Influence of sintering temperature on microstructural changes of ceramic Raschig ring

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Abstract−The thermal behavior of Illitic-kaolinitic clay for manufacturing of low porosity ceramic Raschig rings was characterized during the sintering process. The samples were shaped by extrusion method and fired at different temperatures from 1,100 to 1,300 °C. The main physical-chemical transformations were studied by evaluating changes in shrinkage, water absorption, porosity, mechanical strength, microstructure and mineralogical compositions. The optimum sintering condition was found to obtain maximum mechanical strength. Chemical resistance of ceramic Raschig rings also was determined according standard method. It was shown that the better chemical resistance could be attributed to the different mineralogical compositions, in particular with presence of mullite phase.

Key words: Kaolin, Compressive Strength, Raschig Ring, Sintering, Porosity

INTRODUCTION

Packed towers are widely used in different industries to contact two phases. They were used in chemical processes such as catalytic reactions, combustion, gas absorption, distillation and separation. The most important part of a packed tower is the packed bed. Ceramic packing is widely used in processes in which liquid and gas are contacted together. Distillation, absorption and cooling of air are famous examples for applications of this type of ceramic body. The Raschig ring is the simplest shape of ceramic packing mostly fabricated by manufacturers [1-4].

The most significant mechanism in sintering of low porosity ceramic packing is liquid phase sintering [5]. During the firing of this body a considerable amount of liquid phase is formed, which diffuses by capillary force into the fine pores of solid and reduces the porosity and specific surface area. These transformations of texture cause significant changes in mechanical, thermal and chemical characteristics of pieces determining the properties of ceramic Raschig rings, which relate to shrinkage, water absorption and mechanical strength that define packing quality [6,7].

Chemical reactions that occur during the firing process of clay-based ceramics depend on the type of raw materials in the ceramic body, but the basic reaction step can be outlined as follows [8]:

• Kaolinite crystals contain hydroxyl groups, and the dehydroxylation of these groups to form metakaolin (Al_2O_3, $2SiO_2$) occurs at 400-650 °C.

• α to β-quartz inversion occurs at 573 °C because of having the free quartz in kaolin.

• Metakaolin transforms to spinel type structure and amorphous free silica at 950 to 1,000 °C.

• The spinel phase is a nonequilibrium unstable phase, that certainly transforms to mullite ($3Al_2O_3$, $2SiO_2$) above 1,075-1,200 °C. The content of mullite crystals grows and influences the mechanical strength of the ceramic body.

Three major theories have been developed to explain the strength of clay-based ceramics.

1. Mullite Hypothesis

The mullite hypothesis is one of the oldest theories on the strength of clay based ceramics [8-10]. It was indicated that the strength of a ceramic body depends on the content and morphology of mullite crystals. Two different morphologies are generally described for mullite crystals: primary and secondary. Studies on morphology of mullite have indicated that primary mullite occurs in the form of scaly crystals, whereas secondary mullite is mostly formed in needle shape. It is believed that the secondary mullite is formed from the recrystallization and dissolution of aluminosilicates in melt [10]. Firing temperature and generating properly sized mullite needles are vital in achieving the desired strength. Furthermore, secondary mullite increases strength more than primary mullite because of its acicular morphology and smaller needle diameter, that this effect comes back the elflike interlocking of fine mullite needles [8].

2. Matrix Reinforcement Hypothesis

The difference in thermal expansion coefficients between the matrix (glassy phase) and dispersed particles (quartz and mullite) formed during firing process produces strong compressive stresses on the glassy phase. Also, thermal compressive stresses on the glassy phase due to thermal expansion mismatch lead to strength improvements in clay-based ceramics. This idea of matrix reinforcement is clearly discussed in reference 8.

3. Dispersion-Strength Hypothesis

The results of strength and fracture studies show that the strength of glassy clay-based ceramics manufactured at high temperature is a function of the volume fraction of dispersed phase at low volume fractions, but at high volume fractions of dispersed phase the strength is dependent on the volume fraction and particle size of the dispersed phase [8].

