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Ceramics International 40 (2014) 1093–1098

CERAMICS INTERNATIONAL

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Effect of zircon content on chemical and mechanical behavior of silica-based ceramic cores

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Received 17 November 2012; received in revised form 27 June 2013; accepted 28 June 2013
Available online 11 July 2013

Abstract

In this work, the effect of zircon content on the mechanical and chemical behaviors of injection molded silica-based ceramic cores has been investigated. In order to simulate a casting process condition, the sintered samples at 1220 °C were consequently heated up to 1430 °C. Three point bending tests were carried out on all the prepared samples. The chemical resistance of the prepared cores was evaluated by leaching of samples in 43% KOH solution at its boiling point. Phase evolution and microstructure were investigated by XRD and SEM, respectively. Results showed that increasing zircon content led to an increase in MOR and decrease in leachability owing to the decrease in content of fused silica with lower strength and chemical stability. The leaching rate of sintered ceramic cores was decreased after the simulated casting heat treatment at all zircon contents due to crystallization of cristobalite, with a higher chemical stability, on the surface of fused silica particles.

Keywords: Silica-based ceramic core; Zircon content; Cristobalite transformation; MOR; Leachability

1. Introduction

Ceramic cores are extensively used in hollow shape casting. Proper match between the ceramic core, investment casting ceramic mold and metal blade is essential for proper performance of the casting process. Also, a ceramic core must have other specific properties such as dimensional conformity, mechanical strength, thermal shock resistance, thermal stability, chemical inertness against the super alloy, enough mechanical weakness to prevent the generation of cracks or tears in the casted part and gas permeability [1].

Zircon ($ZrSiO_4$), as an essential component in silica-based ceramic cores, can improve their high temperature properties. It is also useful in investment casting mold due to its low thermal expansion coefficient ($\approx 4.1\times10^{-6}\,°C^{-1}$, 25–1400 °C), low coefficient of heat conductivity ($5.1\ Wm^{-1}\,°C^{-1}$ at 25 °C and $3.5\ Wm^{-1}\,°C^{-1}$ at 1000 °C) and high thermal and chemical stability [2–4].

Wilson et al. reported that increasing the amount of zircon could have beneficial effects on some properties such as creep resistance and flexural strength at 1475 °C. They also reported that silica, with high surface energy, could increase the sintering rate and consequently improve strength/creep resistance of ceramic core. Moreover, they showed that zircon, as an inert secondary phase, could act as a Zener pinning agent at high temperature and prevent consolidation by introducing a pinning force at the grain boundaries [4].

Wang and Hon studied transformation kinetics of fused silica with and without cristobalite seed. They suggested a nucleation and growth model for fused silica crystallization and showed that the cristobalite seed could induce compressive stress resulting from volume expansion of $\alpha\rightarrow\beta$ cristobalite transformation at elevated temperatures [5]. They also investigated the zircon effect on cristobalite crystallization by quantitative XRD. Their results showed that increase in the zircon content, as a nucleation site, could affect the crystallization rate of fused silica and decrease the time exponent (n) in the Avrami equation [3]. On the contrary,

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http://dx.doi.org/10.1016/j.ceramint.2013.06.108

Table 1
Characteristics of the used zircon, cristobalite and fused silica, as raw materials.

Powder	Purity (%)	Important impurities (Type – %)		Powder density (g/cm^3)	PSD			Specific surface area (m^2/g)	Source
					D$_{10}$ (μm)	D$_{50}$ (μm)	D$_{90}$ (μm)		
Fused Silica	98.3	Al_2O_3	0.7	2.06	2.74	27.7	105.05	0.777	Remet
Zircon	87.9	HfO_2	1.4	4.34	2.23	20.4	60.51	1.08	Cookson
		WO_3	1.4						
		Ta_2O_5	1.2						
		ZnO	0.52						
		CuO	0.51						
Cristobalite	99.4	Al_2O_3	0.15	2.24	3.4	14.1	34.02	0.727	Sibelco

Wilson et al. suggested that zircon could not act as a nucleator in fused silica crystallization.

