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The effect of sintering temperature on reliability of extruded ceramic Raschig ring

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The feasibility of illitic-kaolinitic clay in ceramic packing manufacturing was assessed. Industrial illitic-kaolinitic clay was formed by extrusion method in the shape of Raschig ring and was sintered at temperatures between 1100 and 1300 ºC. The samples were characterized after sintering and open, total and closed porosity were determined by standard methods. For better understanding the role of firing temperature on compressive strength and reliability of Raschig rings, the diametric compressive strength tests were performed and the results were analyzed by Weibull statistical theory. The obtained experimental results showed that the Weibull modulus was significantly affected by sintering temperature and decreases as function of total porosity. Furthermore, the microstructures of samples sintered at different temperatures were observed by scanning electron microscopy, SEM, to confirm the statistical results. In conclusion, though the compressive strength of ceramic Raschig rings improves as the total porosity decreases but, the reliability of them strongly depends on sintering temperature.

Key words: Kaolinite-Illitic Clay, Ceramic Raschig Ring, Compressive Strength, Weibull Modulus, Microstructure.

Efecto de la temperatura de sinterización en la fiabilidad de los anillos cerámicos extruidos Raschig

La viabilidad de las arcillas ilítico-caoliníticas en la fabricación de cerámica se evaluó. Las arcilas ilítico-caoliníticas se conformaron por el método de extrusión en forma de anillo Raschig y se sinterizaron a temperaturas entre 1100 y 1300 ºC. Las muestras se caracterizaron después de sinterización y la porosidad abierta, cerrada y total se determinó por métodos estándar. Para entender mejor la influencia de la temperatura de cocción sobre las propiedades de resistencia a la compresión, la fiabilidad de los anillos Raschig y la resistencia a la compresión diamétrica se realizaron los correspondientes ensayos que fueron analizados por la teoría estadística de Weibull. Los resultados experimentales obtenidos mostraron que el módulo de Weibull se vio considerablemente afectado por la temperatura de sinterización y disminuye a medida que lo hace la porosidad total. Por otra parte, las microestructuras de las muestras sinterizadas a diferentes temperaturas fueron observadas por microscopia electrónica de barrido, MEB para confirmar los resultados estadísticos. En conclusión, aunque la resistencia a la compresión de anillos Raschig de cerámica mejora al disminuir la porosidad total. La fiabilidad de los mismos depende en gran medida de la temperatura de sinterización.

Palabras clave: Arcillas ilítico-caoliníticas, anillo cerámico Raschig, Resistencia a la Compresión, Modelo de Weibull, Microestructura.

1. INTRODUCTION

Ceramic packing is a high sintered product successfully used in liquid-gas contact process such as distillation, absorption, cooling towers where mass and heat transfer are require (1,2). The relevant chemical-mechanical characteristics such as chemical resistance, compressive strength and reliability of them make ceramic packing prefers to use in chemical process compared to metal, plastic and carbon types (3, 4).

One of the most important problems regarding operation of packed towers concerns the compressive strength and reliability of packed bed materials. The Raschig rings are widely used as ceramic packing in mentioned process (5, 6). In industrial scale, the ceramic Raschig rings are fabricated by three methods that are extrusion, uniaxial pressing and slip casting. The microstructure of ceramic body is directly related to reliability of packing during the process. The investigation of Villora et. al. showed that extrusion process is the most adequate green forming method that produces maximum reliability (7).

The densification of this product proceeds throughout a viscous phase sintering with developing of a liquid phase that flows by capillary pressure into the interconnected voids among the particles, causing the development of ceramic bounding constituted by a glassy matrix embedding new crystalline phases and part of residual crystals such as quartz. This bounding yields mechanical resistance to ceramic packing (8). The nature of packed bed materials requires suitable heat treatment to improve the mechanical behavior. In addition, the reliability of packed materials also needs to be carefully evaluated, taking into account the strength of them not only during process but also in heat treatment in industrial scale.

It is worth pointing out that based on experimental data, it can be estimated the mechanical reliability of ceramic Raschig rings. By considering these aspects, illitic-kaolinitic clay was chosen for this study. The choice of this raw material was based on its industrial application. To quantify the reliability of Raschig ring and optimize the mechanical strength, the effect due to porosity were first investigated thereafter on the basis of laboratory results, the reliability of Raschig rings was evaluated by statistical Weibull theory. The obtained results are discussed in terms of microstructure and mineralogical analysis.