The aim of the present investigation is based on the evaluation of temperature effects on physical-mechanical properties of ceramic Raschig rings fabricated by using kaolin and shaped by extrusion method. For this purpose the effect of temperature was assessed on microstructures of samples in terms of porosity, mineralogical changes

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Table 1. The chemical and mineralogical analysis of raw material

Chemical analysis		Mineralogical analysis
Oxides	%	Minerals
SiO_2	58±1	kaolinite
Al_2O_3	28±1	illite
Fe_2O_3	0.35	quartz
TiO_2	<0.25	others
CaO	<0.50	
MgO	<0.15	
K_2O	4.50	
Na_2O	<0.20	
L.O.I	6.0	

and mechanical strength.

EXPERIMENTAL PROCEDURE

Processed industrial kaolin consisting of a blend of natural illitic-kaolinitic clay was dry milled on a laboratory scale. The mineralogical analysis of raw material was identified by X-ray diffraction (XRD, Model Siemens 500D, Germany). As shown in Table 1 where chemical and mineralogical analyses are detailed, the main constituents were kaolinite, illite, quartz. Small quantities of calcite and impurities were also found.

Simultaneous thermal analysis of raw material, DTA-TG, with heating rate 10 °C/min was carried out in air atmosphere. A series of Raschig rings were shaped by laboratory extruder (pro to type) at a pressure of 22 MPa measured at the first of the die. The moisture content of the paste was regulated 0.3 kg water/kg dry solid. The green ceramic rings were dried at 110 °C during 24 hours. The dried Raschig rings, Fig. 1, were subjected to firing cycles (Electrical kiln Model EX.1500-6L, Iran) in air atmosphere at a constant heating rate of 5 °C/min up to 600 and maintained for 1 hour at this temperature and then the rings were heated at a constant rate of 10 °C/min to reach different peak temperatures (from 1,100 to 1,300 °C). Soaking time for all samples was considered as 2 hours.

To characterize the sintered samples, the following parameters were chosen: linear shrinkage, water absorption [11], open, total and closed porosity, pore size distribution, average pore size and diametric compressive strength. Shrinkage was measured by using
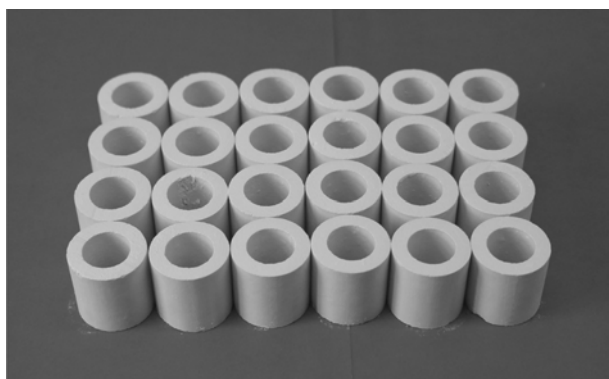

Fig. 1. The dried ceramic Raschig rings.

calipers accurate to 0.1 mm. The total porosity was calculated as follows:

$$\text{total porosity}=1-\text{bulk density/true density} \qquad (1)$$

Bulk and the true densities were measured according to standard methods [11,12].

Mercury intrusion porosimetry (MIP) is a technique used to measure pore size distribution. This method is able to span the measurement of pore sizes ranging from a few nanometers to several hundred micrometers. However, the smallest size of pore in which mercury can intrude depends upon the maximum intrusion pressure applied. Extent of porosity that can be determined by porosimetry test depends, consequently, on the nature of the pores, the size of the smallest pore likely to be encountered in the material and the maximum intrusion pressure applied. The method used to determine the pore size distribution was high pressure mercury pore sizing (Pascal Model 140) that open porosity was calculated from the maximum value of mercury intrusion.

