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Investigation on the effect of silica sand addition in densification of Al_2O_3-SiO_2-ZrO_2 composite

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The possibility of using SiO_2 sand as additive for densification of the Al_2O_3-SiO_2-ZrO_2 (ASZ) ceramic composite was studied. Dilatometry was used to measure the shrinkage behavior of ASZ green bodies under a nitrogen atmosphere from room temperature to 1823 K. The first liquid formed at 1373 K, resulted in a significant reduction of the sintering temperature. It also indicated that the phase transformation occurred during the sintering process had reduced the sintering temperature to1723 K. Alumina, zirconia and mullite phases were detected and confirmed by XRD and FESEM results. Based on those results, it can be concluded that SiO_2 is an additive in lowering the sintering temperature of ASZ composite.

Key words: Alumina, Dilatometry, Silica, Sintering, Zirconia.

Introduction

The mechanical properties of ceramic-based composites for industrial applications are related to their microstructure. In this sense, a study of all the aspects that can modify the microstructure of a ceramic composite during sintering is very crucial. Dilatometry is one of the most powerful techniques for the study of solid-solid phase transformations in ceramic sintering, because it permits the real time monitoring of the evolution of transformations in terms of dimensional changes occurring in the sample by application of a thermal cycle [1].

Alumina-based composites are of relatively low cost, and the ceramic components are manufactured with high output using various ceramic processing such as slip casting, pressing, and injection moulding, without incorporating expensive equipment such as kilns with specially controlled atmosphere. However, the application of alumina-based ceramics is still limited due to high cost of additives and high sintering temperatures [2-5]. Therefore, there are continuous searching for production process of both low-cost alumina starting powder and sintering additives, which are equally inexpensive and enable low sintering temperatures.

Silica sand is the most essential raw material used by foundries for its thermal resistance and availability. However, its usage in ceramic based composites developments is overlooked. The use of silica [6] and other oxides such as MgO, CaO, and CrO as a sintering aid is often reported to increase the densification kinetics and to limit the grain growth in ceramic composites [7]. A first approach on the effect of a silica addition on the sintering of yttrium aluminum garnet doped by neodymium (Nd:YAG) [8] was investigated on the basis of microstructural characterization. However, no work has yet been done on a dilatometric study of the Al_2O_3-SiO_2-ZrO_2 system to use silica as a sintering aid. Thus, the purposes of this paper are to investigate the dilatometric behavior of a mixture of Al_2O_3-ZrO_2 with addition SiO_2 and to understand the sintering phenomena.

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Experimental Procedure

Raw materials

Commercial Al_2O_3 (90 μm) powder of high purity (99.99%), a 3 mole % magnesia stabilized tetragonal zirconia (Mg-ZrO_2) (17 μm) as well as SiO_2 (6.6 μm) was used as a starting materials. The SiO_2 ceramic was produced in the laboratory by the dry milling process from locally found silica sand around Tronoh, Perak, Malaysia.

Powder particle size analysis was done in a Malvern™ Mastersizer operated between the size range of 0.02-3000 μm. The apparatus has a stirring mechanism so that possible agglomeration can be avoided. Multiple recursive trials were made with each batch to account for the statistical size discrepancies of irregularly shaped particles and the last trial was accepted as the final data. The microstructure of the particles was also studied to observe and analyze the shape of the particles.

Sample preparation

The samples involved in this study were pure alumina (sample 1), Al_2O_3 + 10% wt SiO_2 (sample 2) and Al_2O_3 + 10% wt SiO_2 + 10% wt ZrO_2 (Al_2O_3-10SiO_2-10ZrO_2) (sample 3). A number of composition of the Al_2O_3-SiO_2-ZrO_2 composite system used is shown in Table 1. In order to prepare the composite

Table 1. Proportion of each component in the samples.