2. EXPERIMENTAL PROCEDURE

Starting raw material was chosen among the Iranian industrial kaolinitic-illitic clays. The particle size distribution of clay was between 2.9 and 7.6 μm. The chemical analysis of raw material was presented in Table I. The XRD patterns show that kaolinite as the main mineral, illite and quartz are the secondary phases. The water-based paste was prepared with addition of 0.3 kg water/1 kg dry powder and shaped by laboratory extruder in form of Raschig ring. The extruded samples were dried at 110ºC for 24 hours.

The firing of dried Raschig rings were carried out in laboratory electrical kiln with cycle of 5 hours with maximum temperature of 1100, 1150, 1200, 1250 and 1300ºC. The densification behavior was described in terms of open, total and closed porosity and measured by standard methods (9, 10). Ten specimens were used in porosimetry analysis for each set of runs.

The diametric compressive strength test was preformed on samples. At least 25 specimens were tested using a universal testing machine (Adamel Lhomargy DY-26, France) with across head speed of 1 mm/min. To calculate compressive strength, the empirical equation proposed and tested for a number of ceramics by Frocht was used (11). The failure stress of the rings, σ, due to action of maximum tensile stress is given by the following equation:

$$\sigma = \frac{KF}{(D_o - D_i)L} \qquad [1]$$

where F is the load to failure, Do, Di and L are the outside diameter, the inside diameter and width of the ring,

Table I: The chemical and mineralogical analysis of raw material

chemical analysis

L.O.I	Na_2O	K_2O	MgO	CaO	TiO_2	Fe_2O_3	Al_2O_3	SiO_2
6.0	0.20	4.50	0.15	0.50	0.25	0.35	28±1	58±1

respectively. Also K is the stress constant which is a function of the Di/D0 ratio. This constant was taken from empirical relations between K and Di/D0 given by Frocht (11). From dimensions of samples, this ratio is around 0.60 which lies in the part of the Frocht's curve experimentally tested for a number of ceramics (Di/D0= 0.3-0.8) and correspond to K value of 7 (7, 11).

Simple Weibull statistical analysis was carried out on each set of data and suitability of this method for characterizing the compressive behaviour was analysed. The Weibull distribution can be expressed as a cumulative distribution (12, 13):

$$P_n = 1 - \exp\left(-\left(\frac{\sigma - \sigma_t}{\sigma_o}\right)^m\right) \qquad [2]$$

where $P_n(\sigma)$ is the probability of failure at a stress of σ, σ_o is a scaling constant, σ_t is the threshold stress below which no failure occurs in the material that practically can be considered zero for brittle ceramics and m is the Weibull modulus. The scaling constant σ_0, usually called characteristic strength, corresponds to the stress at which the probability of failure is 63.2%. The Weibull modulus controls the shape of the curve, being larger as the scattering degree of the strength decreases. Therefore, larger value of m describes more reliable material. To evaluate $P_n(\sigma)$, the following equation was used:

$$P_n(\sigma) = \frac{n}{N+1} \qquad [3]$$

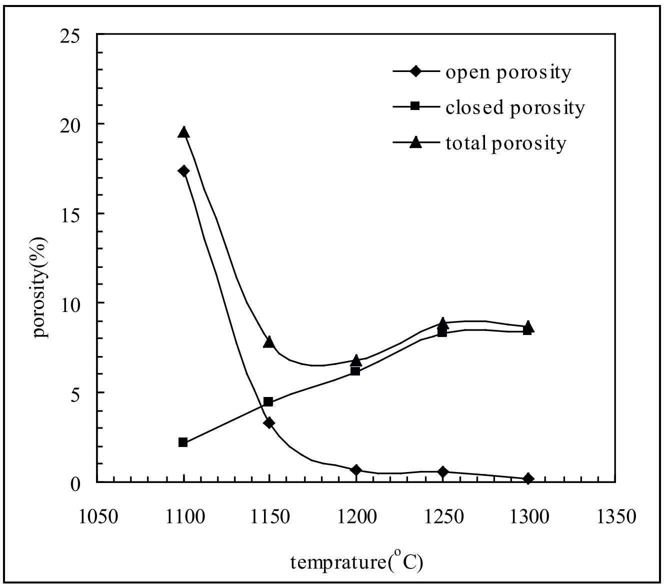

Figure 1: The values of open, total and closed porosity versus sintering temperature