For the diametrical compression tests, the rings were loaded by using steel compression plate in a universal testing machine (Adamel Lhomargy DY-26, France) at a relatively low deformation rate of 1 mm/min.

The mineralogical phases presented in the sintered samples were studied by X-ray diffraction and their microstructure was observed by scanning electron microscopy (SEM, Model EOL. 4401). Also, the chemical resistance of fired ceramic packing was studied according to standard ASTM-C515 [13].

RESULTS AND DISCUSSION

The form of DTA-TG curves shown in Fig. 2 is a characteristic of illitic-kaolinitic composition with a predominantly kaolinite structure. The curves show the slope changes and peaks corresponding to the loss in physically absorbed water at about 100 °C and the loss
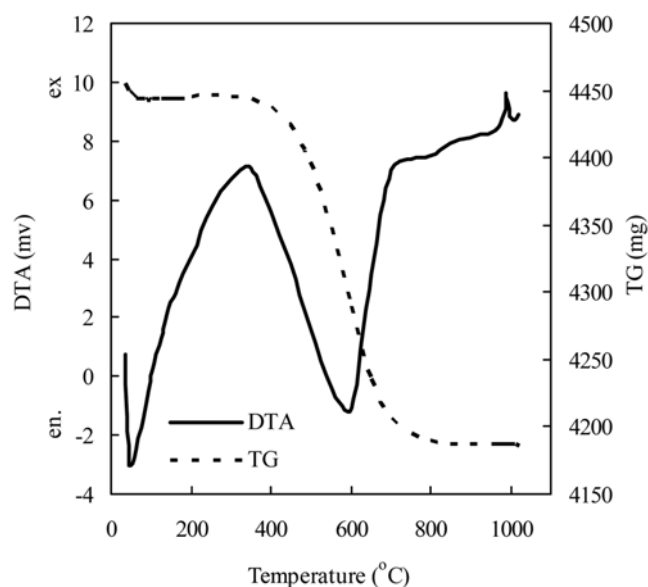

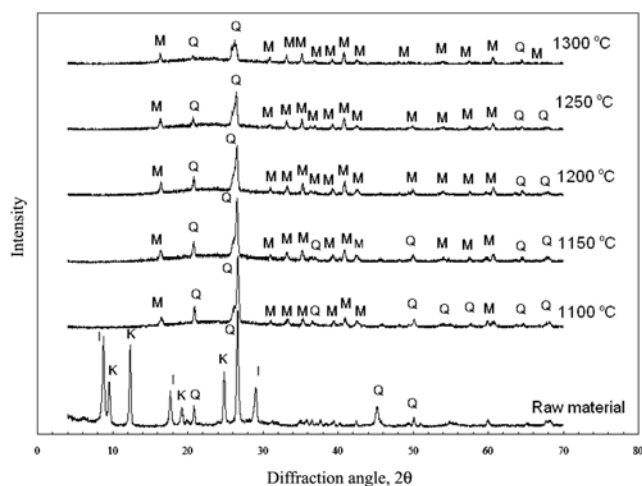**Fig. 2. Simultaneous thermal analysis (DTA-TG) of raw material with heating rate 10 °C/min.**

Fig. 3. The XRD pattern of ceramic Raschig rings at different temperatures. I: Illite, K: Kaolinite, M: Mullite and Q: quartz.

Table 2. Open, total and closed porosity variation as function of sintering temperature

Temperature (°C)	Open porosity (%)	Total porosity (%)	Closed porosity (%)
1100	17.32	19.53	2.21
1150	3.33	7.81	4.48
1200	0.65	6.80	6.15
1250	0.58	8.90	8.32
1300	0.23	8.70	8.47

in structured water of clay at about 400-650 °C. Spinel phase formation also occurs at 980 °C. The XRD pattern changes observed on raising the firing temperature (Fig. 3) were as follows:

• Kaolinite peak completely disappeared and mullite phase was formed between 1,100-1,300 °C. The peak intensity of mullite increases at higher temperatures.