Therefore, lack of information about zircon behavior in silica-based ceramic cores and even their contradictory results led us to study the effects of zircon content on mechanical and chemical properties of silica-based ceramic cores.

2. Experimental procedure

Characteristics of the used zircon, cristobalite and fused silica, as raw materials, are illustrated in Table 1. Purity, powder density and specific surface area were measured with XRF, pyknometer and laser particle size analyzer (LPSA), respectively. Different silica-based ceramic cores, containing 10, 16, 22 and 28 wt% zircon, were injection molded in test bar shape with $150 \times 22 \times 5\ mm^3$ LWH dimension by C-FRAME 100 ton injection machine. Increase in zircon content was accompanied with decrease in fused silica content, while cristobalite content was always 3 wt%.

The prepared samples were then sintered at 1220 °C for 6 h. Some of the sintered samples were subsequently subjected to a simulated casting heat treatment at 1430 °C for 30 min.

Modulus of Rupture (MOR) of both sintered and heat treated samples were determined through a three point bending test by SANTAM STM-5 machine with span distance of 100 mm and 6 N/s loading rate according to ASTM C674. Each reported MOR result was an average of ten tests. Density and residual porosity were also determined by Archimedes method according to ASTM C373.

The leaching rate of $22 \times 10 \times 5\ mm^3$ LWH specimens, after sintering and simulated casting heat treatment, was measured inside 43% KOH solution at its boiling point for 15 and 25 min, respectively. The leaching rate, K, was calculated based on Eq. (3), where ΔW was the total weight loss (g), A was the initial surface area (cm^2), t was the leaching time (h) and ρ was the specimen density (g cm^{-3}).

$$K = \Delta W/(A\rho t^{1/2}) \tag{3}$$

The above formula provides leaching rate independent of sample size and shape, which fits well with diffusion controlled model for leaching process [6].

The approximate quantity of crystalline phases in the sintered and simulated casting heat treated samples was determined by an X-ray powder diffractometer with Ni-filtered CuKα radiation (PW1800- Philips), step size of 0.04° and detecting time of 4 s at each step. Polished cross section and fractured surface of the prepared samples were analyzed by scanning electron microscope (SEM, VEGA TESCAN, Czech) operating at 15 kv.

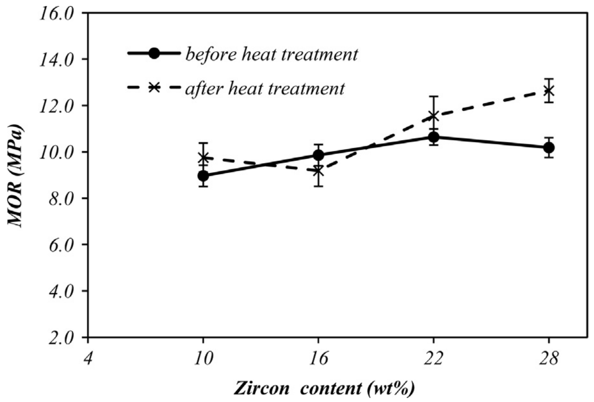

Fig. 1. MOR results of the ceramic cores with various zircon contents before and after the heat treatment.

3. Result and discussion

As shown in Fig. 1, the MOR of sintered and simulated casting heat treated samples slightly increased with increasing zircon content. These results can be attributed to higher strength of the zircon particles in comparison with the fused silica particles.

SEM micrograph (in SE[1] mode) of the simulated casting heat treated sample (containing 10 wt% zircon) in Fig. 2(a) depicts a mixed fracture behavior consisting of both intergranular and transgranular fracture surfaces. The transgranular fracture behavior was detected as smooth surfaces in the fused silica grains while zircon grains exhibited the intergranular fracture behavior.

SEM image of the crack propagation path (in BSE[2] mode) in Fig. 2(b) also confirms persistence of zircon grains against the crack growth, while crack easily propagates through the fused silica grains. In fact, crack propagation occurs more

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[1] Secondary Electron.

[2] Back Scattered Electron.