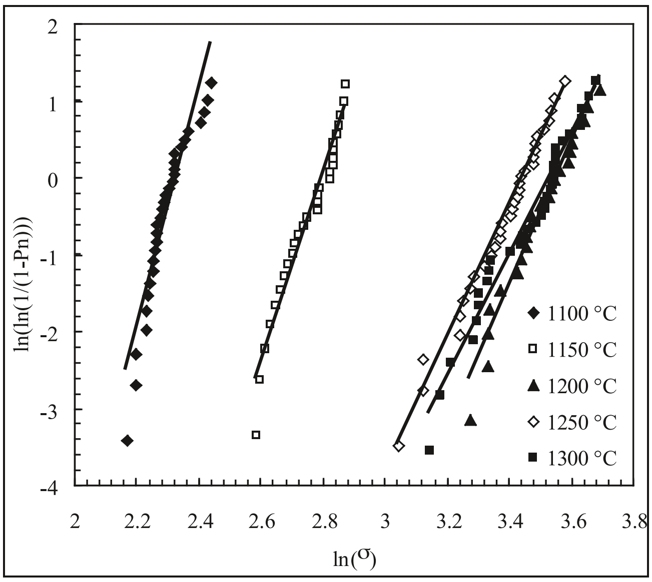

Figure 2: Weibull plots for five series of samples sintered at different temperature

where N is the total number of testing specimens and n is the specimen rank in ascending order of failure stress. This equation gives an unbiased estimation of the n^{th} failure and is recommended when the number of testing specimens is between 20 and 30.

The mineralogical compositions of the sintered ceramic Raschig rings were identified by using X-ray diffractometry with Cuk_α radiation (XRD Model Philips, PW1130/90). The microstructures of the sintered specimens were observed to determine pore gradients by scanning electron microscope, SEM (Model EOL. 4401), on the cross-sectional surfaces.

3. RESULTS AND DISCUSSION

Figure 1 shows the variations of open, total and closed porosity of samples with temperature. The total porosity of ring reaches to minimum at 1200 ºC where the same value of closed porosity was found. For the temperatures more than 1200 °C the open porosity (difference of total and closed porosity) is almost zero. It can be observed that total porosity decreases with increasing temperature and the densification rate dropped (slop of curve) as samples are sintered, except for the temperature over 1200 ºC. The increasing in total and closed porosity is due to expansion of air inside the occluded pores. To verify if the proposed probability of failure function is representative for Weibull distribution, Eq. [2] was put into the following logarithmic form:

$$\ln\ln\left(\frac{1}{1-P_n}\right)=m\ln\sigma-m\ln\sigma_o \quad [4]$$

The Weibull parameters were calculated from slope, m, and those of the ordinate at origin, $m\ln\acute{o}_0$, of the straight lines in Figure 2. Table II was summarized the Weibull parameters corresponding to the linear adjustments. In Figure 3 the probability of failure as a function of stress calculated from the Weibull parameters were depicted with the experimental values corresponding to Eq. [2]. Table II data shows that Weibull modulus decreases considerably when sintering temperature rises whilst the values of σ and σ_o increases until a maximum value at 1200°C.

Table II: The Weibull parameters and average compressive strength sintered ceramic Raschig ring as function of temperature

sintering temperature(°C)	Weibull modulus	normal stress	R	average strength
1100	15.4	10.3	0.94	9.5±2.1
1150	12.3	16.4	0.98	15.6±3.1
1200	9.4	34.9	0.98	32.4±2.1
1250	8.6	31.4	0.99	29.3±3.1
1300	7.8	34.3	0.98	32.0±3.2

The σ and σ_o value is positively correlated to porosity values. The only exception being for samples sintered at 1300 °C whose highest total porosity does not account for its worse performance. It is important to notice that mullite content increase at 1300°C as shown in X-ray pattern in Figure 4. The increment of mullite phase improves the compressive strength though the total porosity increases considerably (14, 15).

The variation in reliability of ceramic Raschig rings can be explained by microstructure of ceramic bodies. The SEM micrographics reported in Figure 5 reflect to the defect differences among the samples sintered at different temperatures. The presence of elongated defects that were large and uniform in size for sample sintered at 1200 is evident. This type of defect was also found for the other samples sintered at different temperatures.