• The illite peak intensity eventually disappears. Owing to its alkaline content, illite acts as fluxing agent.

• The quartz peak intensity gradually decreases remarkably at high temperatures. The viscosity of glassy phase varies with temperature in the same way, and these patterns indicate that the quartz dissolution process is closely related to variation in the viscosity of glassy phase with temperature.

The value of linear shrinkage and water absorption with sintering temperature is shown in Fig. 4. The more significant change
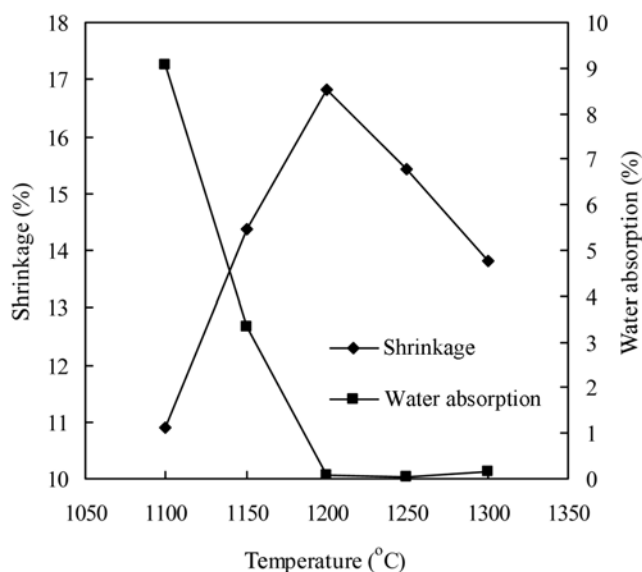
with rising temperature is the following. The linear shrinkage of samples increases up to a maximum value at temperatures close to 1,200 °C. At higher temperatures shrinkage decreases considerably. It is interesting that the value of water absorption decreases until approximately zero value and remains constant after 1,200 °C.

The pore system in ceramic-based materials consists of two main types of pores: open and closed pores. An open pore is a cavity or channel that communicates with the surface of the ceramic body. Closed pores are inside the material and are completely isolated from the external surface. Closed pores influence parameters like density, mechanical and thermal properties. Table 2 shows open, total and closed porosity variation as a function of sintering temperature. The values of open and total porosity decrease progressively with increasing sintering temperature. The value of open porosity reaches zero like water absorption around 1,200 °C and remains constant, whilst the total porosity of samples decreases up to a minimum value at 1,200 °C. Therefore, water cannot diffuse into the closed pores and its value remains constant near zero. On comparing the evaluation of open and total porosity with sintering temperature, both are observed to be very similar at low temperatures and indicate that most pores are open. However, as sintering temperature rises, the value of closed porosity increases and the difference between the two curves grows until reaching to high values at about 1,200 °C. At this and higher temperatures the body porosity may

Fig. 4. The linear shrinkage and water absorption variations of ceramic Raschig rings with sintering temperature.
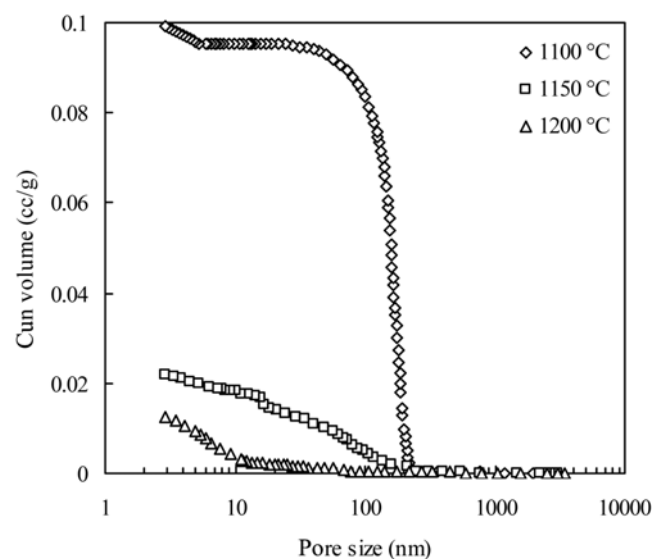

Fig. 5. The pore size distributions of open pores for the test samples sintered at different temperatures.

be assumed as closed porosity.