Sample no:	Composition (wt %)		
	Al_2O_3	SiO_2	ZrO_2
S1	90	0	10
S2	85	5	10
S3	80	10	10
S4	70	20	10
S5	65	25	10

sample mixtures, the constituent powders were weighed in a precision balance (A&D weighing) in various proportions and mixed thoroughly. In the process of preparing the mix, it was ensured that the powder mix was evenly distributed. This was achieved through the use of a dispersant (alcohol) which helped in avoiding agglomeration. Polyvinyl alcohol (PVA) was also used as a binder for the composite system. The mixture was ball milled for 7 hr in the alcohol medium to obtain a homogeneous mixture.

The mixture was then cold pressed (450 MPa) in a high alloy steel mold fabricated in house using a hydraulic press (Flowmech Engineers Pvt. Ltd). A dilatometric study was then carried out under an argon atmosphere. The thermal cycle for the dilatometric study was set according to Fig. 1. The coefficient of thermal expansion (CTE) of the compacted composite was measured using an alumina rod dilatometer (BAHR Thermoanalyse GmbH 2000 Model DIL801L).

The samples were smoothly ground, polished using a SiC paste and cleaned. The phase composition and crystalline properties of the samples were studied using X-ray diffraction (XRD) (Philips 1730 diffractometer) with Cu Kα radiation. The microstructural features of the composite were observed by scanning electron microscopy (SEM) (Philips XL30) with simultaneous chemical

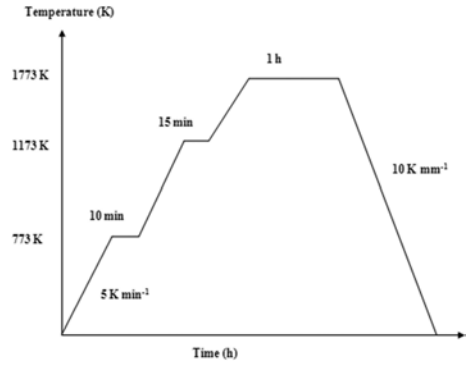

Fig. 1. Thermal cycle for the dilatometer study.

analysis using energy dispersive x-ray spectroscopy (EDS).

Likewise, the five samples of different proportions of silica sand as shown in Table 1 were taken and measured for their density and hardness after sintering.at 1722 K for 1 hr. The densities of the bulk sintered samples were measured by the Archimedes water immersion method while their hardness was obtained under a 1000 g load for 15 seconds using Vickers indentation. Vickers hardness (Hv) was determined from a minimum of 10 indents and then it was calculated with Equation 1 [9].

$$H = 1.85\left(\frac{P}{D^2}\right) \quad (1)$$

where P is the load in kg and D is arithmetic mean of the two diagonals, d_1 and d_2 in mm as shown in figure 5.

Results and Discussion

Particle size and shape study

As shown in figures 2a, 2b and 2c, the powders have a Gaussian particle size distribution and they have an average particle size of 90, 6.6 and 17 μm with an estimated specific surface area of 0.07, 2.10 and