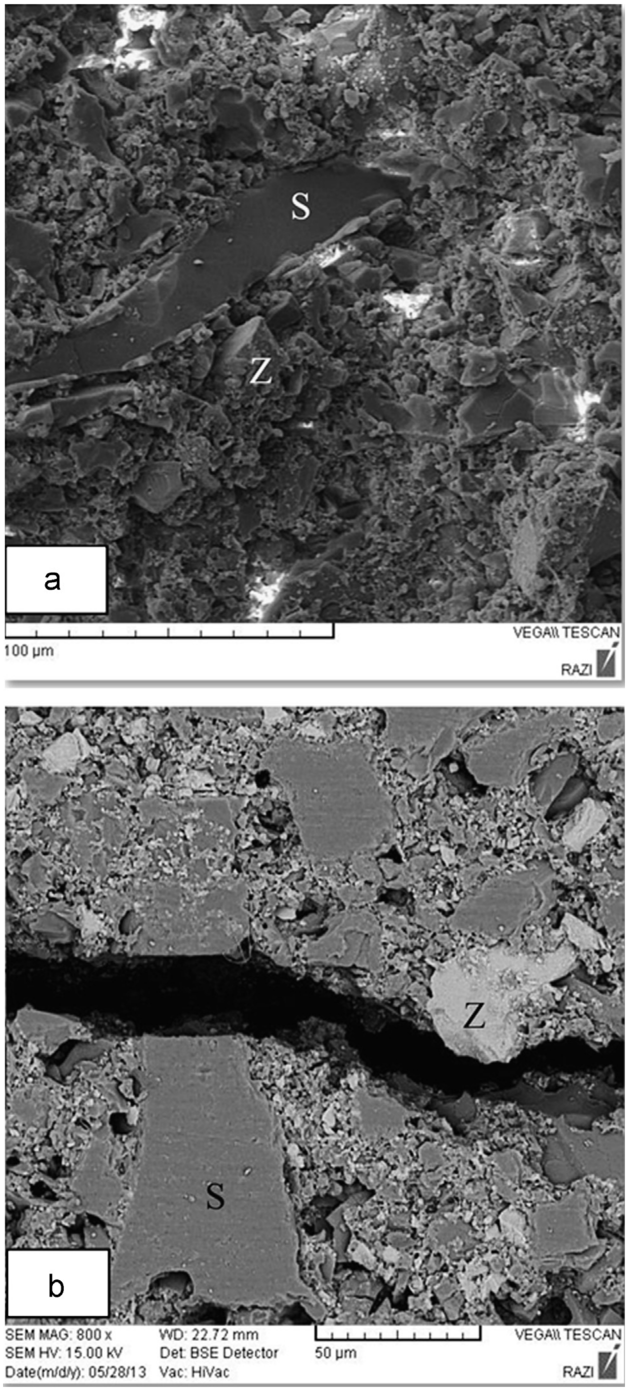

Fig. 2. SEM images of the simulated casting heat treated sample containing 10 wt% zircon: (a) the fractured surface, and (b) the crack propagation path (S: silica grain; Z: zircon grain).

easily in the fused silica particles than in the zircon particles. Therefore, increase in zircon content, which was accompanied with decrease in fused silica content, resulted in slight increase of MOR.

XRD patterns of the samples with various zircon contents are shown in Fig. 3. In addition, Fig. 4 presents the changes of cristobalite to zircon weight percent ratio in the raw mixtures and cristobalite to zircon main peak ratio versus zircon content, before and after simulated casting heat treatment (extracted