The evaluation of the above properties with sintering temperature corresponds to their behavior during the firing process in the presence of liquid phase. Actually, linear shrinkage, water absorption and porosity variation are conditioned by two effects. First, the capillary pressure due to surface tension of liquid phase tends to reduce the pore size, which increases the linear shrinkage and reduces water absorption, open and closed porosity. Second, the expansion of the gas remaining in the pores tends to expand the ceramic body, and therefore the linear shrinkage is lowered.

The pore size distributions of open pores for the test samples sintered at different temperatures are presented in Fig. 5. The geomet-
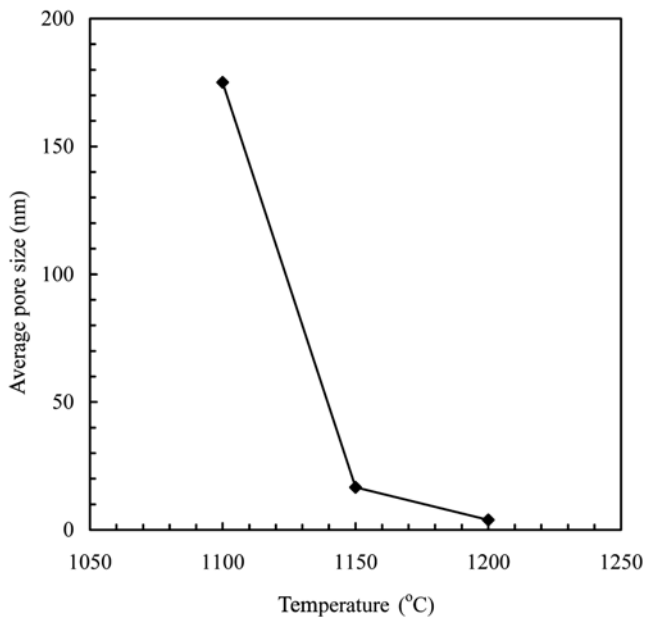

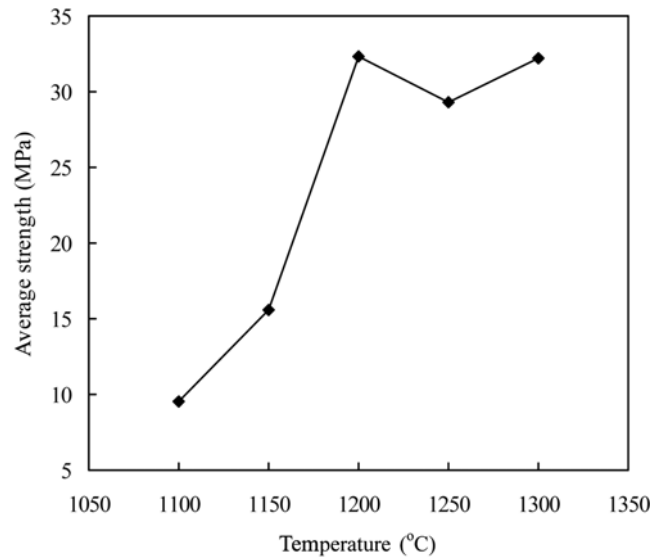Fig. 6. The value of average pore size versus firing temperature.