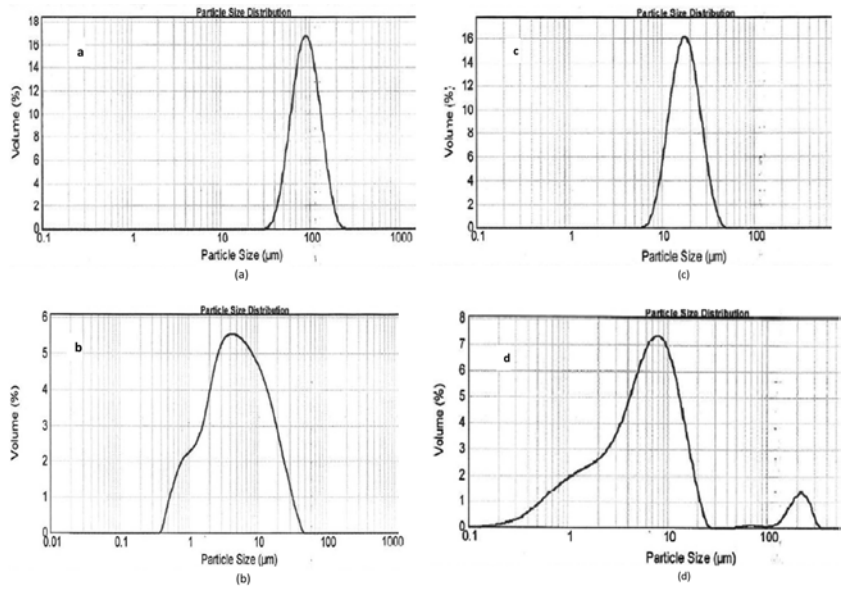

Fig. 2. Particle size distribution of (a) silica sand (b) alumina (c) zirconia (d) as-milled Al_2O_3-SiO_2-ZrO_2 composition.

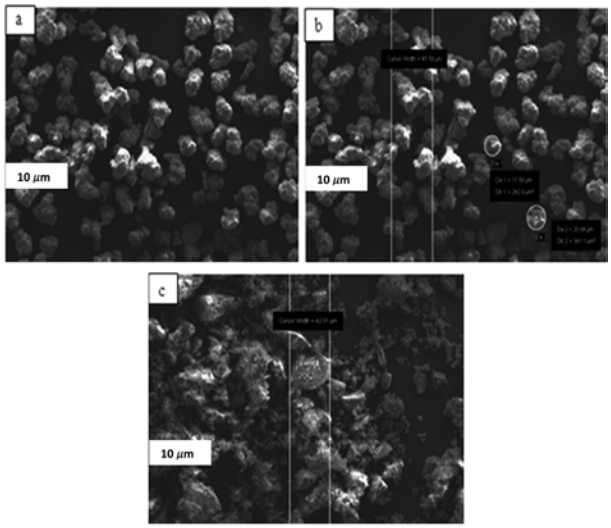

Fig. 3. SEM image of the initial powders (a) alumina (b) zirconia (c) silica.

0.36 m^2/g, respectively. Figure 2d shows that the average median particle size of the ball milled mix of the three ceramic powder system is 6.50 μm and the specific surface area is a 2.2 m^2/g.

The micrograph morphology of the powders was also studied and the results are shown in figure 3 for alumina, silica, and zirconia powders, respectively. They were analyzed for size distribution and the particle shape in order to predict the packing property behavior. The mix particle size distribution was wide and this would result in an increase of the packing density because the finer particles would fit within the large particles [10]. Particle shape influences the sintering primarily through its effect on the packing of the green body. Deviation from a spherical or equiaxed shape leads to a reduction in the packing density [10] and packing homogeneity, resulting in a reduction of densification. It is noted that although the powder size distribution seems uniform, there is an indication of aggregate or agglomerates, which could cause difficulty in the packing of particles during compaction the stage and consequently in the densification during sintering.

Densification and dilatometric behavior of the sintered part

Final densities and hardness of sintered samples, containing various silica contents, are reported in figure 4. It showed, for a concentration up to 5% wt of silica, both density and hardness decreased but for concen-trations of 5-10 wt % of silica the density tends to increase where as hardness continued decreasing.

The drop in bulk density as the concentration of silica increases can be explained by two factors: first, as a consequence of increased porosity, and second, as a result of the increased amount of the mullite phase, which is less dense than alumina. It appears that silica could play a role in the sintering behavior of Al_2O_3-

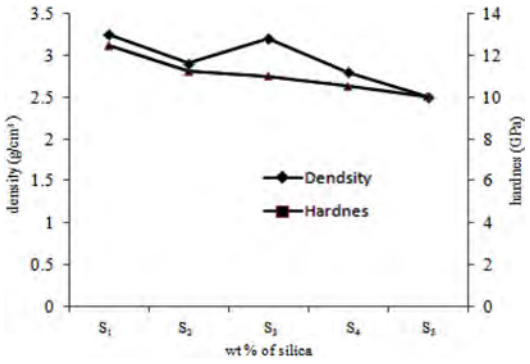

Fig. 4. Densification trend with respect to the silica composition.