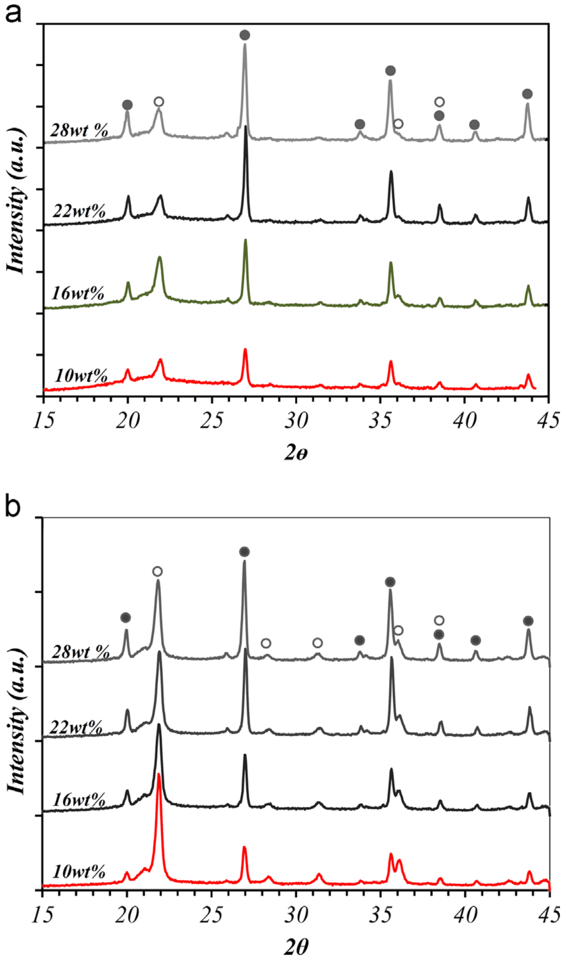

Fig. 3. XRD patterns of the sintered samples with various zircon contents: (a) before and (b) after the simulated casting heat treatment (○; cristobalite, ●; zircon).

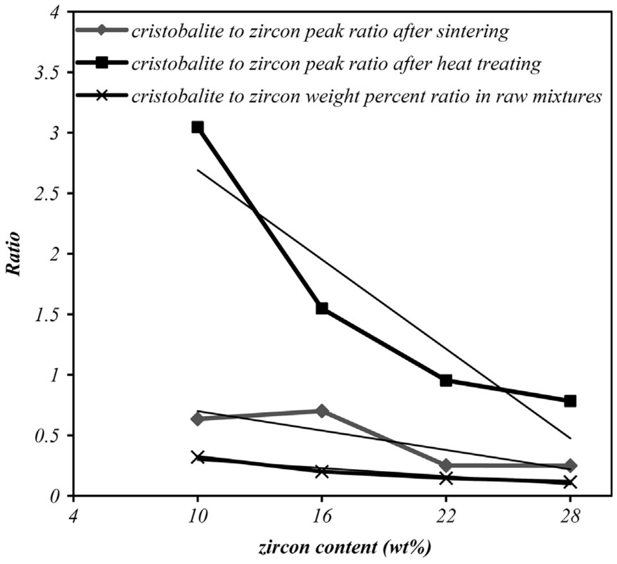

Fig. 4. Cristobalite to zircon weight percent ratio in raw mixtures and cristobalite to zircon main peak ratio, before and after the simulated casting heat treatment, versus zircon content.

from Fig. 3). Since cristobalite crystallization occurs on the surface of fused silica particles during heat treatment, as shown in Fig. 5(a), increase in zircon content and therefore decrease in fused silica content can result in decrease of in-situ formed cristobalite content. This result is contrary to the Wang and Hon report [3], but it is in a good agreement with the Wilson et al. result [4].

