water were used as a standard for $TiCl_3$. Both standards gave same value. The surface tension measurement was also conducted in the Department of Applied Physic at Curtin University of Technology. The method used is plate removal. The porosity was measured in School of Chemical Engineering and Industrial Chemistry, University of New South Wales, Sydney. The measurement was conducted on Micrometric 92220II mercury porosimeter.

RESULT AND DISCUSSION

After preforms were pre-sintered, the bulk density and porosity were measured based on Archimedes principle. Table 1 and 2 listed physical properties of preforms and infiltrants. Apparently, the porosity of the preforms sintered 900, 1000 and 1100°C are very close. It can be assumed as ideal number for the purpose of infiltration.

Table 1. Physical properties of preforms

Sintering (°C)	Porosity (%)	Bulk density (g/cm^3)
900	45.0±1.1	2.125±0.020
1000	45.9±1.4	2.123±0.021
1100	44.6±1.4	2.193±0.022

Table 2. Physical properties of infiltrants

Infiltrants (at 23°C)	Surface tension, γ (N/m)	Viscosity, η (Ns/m^2)
Water	$(7.225 \pm 0.032) \times 10^{-2}$	$(9.5 \pm 0.7) \times 10^{-4}$
$TiCl_3$	$(7.046 \pm 0.031) \times 10^{-2}$	$(5.3 \pm 0.4) \times 10^{-3}$

For modelling the kinetic infiltration in terms of effect of pre-sintering temperature, type of infiltrant, vacuum/nonvacuum and multiple infiltrations, firstly the pore radius of alumina preform was calculated based on preform-water system (sintered at 1000°C). In addition, alumina preform-water system can be a good reference to other system because water is well known and also its reference data is more complete than others. To calculate the pore radius of alumina preform, the Washburn formula is used [4].

$$h = (\gamma \cos \theta \; r/2\eta)^{1/2} \, t^{1/2} \qquad \text{.......................} \qquad (1)$$

where h and t are height of liquid and time respectively whereas γ, θ, r and η are surface tension, contact angle, pore radius and viscosity. By assuming the contact angle is zero [5] one can calculate the pore radius of preform if height and time of infiltration are known. The factor $(\gamma \cos \theta \; r/2\eta)^{1/2}$ can be assumed as constant, k or rate of infiltration can be calculated from the measurement data (Figure 1).

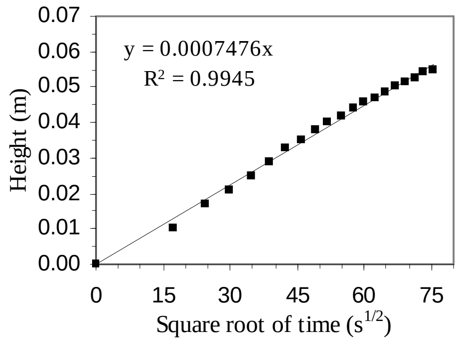

Figure1. Height of infiltration of water into alumina preform (sintered 1000°C) as a function of square root of time.

From the measurements (without vacuum) it was found that pore radius of alumina preform is 0.0147 μm. This is in good agreement with the average radius based on porosity measurement, r of 0.0170 μm (Figure 2). As comparison to the pore radius, it was also taken SEM photo of pre-sintered alumina preform as Figure 3. If the black images were assumed as pores, so that pore radius is (0.40 ± 0.11) μm. This number is larger than pore radius calculated based on Wasburn and porosimeter. Might

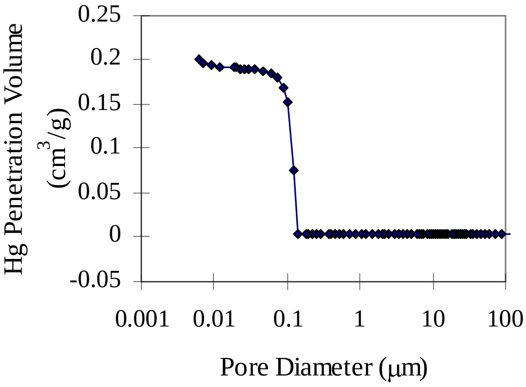

Figure 2. Porosity of alumina preform sintered at 1000°C.

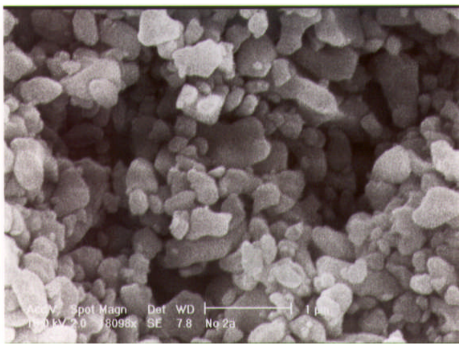

Figure 3. SEM photo of alumina preform sintered 1000°C.

be the pore radius from SEM reflects the pore radius bulge [6] and does not reflect the effective pore radius. Only the effective pore radius responds to infiltration process [7].