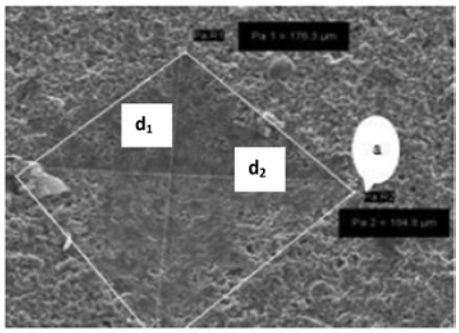

Fig. 5. A representative SEM image of the indented sample.

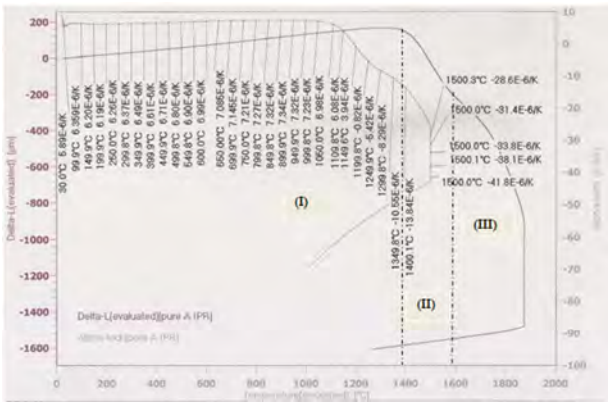

Fig. 6. Delatometric plot of sample 1pure alumina (conversion to Kelvin (K) may be used '°C+273').

SiO_2-ZrO_2 composites between the concentrations for which the density is higher as shown in the figure 4.

The Vickers hardness (H_V) was determined using Equation (1) and the calculated value was decreasing, for it is expected that the composite is getting tougher. Fig. 5 shows an SEM micrograph of a Vickers indent with the value of D (d_1 and d_2 from the picture) in Equation (1).

A dilatometric study of the sintering process is very useful because it shows the length change of green bodies during heat treatment while the curve shows different phenomena. Figures 6, 7 and 8 show delatometric plots of sample 1 (pure Alumina), sample 2 (10% wt. SiO_2) and sample 3 (10% wt SiO_2 + 10% wt. ZrO_2), respectively. The plots depict the shrinkage behavior of each of the different samples as a function of tem-perature.

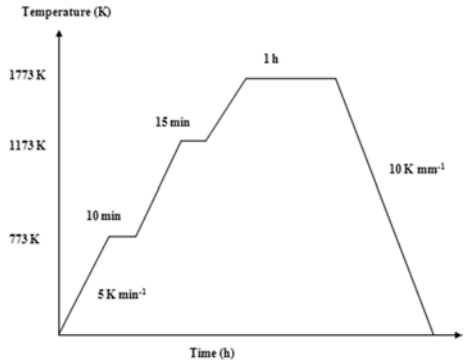

Fig. 7. Dilatometric plot of sample 2 (10% wt SiO_2), (conversion to Kelvin (K) may be used '°C + 273').

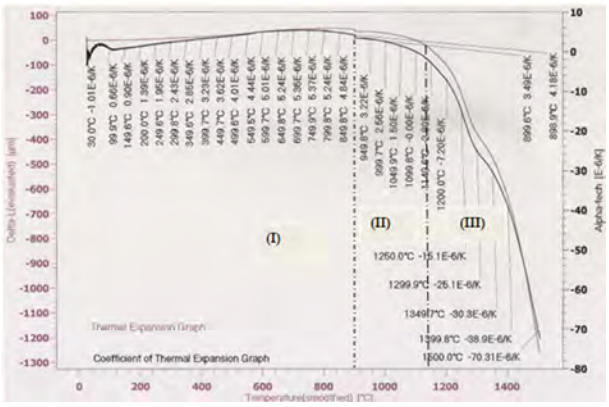

Fig. 8. Dilatometric plot of sample 3 (10% wt SiO2 + 10% wt ZrO2), (conversion to Kelvin (K) may be used '°C + 273').