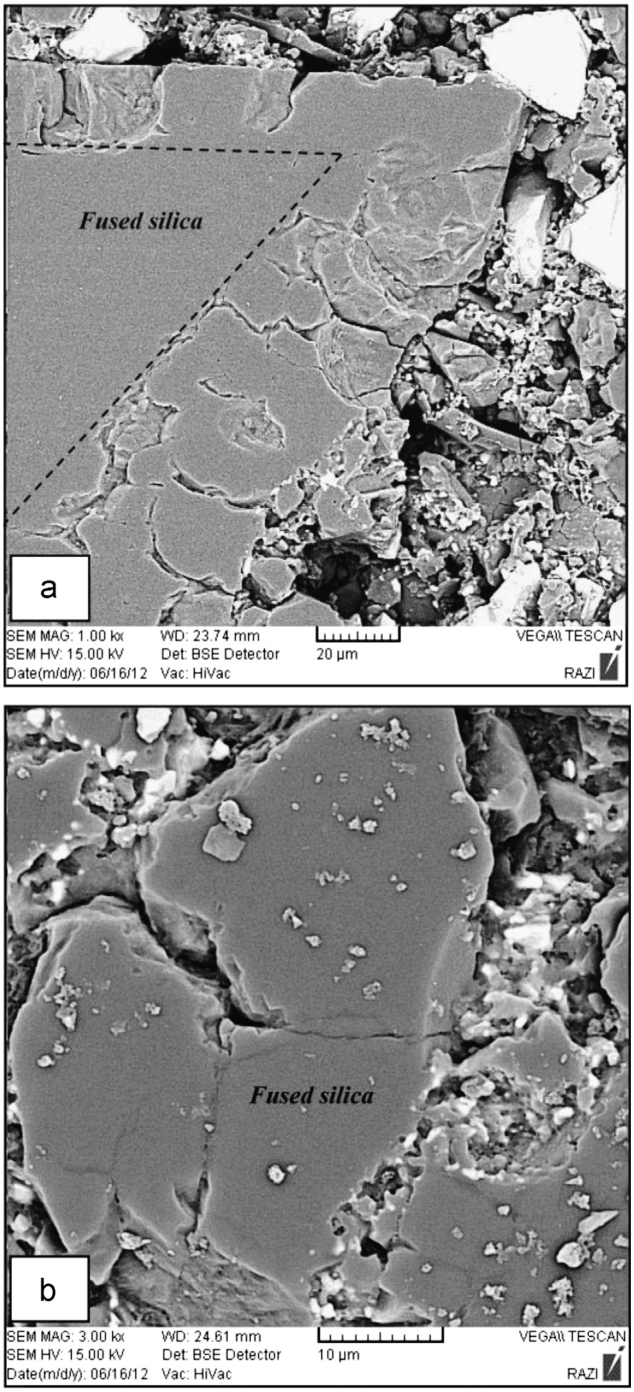

Fig. 5. SEM micrographs of the heat treated samples, containing 10 wt% zircon: (a) cristobalite surface crystallization on the fused silica grain, and (b) crack formation in the fused silica grain.

To investigate the sole effect of zircon on the fused silica crystallization, samples containing fused silica with and without 10 wt% zircon were additionally shaped and sintered at 1220 °C for 6 h. Some of the sintered samples were also heated at 1400 °C for 1 h. 10 wt% alumina powder, as reference, was added to each heated sample before X-ray analysis. Fig. 6 shows the XRD results. The main peak intensity ratio of cristobalite to alumina after various heat treating cycles (extracted from Fig. 6) is presented in Fig. 7. As it seems, fused silica crystallization at 1220 °C is negligible and zircon does not have considerable effect on it. These results also show that, at elevated temperatures (1400°–> C),°C), zircon addition decreases formation of the in-situ cristobalite.

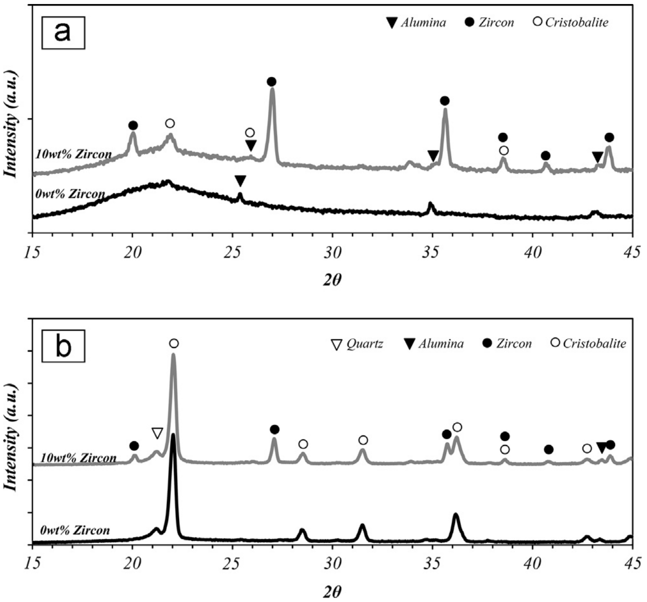

Fig. 6. X-ray diffraction patterns of the sintered samples at 1220 °C for 6 h with and without zircon: (a) before and (b) after heat treatment at 1400 °C for 1 h.

