Low Temperature In-situ Reaction Sintering of Zircon: Alumina Composites Through Spark Plasma Sintering

M. C. Anjali, P. Biswas, D. Chakravarty, U. S. Hareesh, Y.S. Rao and R. Johnson

Abstract:
Pure Zircon and Zircon: Alumina (ZrSiO₄: α-Al₂O₃) composite powders were subjected to densification studies employing spark plasma sintering (SPS). Physicochemical and microstructural properties of the samples were evaluated and compared with that of conventionally sintered (CRH-Constant Ramp and Hold) compacts. Density measurements and microstructural evaluation revealed a low temperature densification of Zircon: Alumina at temperatures as low as 1300°C by SPS. Increase of temperature to 1350°C had shown negligible changes in density and on further heating the sample melts at 1400°C as a result of excessive formation of liquid phase. However, pure zircon could not be densified in the absence of alumina under SPS conditions. It is evident that addition of alumina enhances partial low temperature decomposition of zircon under the influence of plasma generated during SPS. Mullite formed as a result of this insitu reaction between alumina and silica acts as a bonding phase as revealed by the X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Electron dispersive scanning (EDS) analysis.

Keywords: Zircon, Spark Plasma Sintering, Mullite, X-ray Diffraction, SEM

1. Introduction

Zircon ceramic is an excellent refractory material with high chemical inertness and low thermal expansion coefficient. However, utilization of zircon is inadequate due to its inherent poor sinterability. Sintering of zircon has been a subject of several studies [1-5] and generally reaction sintering of alumina and zircon mixture in stoichiometric proportions lead to the decomposition reaction of zircon (ZrSiO₄→ZrO₂ + SiO₂) followed by the reaction between alumina and silica forming mullite and zirconia composites (Al₂O₃ + ZrO₂ + SiO₂ →ZrO₂ + Al₆Si₂O₁₃) [6-10]. Though the sinterability can be improved by this method, a temperature beyond 1550°C is essential by conventional Ramp and Hold (CRH) sintering to achieve sintered specimens with higher densities and correspondingly low porosities even with highly reactive submicron size powders. In addition to this, according to the stoichiometric reaction 3Al₂O₃ + 2ZrSiO₄ →Al₆Si₂O₁₃ +ZrO₂, the reaction mixture should have 45.54% by weight of Al₂O₃ and 54.35% by weight of ZrSiO₄ and corresponding reactions results in volume changes that competes with the densification shrinkage necessitating very critical processing conditions. Further the zirconia produced as a result of the reaction imparts volume changes while transformation to monoclinic zirconia during cooling leading to

*) Corresponding author: royjohnson@arci.res.in
microcracking and exhibiting poor mechanical properties. Hence addition of Al₂O₃ in non-stoichiometric amounts which forms transient liquid phase has also been experimented to improve the sinterability [11-16].

T. Ebadzadeh et al [1] have compared microwave assisted sintering of pure zircon with conventional ramp and hold sintering and reported a maximum relative density of 88% with microwave assistance against 80% with conventional sintering. E. Rocha-Rangel et al [9] have produced ZrO₂-toughened mullite ceramic composites by spark plasma reaction sintering using a mixture of zircon, α-Al₂O₃ and aluminum metal. They reported the decomposition of zircon and the formation of mullite at an SPS temperature of 1420°C which finishes at 1560°C and the relative density achieved was reported to be around 95.5%. K. A. Khor et al [6] have reported the densification of plasma spheroidized zircon and alumina mixtures by spark plasma achieving a density close to 99.5% relative density. Authors have attributed the observed high density to plasma spheroidization of the zircon: alumina mixture. However, low temperature in-situ reaction sintering of zircon: alumina composites through SPS technique have not been reported so far.

The objective of the present study is to explore the densification behaviour of pure zircon and zircon with alumina as a sintering aid by the spark plasma sintering technique (SPS) and to provide a comparative evaluation with the conventional sintering. Investigations were also carried out to elucidate low temperature in-situ reaction during SPS and effect of alumina addition on sintering. The samples are studied for their phase evolution by XRD and compositional analysis through EDS followed by characterization for their micro-structural development and hardness measurements.

2. Experimental Work

Characterization of Raw materials

Commercially procured high purity zircon (Australian origin) and alumina (AHPA Ceralox, Sasol, USA) were characterized for their particle size and phase identification using XRD (D8 Bruker, Germany). Further morphology of the powder was recorded using the Scanning Electron Microscope (FESEM, Hitachi, Japan).

Compaction and conventional sintering

Zircon (ZrSiO₄) and the mixture of zircon and alumina (α-Al₂O₃) mixed in the ratio of 90:10wt% were attrition milled in isopropyl alcohol for 1 hour in presence of a polyvinyl pyrrolidone as a binder and were further dried and compacted into discs of 10mm diameter by applying 250 MPa pressure. The compacted samples were characterized for their green densities and were conventionally sintered at 1600°C for 1 hour in a PID controlled Muffle furnace (Nabertherm, Germany) at the rate of 120°C/hour.