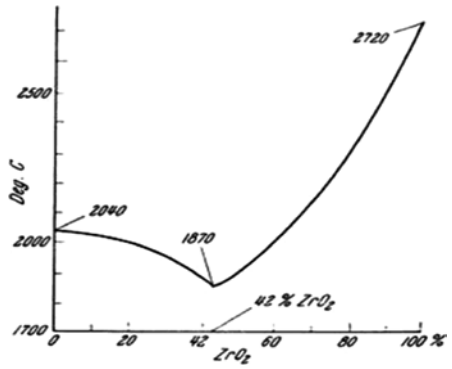

Fig. 9. Phase diagram for the alumina- zirconia system [11].

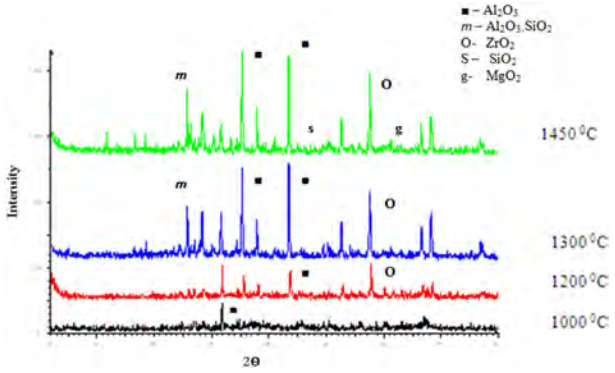

Fig. 10. X-ray diffraction diagrams for sample (Al_2O_3-10SiO_2-20ZrO_2) sintered between 1273 K and 1723 K. (conversion to Kelvin (K) may be used '°C + 273' in the figure).

A representative dilatometric plot of a pure alumina with some imputities (sample 1) is shown in figure 6. Upon heating, the change in length (ΔL) was the net result of two opposing mechanisms of linear thermal expansion and pore closing. Up to ~ 1673 K (region I), the composite expanded due to limited retraction rates characteristic of surface diffusion. The first necks could be observed. As the temperature increased, grain boundary and volumetric diffusion became the dominant mechanisms, as suggested by a significant change in the slope of the plot from region I to region II. The thermal expansion was roughly counterbalanced by the retraction rate. Further heating to around 1873 K was characterized not only by sintering but also homo-genization with mutual diffusion of impurities in the system.

In Fig. 7, with the addition of 20% wt to the Al_2O_3-ZrO_2 system (sample 2), we can observe that the rearrangement of the particles and creation pores starts at a lower temperature. The dilatometric behavior of the composite showed, starting from ambient to approximately 1153 K, a slight expansion was noticed and ruled by a mechanism similar to that discussed for sample 1. The slope of the dilatometric plot changed in the range of 1153-1473 K, corresponding to the onset of the contraction process. The slope in region II of the plot can be explained by the formation and growth of inter particle necking. Region III, between 1473 K and 1793 K, was characterized by volumetric diffusion and a phase transformation. A densified composite was formed around 1673 K, resulting in rapid contraction.

The dilatometric plot corresponding to sample 3 (Al_2O_3 + 10% wt SiO_2 + 10% wt ZrO_2) is illustrated in figure 8. The shape of the curve indicates almost the same occurrence as of figure 7, even though a 10% wt ZrO_2 was added to it. There were also dilatometric graphs from this experiment as a longer percentage of zirconia was added but the shape of the profile results were the same as figure 8. This implies that the effect of zirconia on the densification of the system is minimal but the exact effect may need further investigation to reach a concrete understanding.

According to the phase diagram of liquidus curve of Al_2O_3 -ZrO_2 in Fig. 9, the lowest eutectic temperature in the system is around 2123 K [11]. However, the overall liquid forming temperature is lower than the nominal eutectic temperature because of the present of SiO_2 in the liquid phase. This confirms that the Al_2O_3-SiO_2-ZrO_2 acts as a very good solvent for SiO_2, which is also a prerequisite for a good sintering additive.