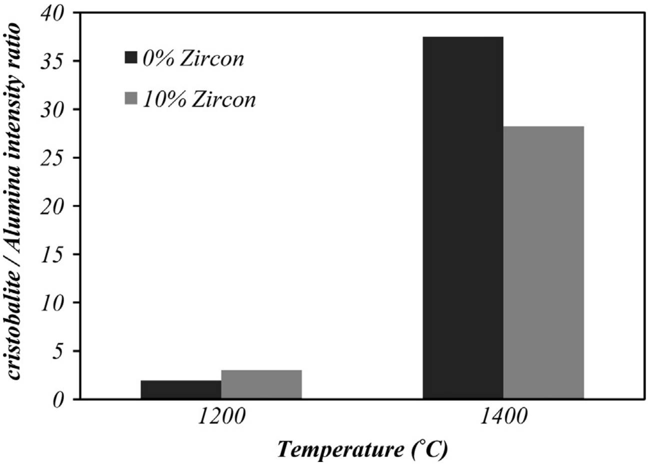

Fig. 7. 100% peak intensity ratio of cristobalite to alumina for the sintered samples at 1220 °C for 6 h with and without zircon before and after heat treatment at 1400 °C for 1 h.

Lower total cristobalite content and therefore formation of fewer microcracks (resulting from $\beta \rightarrow \alpha$ phase transformation) is an evidence for increasing of MOR for the heat treated samples, when zircon content increases [5,7]. SEM image of the polished surface of heat treated samples in Fig. 5(b) demonstrates formation of cracks in the fused silica particles. Comparing the slope of cristobalite to zircon weight percent ratio graph with two others, in Fig. 4, demonstrates that cristobalite content in the heat treated specimens decreases with higher rate in comparison with both raw batches and sintered samples, when zircon content increases. Therefore, MOR of the simulated casting heat treated samples increases with higher rate than that of the sintered samples, when zircon content increases.

It seems that positive effect of the improvement in sintering during simulated casting heat treatment at higher temperature could compensate negative effect of higher in-situ cristobalite formation during this treatment on MOR results. Therefore, MOR of the simulated casting heat treated samples are almost the same as the sintered ones. However, in the case of sample with the highest zircon content, this positive effect could even overcome the mentioned negative effect, due to the lowest difference in cristobalite content in this sample before and after heat treatment (Fig. 4), which results in higher MOR after heat treatment in comparison with the sintered one at the highest zircon content (Fig. 1).

Porosity, as another effective parameter, can also affect the strength of ceramic core. As Fig. 8 shows, open porosity of the core body increases with increasing the zircon content, before and after the heat treatment. Zircon with very high melting point increases the sintering temperature and consequently the residual porosity of the silica based ceramic core. Higher residual porosity of the heat treatment samples in comparison with the sintered ones, in spite of the higher heating temperature and consequently better sintering, is due to the fused silica crystallization into cristobalite form and its polymorphic transformation from β to α during cooling, which introduces several cracks to ceramic core (Fig. 5). However, it seems that effects of the previously mentioned parameters overcome the effect of porosity due to its very small changes.

Fig. 9 presents the effect of zircon content on leaching rate of the sintered and simulated casting heat treated samples. To explain these results, leachability of the fused silica, cristobalite and zircon powders, as the main components in silica based ceramic core, with the same particle size has also been investigated inside 43 wt % KOH solution at its boiling point for 5 min. The weight loss of each powder after the leaching test is presented in Fig. 10. As it seems, the fused silica powder shows the lowest corrosion resistance with more than 50% weight loss, while cristobalite powder has more resistance in KOH (< 10% weight loss) and zircon presents the highest resistance against leaching solution. In fact, since increase in zircon content (with higher chemical resistance) was accompanied with decrease in fused silica, leachability of the silica-based ceramic core was decreased with the increase of zircon content. Lower leaching rate of the simulated casting heat treated samples in comparison with the sintered ones at any zircon content is also due to the formation of in-situ cristobalite on the surface of fused silica grains with lower leachability in comparison with the fused silica.