Spark plasma sintering of specimens

Zircon (ZrSiO₄) and the mixture of zircon and alumina (α-Al₂O₃) prepared above were subjected to SPS sintering (Model Dr. Sinter 1050) into 20mm discs in a graphite die with a heating rate of 100°C/min to the temperatures of 1300°C, 1350°C and 1400°C at a pressure of 50 MPa for a dwell time of 10 minutes.

Characterization of Samples

Sintered discs prepared by both the sintering techniques were characterized for their density and porosity using Archimedes principle and the theoretical densities were calculated by rule of mixtures (theoretical density of pure zircon and alumina are 4.65 and 3.9865 g.cm⁻³
respectively). Specimens were also subjected to XRD analysis to identify additional phases emerging from both sintering processes. Microstructural analysis of polished and thermally etched samples were carried out using SEM (Hitachi 2400, Japan) simultaneously with composition analysis of the samples by EDS. The samples were characterized for micro hardness under a load of 500g using micro hardness tester (UHL VMHT).

3. Results and Discussions

Raw materials characterization

Table I represents the characterization data of the raw materials. XRD patterns of high purity zircon and alumina samples are presented in Fig. 1. XRD patterns of the samples have shown ZrSiO$_4$ and $\alpha$-Al$_2$O$_3$ as the prominent phase in case of zircon and alumina samples respectively. The average particle sizes were around 4.5$\mu$m for zircon and 0.3$\mu$m for alumina as is evident from SEM micrograph shown in Fig. 2.

Fig. 1. X-ray diffraction pattern of as received Zircon and Alumina.
Tab. I. Characterization data of raw materials.

|                  | Zircon            | Alumina          |
|------------------|-------------------|------------------|
| Purity           | >98.5%            | 99.99%           |
| Phase Analysis (XRD) | 100% zircon phase (As shown in Fig. I) | 100% α-alumina (As shown in Fig. I) |
| Particle size    | 4.5 µm (As shown in Fig. II) | 0.5 µm (As shown in Fig. II) |

Fig. 2. Morphology of as received (a) Zircon and (b) Alumina powder.

Sintering studies of zircon: alumina composites

Table II presents the sintering parameters and densities of pure zircon and zircon with alumina additive densified using CRH and SPS sintering techniques. In CRH mode, though the samples were exposed to a temperature of 1550, 1600 and 1625°C the samples with a dwell time of 60 minutes the density of the samples could not be improved significantly even with addition of alumina. The maximum density exhibited by the samples was found to be 3.88 g/cm³ in case of pure zircon against 3.77 g/cm³ with alumina addition. This is due to the high coordination of the bisdisphenoid ZrO₂ in the tetragonal structure with SiO₄.
tetrahedra [17], though XRD patterns depicted in Fig. 3 indicated evidence of mullite formation. This is further evident from the highly porous microstructures in Fig. 5 a and b for pure zircon and zircon with alumina additives respectively sintered at 1600°C.

It is evident that unlike CRH samples SPS sintering of zircon with alumina addition has resulted in densification achieving a density of 4.23 gcm-3 in comparison to the maximum of 3.77 gcm-3 achieved through CRH sintering technique. Density remained almost constant at 4.16 gcm-3 on increase of temperature to 1350°C which on further increase of temperature to 1400°C resulted in formation of excess liquid phase and melting of the formulation. It is also evident from the table II that surprisingly there is no significant effect
of SPS sintering on pure zircon exhibiting a density of 3.85 gcm-3 versus 3.88 gcm-3 as in the case of CRH technique indicating the role of alumina as a sintering additive. The XRD pattern depicted in Fig. 4 also revealed the evidence of mullite formation even at a low temperature of 1300°C under SPS condition.

![Fig. 5. Microstructure of zircon alumina composite densified by (a) CRH 1600°C/1h, (b) Pure Zircon 1600°C /1h, CRH, (c) SPS 1300°C/10min, (d) SPS.](image)