The microstructures of samples sintered at different temperatures were presented in Figure 6. The fracture surface

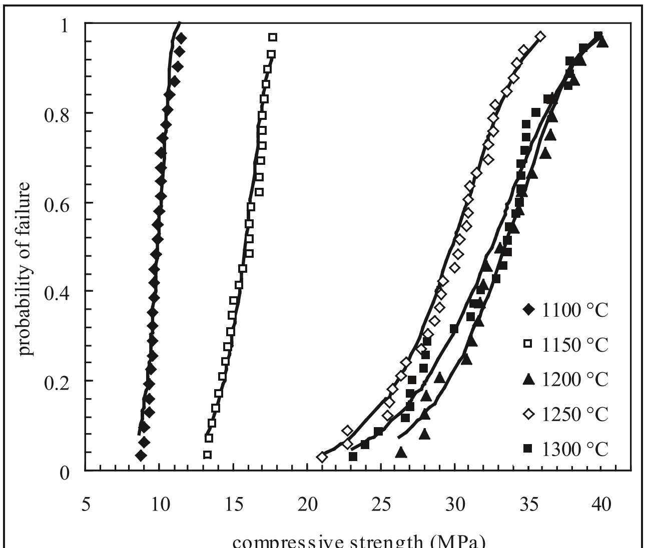

Figure 3: The probability of failure as function of compressive strength at different sintering temperature

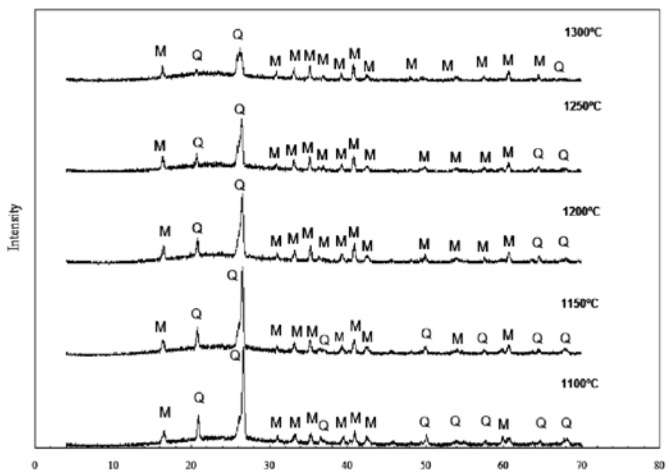

Figure 4: XRD pattern of samples sintered at different temperature (Q: qurtz, M: mullite)

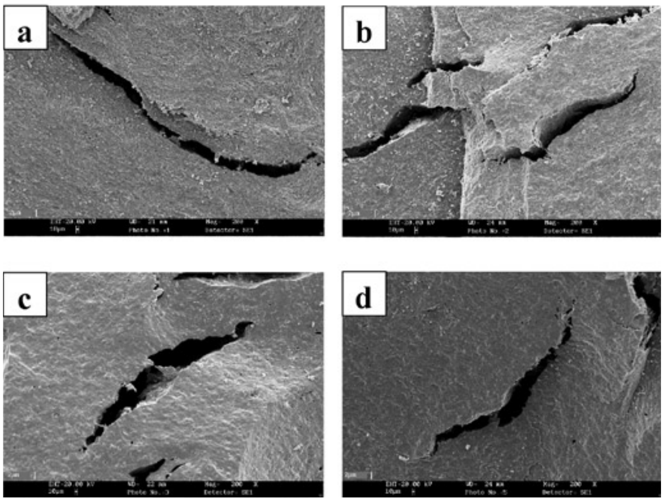

Figure 5: The defects of samples sintered at (a) 1100, (b) 1150, (c) 1200 and 1250 ºC

of body sintered at 1100°C is characterized by the presence of interconnected pores essentially, distributed homogenously in the ring fracture surface whose size are significantly larger than those sintered at 1200°C. Spherical pores were observed in mature microstructure where a sort of equilibrium between the gas pressure and capillary pressure was reached. At 1150°C some of the pores were closed and the homogeneity of ceramic ring decreases. The pores were closed when sintering temperature reach to 1200°C. The pore size increases when the sintering temperature rises to 1250°C and heterogeneous distribution of pores was found at this condition. The variation of Weibull modulus significantly depends on microstructure homogeneity. As sintering temperature increases the homogeneity of microstructure changes significantly and the Weibull modulus drop consequently.