Effect of Pre-Sintering Temperature

Effect of pre-sintering temperature can be looked at Figure 4. The infiltrant is $TiCl_3$ liquid without vacuum. The graph represents between height and square root of time. Figure 4 indicates that rate of infiltration of preform sintered 1000°C is higher than 900 and 1100°C. The explanation to 1100°C can be caused by porosity even only differ slightly. The preform sintered of 900°C indicates that rate of infiltration is slower than that two others. By assuming that if one preform sintered in lower temperature, the porosity is larger. Suppose that assumption is right so that the rate of infiltration must be higher. This fact indicates that the porosity is not only the parameter to contribute the rate of infiltration.

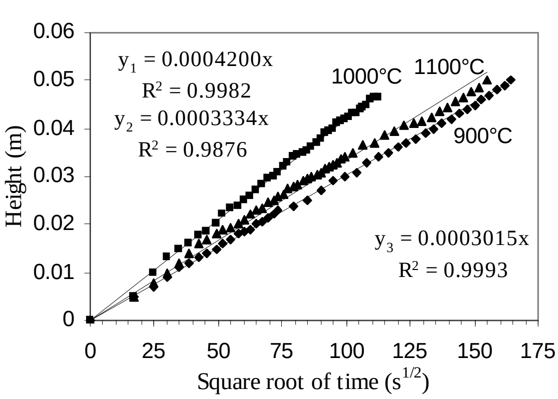

Figure 4. Effect of pre-sintering at 900, 1000 and 1100°C.

Effect of Infiltrants

For looking the effect of infiltrants, the preforms were infiltrated with water and $TiCl_3$. From Table 2, their surface tensions are very close, but the viscosities are different. Figure 5 indicates that rate of infiltration of water is higher than $TiCl_3$. This can be influenced by the viscosity. From equation 1, if viscosity, η increases the rate of infiltration decreases. As in Table 2, the viscosity of $TiCl_3$ is higher than water.

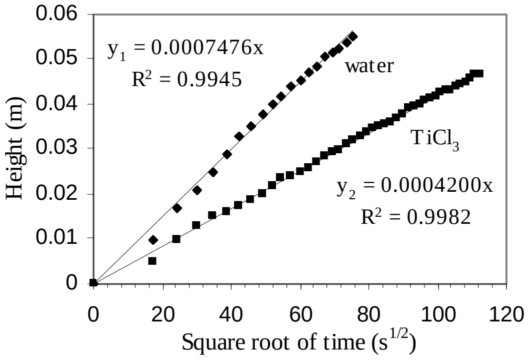

Figure 5. Effect of infiltrants using water and TiCl3.

Effect of Vacuum

The effect of vacuum to rate infiltration on the preform is presented in Figure 6. It is very clear that vacuum helps the infiltration process faster. It means that if a preform indicates slow infiltration, the vacuum can be applied as other candidate manner to enhance the rate of infiltration.

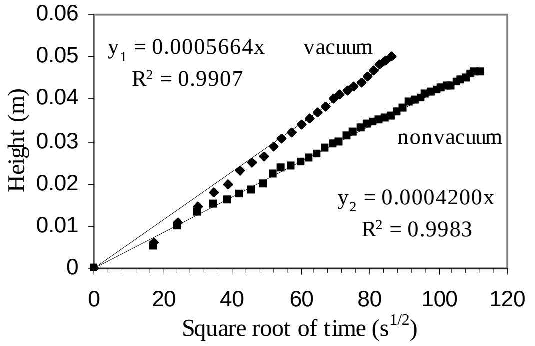

Figure 6. Effect of vacuum with TiCl3.

Besides acting as sucker to preform, vacuum makes the pressure around preform lower than 1 atm. By using Semlak formula modified by Travitzky [8]:

$$h = r/2\eta^{½} (Pa + 4\gamma \cos \theta/2r)^{½} t^{½} \quad .... \quad (2)$$

where h and t are height of liquid and time whereas γ, θ, r and η are surface tension, contact angle, pore radius and viscosity. Pa is applied pressure during experiment. From equation 2 if pressure decreases the rate of infiltration increases.