**Tab. II** Sintering Parameters and Sintered densities of the pure zircon samples.

| Sl. No | Sample Identified | Sintering technique | Sintering temperature (°C) | Dwell Time (Min) | Density (gcm⁻³) | % TD | Hardness (Kg/mm²) | Grain Size (μm) |
|--------|------------------|---------------------|-----------------------------|-----------------|-----------------|------|------------------|----------------|
| 1      | ZrSiO₄           | CRH                 | 1550 1600 1625              | 60 60 60        | 3.66 3.88 3.47  | 78.70| 83.44 74.62      | 600 30          |
| 2      | ZrSiO₄ + α-Al₂O₃ | CRH                 | 1550 1600 1625              | 60 60 60        | 3.33 3.77 3.19  | 72.70| 82.31 69.65      | 642 5           |
| 3      | ZrSiO₄           | SPS                 | 1300                         | 60              | 3.85           | 82.79| 680              | 25             |
| 4      | ZrSiO₄ + α-Al₂O₃ | SPS                 | 1300 1350 1400              | 10 10 10        | 4.23 4.16 Melted| 92.35| 90.8 1280        | 25 -            |
Further, the micro-structural observations also confirm the measured density values. It can also be observed that large ZrSiO$_4$ grains are surrounded by smaller ones that appear in bright contrast. EDS examination of the elemental composition and their quantitative interpretation confirmed the formation of mullite at low temperatures of 1300°C (Fig. 6). The high density values obtained for zircon with alumina addition can be attributed to the enhanced densification rate due to mechanisms like particle rearrangement and breaking up of agglomerates aided by the applied pressure and faster heating rates under SPS sintering conditions. Applied electric field also promotes the diffusion of Al$^{3+}$ ions through the siliceous phase produced as a result of the minor decomposition of zircon at the SPS temperature of 1300°C (Fig. 4). It is also evident from the mullite peak appeared in the XRD pattern. Indentation hardness of the pure zircon sintered by CRH, zircon-alumina samples sintered by CRH (1600 and 1625°C) and SPS indicated average value of 600, 642, 692, 1280 Kg/mm$^2$ respectively (average of 10 readings) for the samples with highest sintered densities. Further the corresponding grain sizes are also presented in the Tab. II. The high hardness value of 1280 Kg/mm$^2$ for the sample sintered at 1300°C in SPS also complemented by dense microstructure.

4. Conclusion

Density measurements of SPS sintered zircon: alumina formulations revealed a low temperature densification as low as 1300°C. However, pure zircon could not be densified in the absence of alumina under identical SPS conditions indicating the effectiveness of alumina as a sintering additive.

Zircon: alumina formulations could not be sintered even at 1625°C when CRH methodology is employed, though the presence of mullite peaks is evident from the XRD
pattern. This confirms a combination of unique mechanism operative under SPS condition and enhancement of diffusion of Al\(^{3+}\) ions through the siliceous phase produced as a result of zircon decomposition. Complementary results are obtained from microstructural, EDS analysis and knoop hardness confirms the densification of the specimens by the SPS process.

5. References

1. T. Ebadzadeh, M. Valefi, J. Alloys. Compd., 448 (2008) 246.
2. W. P. C. M. Alahakoon, S. E. Burrows, A. P. Howes, B. S. B. Karunaratne, M. E. Smith, and R. Dobedoe, J. Eur. Ceram. Soc., 30 (2010)2515.
3. M. Awaad and S. H. Kenawy, Brit. Ceram Trans., 10 (2003) 69.
4. P. Tartaj, J. Am. Ceram. Soc., 88 (2005) 22.
5. W. Y. Wang, A. H. Wang, D. W. Zeng, Z. K. Bai, C. S. Xie, W. L. Song, and X. C. Zhu, Mater Char., 56 (2006) 227.
6. K. A. Khor, L.G. Yu, Y. Li, Z.L. Dong, Z.A. Munir, Mater. Sci. Eng. A., 339 (2003) 286.
7. K. A. Khor, Y. Li, Mater.Lett., 48 (2001) 57.
8. A. Bradecki, S. Jonas, Ceram. Int., 36 (2010) 211.
9. E. Rocha – Rangel, S. D. de-la-Torre, I. Umemoto, H. Miyamoto, H. Balmori-Ramirez, J. Am. Ceram. Soc., 88 (2005) 1150.
10. S. Yugeswaran, V. Selvarajan, P. Dhanasekaran, L. Lusvarghi, Vacuum., 83 (2009) 353.
11. H. Majidian, T. Ebadzadeh, and E. Salahi, Ceram. Inter., 36 (2010) 1669.
12. I. A. Aksay, D. M. Dabbs, M. Sarikaya, J. Am. Ceram. Soc., 74 (1991) 2343
13. L. B. Garrido and E. F. Aglietti, Mater. Sci. Eng. A., 369 (2004) 250.
14. N. M. Rendtorff, L. B. Garrido, E. F. Aglietti, Ceram. Int., 35 (2009) 2907.
15. J. S. Moya, R. Moreno, J. Requena, R. Torrecillas, G. Fantozzi, J. Am. Ceram. Soc., (1991) 27
16. S. K. Zhao, Y. Huang, C. A. Wang, X. Xian Huang, J. Kun Guo, Mater. Lett., 57 (2003)1716.
17. A. M. Abdelkader, A. Daher, E. El-Kashef, J. Alloys. Compd. 460 (2008) 577.