Due to the occurrence of the liquid phase in the pressureless sintering process, the formation of amorphous glassy phases after cooling was expected. But the XRD pattern in Fig. 10 showed a remarkable increase in the

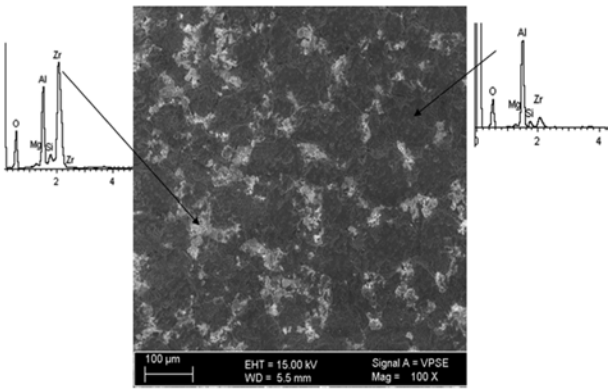

Fig. 11. SEM + EDS image of the sintered representative sample of the composite Al_2O_3-10SiO_2-20ZrO_2.

diffraction lines intensities, which can be explained by the increase of a new crystalline phase called mullite. The sintering of Al_2O_3-10SiO_2-10ZrO_2 composites at different temperatures indicates that no significant transformation takes place up to 1273 K. When heated to more than 1273 K, the samples begin to crystallize and the ZrO_2 phase starts to form. With an increase of temperature up to 1473 K the diffraction peaks of t-ZrO_2 and mullite are more evident as depicted from figure 10. These observations agree with the findings of the dilatometric study discussed above in this paper.

The representative X-ray diffraction results of the composites produced are shown in Fig. 10. This also showed that the composite were composed of Al_2O_3, ZrO_2 and mullite with a little SiO_2, phases which is constituent with the SEM observation shown in Fig. 11. It can be deduced that the starting materials SiO_2, and Al_2O_3, reacted completely to form mullite during the sintering process. The XRD pattern in figure 10 showed intense sharp peaks indicating good crystallinity of the ASZ based system for all compositions. The synthesis reactions can be summarized as follows:

$$4Al_2O_3 + 2SiO_2 + (1 + x)\ ZrO_2 \rightarrow 3Al_2O_3.\ 2SiO_2 + Al_2O_3 + x\ ZrO_2 \quad (2)$$

Fig. 11 is a typical SEM image of the Al_2O_3-10SiO_2-10ZrO_2 composite which shows the morphologies of zirconia and mullite particles within the alumina matrix. The chemical composition analysis with EDS along the line was more or less perpendicular to the $Al_2O_3/ZrO_2/3Al_2O_3$. $2SiO_2$ interface which showed that interdiffusion had occurred at the interfacial zone. Some zirconia was dissolved in the alumina matrix, while some SiO_2 particles were dissolved within the interface of the grain boundary to form a silicon oxide solid solution. This implies SiO_2 has been mainly assisting in the liquid phase sintering of the final composite. The SEM observation of the composite also showed that the distribution of ZrO_2 particles in the Al_2O_3 is uniform except for the small agglomerations in a few parts. The interfacial interdiffusion should enhance the surface adhesion.

It was also shown that mullite and zirconia particles with sub-micrometre in particle size were mainly located at grain boundaries, while finer ones were within matrix, inferring that larger mullite and zirconia particles suppress grain boundary movement of the alumina matrix. There was a good densification in the composites and a high level of bonding between grains and the matrix. This is supposed to be achieved due to the combination of solid state reaction bonding and liquid phase sintering mechanisms as has been analyzed in the dilatometric study.

Conclusion

In this paper, the chemical reactions and phase evolution during pressureless sintering followed by characterization using means of SEM + EDS, X-ray and dilatometric analysis were done. Results showed that the first liquid forms as low as 1373 K, sharing in a significant reduction of the sintering temperature. The final phase composition of the system obtained at 1723 K consists of crystalline alumina, mullite and zirconia phases. The results showed that the SiO_2 was a very effective lowtemperature sintering additive for ASZ composites. An optimum quantity of SiO_2 sand for the maximum densification was determined.

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