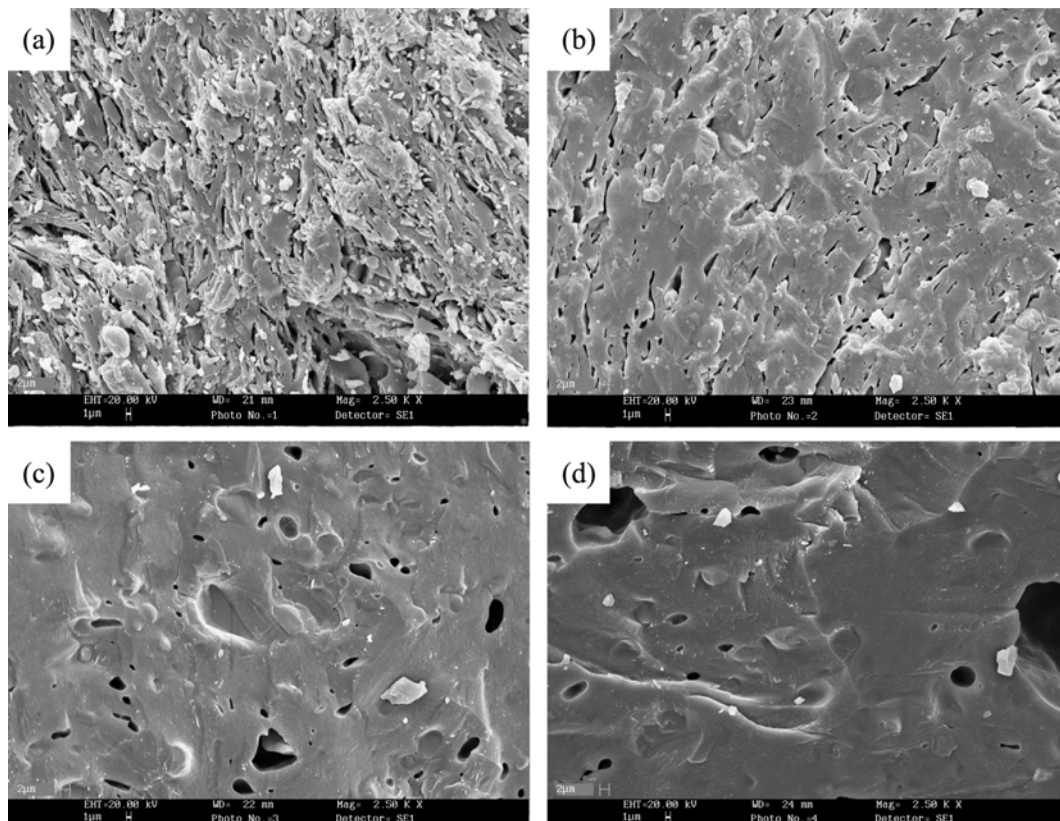Fig. 7. Diametrical compressive strength of samples as a function of sintering temperature.

Fig. 8. The SEM analysis of ceramic Raschig rings sintered at (a) 1,100, (b) 1,150, (c) 1,200 and 1,250 ℃.

ric mean diameter was determined from the pore size distribution curves. The values of mean pore size versus firing temperature have been plotted in Fig. 6. It can be observed that the open pore volume decreases with rising sintering temperature up to 1,200 °C. The evaluation of pore size distribution shows that the smallest pores disappear at low temperatures during sintering. However, average pore size progressively decreases with temperature. At higher temperatures, in advanced states in which most of pores are closed, therefore, the average open pore size reaches zero.

Diametrical compressive strength of samples as a function of sintering temperature is shown in Fig. 7. The strength of samples increases with temperature until reaching a maximum at 1,200 °C. This is due to the fact that the liquid glassy phase content is developed mainly by fusion of clay minerals and quartz particle dissolution, whilst the viscosity of liquid phase decreases considerably. Both factors are the main reason for dropping of the porosity. After 1,200 °C, all the pores are closed and closed porosity and pore size increase, and as result the mechanical strength is reduced.