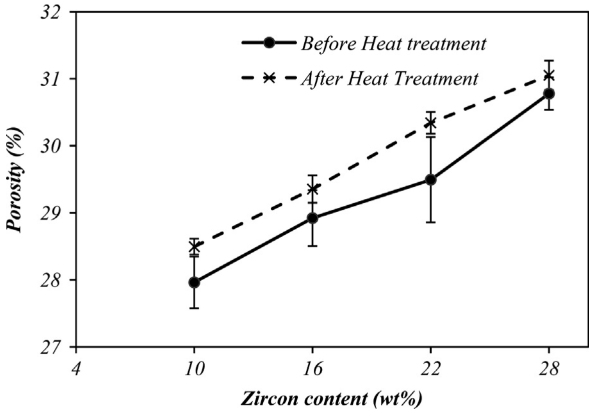

Fig. 8. Porosity of the sintered samples containing various zircon contents, before and after heat treatment.

4. Conclusion

In this work, effects of zircon content on properties of injection molded silica-based ceramic cores have been investigated. Results showed that increase in zircon content caused

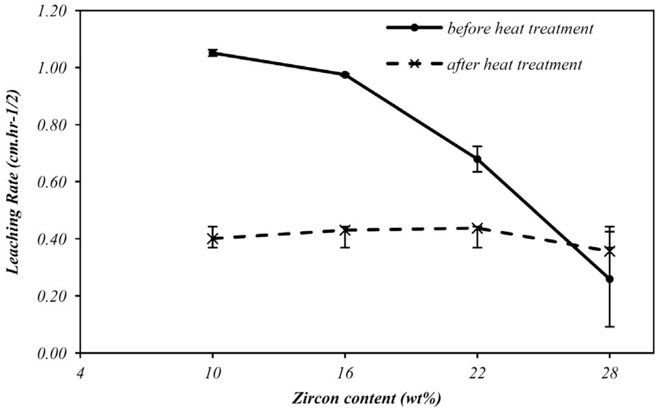

Fig. 9. Effect of zircon content on leaching rate of the sintered samples before and after the simulated casting heat treatment.

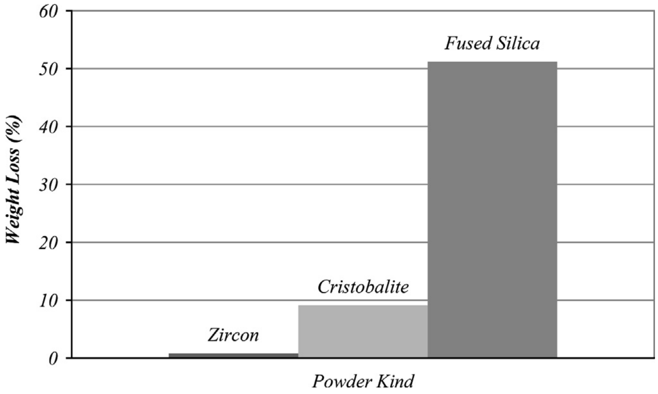

Fig. 10. A comparison between leachability of cristobalite, fused silica and zircon with the same particle size.

an increase in MOR and decrease in leaching rate, due to the decrease in content of fused silica with lower strength and chemical resistance.

Moreover, leaching rate of the simulated casting heat treated samples at any zircon content was lower than that of the sintered samples due to the higher chemical resistance of cristobalite phase that was crystallized on the surface of fused silica particles during the simulated casting heat treatment.

However, MOR results of the simulated casting heat treated samples were almost the same as MOR of the sintered samples, especially at lower zircon contents. It seems that improvement in sintering compensated the negative effect of in-situ formed cristobalite during the simulated casting heat treating and its further $\beta \rightarrow \alpha$ phase transformation during cooling. This result is contrary to the Wang and Hon report [3], but it is in a good agreement with the Wilson et al. result [4].

Acknowledgment

The authors gratefully acknowledge the MAPNA Turbine Blade Eng. & Mfg. Co. PARTO, Research and Development Department of MAPNA and PARTO for their funding and also Mr. H. Alizade and Mr. M. Abrishami for their technical assistant.

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