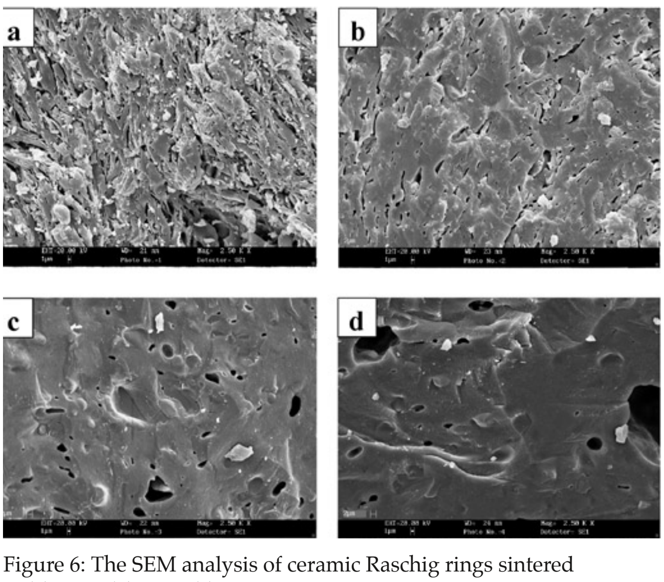

Figure 6: The SEM analysis of ceramic Raschig rings sintered at (a) 1100, (b) 1150, (c) 1200 and 1250 ºC

4. CONCLUSIONS

In the present work, the reliability of ceramic packing, in the shape of Raschig ring, was investigated. From the obtained results can be concluded that the mechanical compressive strength increases with rising of sintering temperature until a maximum value that is correlated with decreasing porosity. The mullite content is another reason for improvement of compressive strength at higher temperature where the closed porosity increases by the air pressure inside of closed pores.

The used kaolinitic-illitic clay for fabricating ceramic Raschig rings exhibited a considerable decrease in Weibull modulus and reliability of rings with sintering temperature. This variation in reliability of ceramic Raschig ring was found due to decreasing homogeneity of ring microstructure during sintering process.

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REFERENCES

1. R.E. Treybal, Mass transfer operation, McGraw-Hill Publishing Co, 3rd, Tokyo, Japan, 1980
2. L.P. Reiss, Cocurrent gas-liquid contacting in packed columns Ind. & Eng. Che. Pro. De. & Dev., 6, 486-499, (1967)
3. R. F. Strigle, Random packing and packed tower, Huston TX, Gulf Publication Co, 1987
4. Dipl.-Ing. Kai Sundmacher, Activity evaluation of a catalytic distillation packing for MTBE production, Chem. Eng. & Tech.16, 4, 279-89, (2004)
5. W.L. McCabe, J. C. Smith, P. Harriott, Unit operations of chemical engineering, McGraw-Hill, 6th ed., New York, USA, 2001
6. J. L. Bravo, J. R. Fair, Generalized correlation for mass transfer in packed distillation columns, Ind. Eng Chem. Process Des. Dev., 21, 162-170, (1982)
7. J.M. Villora, P. Callejas, M.F. Barba, C. Baudı´ n, Statistical analysis of the fracture behavior of porous ceramic Raschig ring, J. Eur. Ceram. Soc., 24, 589-94, (2004)
8. J.S. Reed, Introduction to Principles of Ceramic Processing, John Wiley & Sons, New York, USA, 1995
9. ASTM-C21, Standard Test Method for Water absorption, Bulk density, Apparent porosity of Fired Ceramic, Annual Book of ASTM Standards, 1995
10. ASTM C373, Standard Test Method for Water Absorption, Bulk Density, Apparent Porosity, and Apparent Specific Gravity of Fired Whiteware Products, 2006
11. Bortz, S.A. and Lund, H.H., The brittle ring test. In The proceedings of a conference conducted by the School of Engineering and the College Extension Division, North Carlonina State College in cooperation with the Office and Ordnance Research, ed. Interscience Publishers, New York-London, 1961
12. G. Jianghong, A new probability index for estimating Weibull modulus for ceramics with the least-square method, J. Mater. Sci. Letters,19, 827-29, (2000)
13. K. Trustrum, A. Des. Jayatilaka, On estimating the Weibull modulus for a brittle material. J. Mater. Sci., 14, 1080-84, (1979)
14. W.M Carty, U. Senapati, Porcelain-raw materials, processing, phase evolution, and mechanical behavior, J. Am. Ceram. Soc., 81, 3-20, (1998)
15. C. Aksel, The effect of mullite on the mechanical properties and thermal shock behaviour of alumina–mullite refractory materials, Ceramics International, 29, 2, 183-188, (2003)

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