The compressive strength of ceramic Raschig rings has been explained by developing by mullite hypothesis. The interlocking mullite crystals are responsible for the enhanced strength. Regardless, porosity values for samples sintered at 1,300 °C, mullite content and shapes were generally considered. The higher mullite content and the more elongated at high temperatures results in the higher values of strength for samples sintered at 1,300 °C. The morphology of crystalline phase influences mechanical properties. The elongated phenomena of mullite could be explained by the viscosity of the liquid glassy phase. That is essentially due to the lower viscosity of the liquid phase formed at higher temperatures that allows better growth of mullite crystals [10].

Fig. 8 shows the microphotographs corresponding to samples sintered at different temperatures. In the sample sintered at 1,100 °C, the interconnected pores can be observed. However, at 1,150 °C some of the pores are found to form closed pores. As temperature rises, the percentage of fracture area of samples which make up glassy filaments increases remarkably. At 1,150 °C the samples contain irregularly formed pores. In this case, some of pores appear to be open, and closed pores can be found. At higher temperatures than

1,200 °C the same kind of texture is observed, and vitreous matrix is developed in which the pores are starting to be as spherical shape, and most of the pores have been closed at 1,200 °C. At advanced sintering temperature (1,250 °C) pore volume is observed to increase, owing to expansion of gas inside the pores.

Fig. 9 shows the value of weight loss of ceramic Raschig rings in acid solution. The weight loss can be observed to decrease with increasing firing temperature. This decrease is much more marked at high temperatures in which porosity of samples has hardly been lowered. On comparing the values of weight loss, it was found that the optimum condition for obtaining the maximum strength satisfactorily covers the optimum condition for chemical resistance. The main reason for this behavior is due to decreasing open porosity and forming new crystals, especially mullite at higher temperatures.

CONCLUSIONS

A typical ceramic packing in shape of Raschig rings was manufactured from illitic-kaolinitic processed clay using extrusion method. Samples were sintered at different temperatures from 1,100 to 1,300 °C by steps of 50 °C. The densification of samples has been shown to take place by liquid phase formation. The development of melted phase caused closed pores, which increases the heterogeneity of a ceramic body and decreases the compressive strength of the ceramic Raschig ring. At higher temperatures than 1,200 °C the strength is dependent on the homogeneous glassy matrix and mullite formation in a ceramic body. The content of mullite crystals is another reason for increasing strength. The porosimetry experiments show that average open pore size of ceramic packing falls down at higher sintering temperatures. Scanning electron microscopy studies also revealed that small spherically shaped pores were formed at optimum sintering condition. The chemical resistance of ceramic packing was investigated, and the results show satisfactory chemical resistance for the body sintered at optimum temperature where the maximum mechanical strength was obtained.

ACKNOWLEDGMENT

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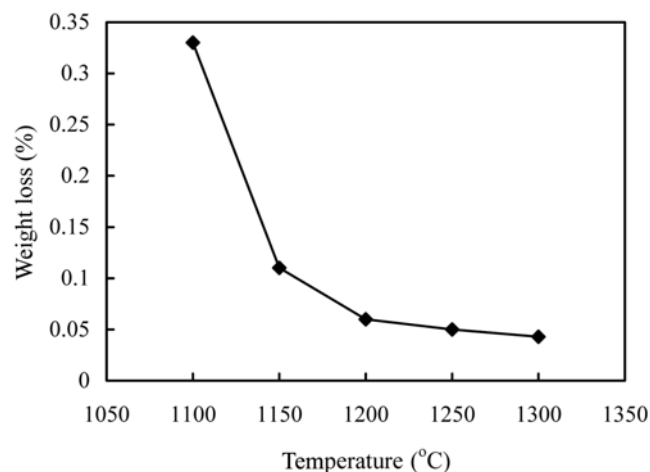8. W. M. Carty and U. Senapati, *J. Am. Ceram. Soc.*, **81**, 3 (1998).

Fig. 9. The value of weight loss of ceramic Raschig rings in sulfuric acid solution (78%).

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