Effect of Multiple Infiltrations

Effect of multiple infiltrations is presented in Figure 7 between height and square root of time. Every cycle indicates that the curves are relatively linear line. Vacuum can help the filling of capillary. As mentioned in equation 2 with the decrease of pressure, the rate of infiltration increases. By using equation 1, if pore diameter decreases the rate of infiltration also decreases. Comparing to this experiment, the first cycle took longer time than cycle 2 and 3 and cycle 2 longer than 3. Logically $TiCl_3$ liquid reduced the pore radius of alumina preform in the first cycle as consequnce of filling process of liquid into wall of capillary. So that the rate of infiltration in cycle 2 and 3 should decrease. This phenomenon looks contradictive to experiment.

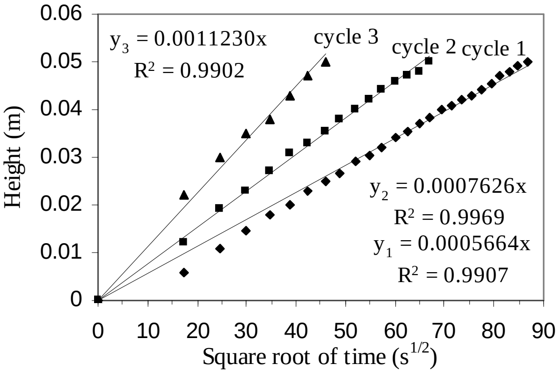

Figure 7. Effect of multiple infiltrations with TiCl3 under vacuum. Preform was sintered to 1000 C.

To explain this phenomenon, other formula can be used following Kozeny-Carman equation.

$$h\, dh/dt = k/T^2 \quad .... \quad (3)$$

$$k = p^3 CsP/(hS(1-p^2))$$

where h and t are height and time, whereas T, Cs, P, S, and p are tortuosity, shape factor, pressure, spesific surface and porosity. Assume that the channels in preform are straight line. In fact they are tortous in shape. Actually in the time required to travel through the preform, an element of liquid volume transverses a distance that greater than the length of preform. During the first cycle, the path is still maximum so that the tortuosity factor is large. From equation 3, if tortuosity, T is large so time for nfiltration takes longer for the same height. Assume that the tortuosity decreases after filling process in the first cycle and it causes the rate of infiltration increase in cycle 2 and 3.

Other formula explored in terms of the rate of infiltration in this paper is Yokata et al. [3].

$$h = 2/T (p\, Cs\, g \cos q\, r/2h)^{½} t^{½} \quad .... \quad (4)$$

Equation 4 involves the tortuosity and shape factor as equation 3. By using T of 1.4142, Cs of 0.4 (these values were recommed by Carman) and pore radius of 0.0147 mm (as calculated from equation 1), k factors are 64.83 x 10^{-5} $ms^{½}$ and 27.11 x 10^{-5} $ms^{½}$ for water and $TiCl_3$ respectively. Meanwhile by using equation 2, the k factors are 75.14 x 10^{-5} $ms^{½}$ and 31.40 x 10^{-5} $ms^{½}$ for water and $TiCl_3$ respectively.

The summary of k values from experiment for every treatment in terms of effect of pre-sintering temperature, infiltrant, vacuum and multiple infiltration was listed in Table 3. Comparing to the experiment, k value of water is good agreement with the calculation by using equation 2 and 4. However, equation 2 is closer to the experiment than equation 4 because it used the pressure factor. As showed in effect of vacuum, the pressure factor is very important in enhancing the rate of infiltration. The calculation of pore radius based on water and alumina preform system gave k factor for $TiCl_3$ alumina preform system is lower than k factor from experiment. This can be caused by assuming that the contact angle for both infiltrant is zero.

CONCLUSION

Experiment results showed that the kinetic of water and titanium trichloride alumina preform system is parabolic in time or linier in square root of time. The radius pore assumed from SEM photo is too big to involve to the calculation. Washburn formula is a good agreement to experiment to calculate the pore radius and to porosity meter measurement. The viscosity of infiltrant also influence the rate of indiltration as showed in effect of infiltrants. The rate of infiltration is depent on pressure. The rate of infiltration, k are 64.83 x 10^{-5} $ms^{½}$ and 27.11 x 10^{-5} $ms^{½}$ for water and $TiCl_3$ respectively without involving pressure in the calculation. On the other hand, by using pressure, the k factors are 75.14 x 10^{-5} $ms^{½}$ and 31.40 x 10^{-5} $ms^{½}$ for water and $TiCl_3$ respectively. The time of infiltration is faster in vacuum than in nonvacuum. Besides vacuum, multiple infiltrations also increases the rate of indiltration. The other parameter of preform as pre-sintering temperature influences the rate of infiltration. In multiple infiltrations, the tortuosity of preform can be used to explain why cycle 1 is slower than cycle 2 and 3.

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