

Effect of SPS Process Parameters on the Densification Behaviour of Yttria Stabilized Zirconia

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ABSTRACT

Zirconium dioxide (ZrO_2) doped with Yttria exhibits superplastic behaviour, corrosion resistance and excellent ion conducting properties [1] at moderate temperatures and thus it can be used as an electroceramic to measure the pH of high temperature water used in fuel cells. Several fabrication processes are available for preparation of zirconia ceramics. This research focused on the study of using Spark Plasma Sintering (SPS) process to prepare Yttria Stabilized Zirconia (YSZ) ceramic.

8 mol% YSZ was subjected to varying SPS sintering conditions. Samples were sintered by changing the heating cycle, dwell time, sintering pressure and cooling cycle. Subsequently, these parameters were related to the densification characteristics of the as-sintered YSZ. The results of specific gravity measurements and microstructure evaluation suggest that stepped heating followed by a slow cooling results in YSZ with highest relative density (99.9%).

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INTRODUCTION

The present-day automobile market is dominated by petrol or diesel powered vehicles. Methods to reduce the CO_2 emissions from these engines has become an important research area worldwide, and resulted in the development and application of various process gas sensors to monitor engine operating efficiency and performance. Specifically, oxygen sensors have been found to be very beneficial for controlling emissions by allowing for efficient engine management [1]. One of the leading ceramics used for oxygen sensors is Zirconia (ZrO_2).

Zirconia has a high hardness, low coefficient of friction, high elastic modulus, chemical inertness, thermal shock resistance and low thermal conductivity [2]. However, Zirconia undergoes a phase transformation at elevated temperatures. To avoid this undesirable transformation, Yttrium (III) dioxide (yttria) is added to zirconia to form Yttria Stabilized Zirconia (YSZ).

YSZ has also been recognised as a promising electrolyte in solid oxide fuel cells, because it shows high ionic conductivity at elevated temperatures [3]. Early work by Chen *et al.* investigated the microstructure of YSZ ceramic prepared by Spark Plasma Sintering (SPS) process [4]. Their investigation aimed at producing high density YSZ ceramic through process cycling (i.e., controlled arrest or repeat of sintering temperature / pressure / time during processing). They found that the relative density and the ionic conductivity of the ceramic samples initially increased with the increase in the sintering

cycles and the sintering pressure, but after three cycles a plateau in density and conductivity was observed. Their results also suggest that a maximum relative density of 99.1% was achieved at 1400 °C, for four consecutive sintering cycles at 3min/cycle and applied uniaxial pressure of 23MPa.

Chaim *et al.* [5] studied the densification of Yttrium oxide ceramic by spark plasma sintering. They examined different heating rates, temperature ranges and pressure levels in order to determine the densification characteristics of the ceramic under different processing conditions. According to their results, high density ceramic was fabricated at 100MPa and 1400 °C sintered for 5 min. On the basis of the densification plots obtained, the densification of the powders started at approximately 650 °C under a pressure of 100MPa and continued up to 900 °C. Peak of densification was observed at 750 °C at 100MPa sintering pressure. Their study also suggested a relationship between the heating rate and the densification. The faster the heating rate, the faster was the grain growth and the higher the relative density. However, excessive grain growth resulted in a loss of the mechanical properties of the ceramic. Also, the sintering temperature was found to have the most significant impact on the grain size, where a continuous increase in the sintering temperature was directly proportional to an increase in the grain size. The relative density of the samples was found to increase only up to 1400 °C, while further increase in the sintering temperature did not affect the relative density of the sample [4].

Based on these studies and findings, the present work focused on a comprehensive and systematic study of densification behavior during Spark Plasma Sintering of YSZ. The effect of different processing parameters on the specific gravity and microstructure are reported.

EXPERIMENTAL PROCEDURE

Spark Plasma Sintering

Commercially available 8mol% YSZ powders (from Inframat Advanced Materials, USA) were used for all experiments. 7g of the powder was placed in a graphite die of a Thermal Technologies 10-3 Spark Plasma Sintering (SPS) machine. The resulting as-sintered discs were 20 mm in diameter and ~ 3 - 4mm thick. For all experiments, sintering was performed in inert Argon atmosphere. SPS process parameters: sintering temperature, heating rate, hold time, cooling rate and sintering pressure were programmed into a Eurotherm controller and their impact on the densification and microstructure was studied. Densification was measured from the relative compression of the sintering die during processing (as recorded by the Eurotherm controller). A summary of the processing parameters investigated in this work is provided in [Table 1](#). All samples were prepared with 100 °C/min heating rate. Based on earlier experiments, sintering 1400 °C required an increase in sintering pressure from 30MPa to 50MPa.

Table 1. Sintering process parameters

SAMPLE NAME	HEATING CYCLE				COOLING CYCLE
	600°C	1000°C	1300°C	1400°C	COOLING RATE
S.1.1	3mins; 0MPa	—	3mins; 30MPa	—	Ambient cooling
S.1.2	—	3mins; 30MPa	3mins; 30MPa	—	Ambient cooling
S.1.3	3mins; 0MPa	3mins; 30MPa	3mins; 30MPa	—	Ambient cooling
S.3.1	3mins; 0MPa	—	—	3mins; 50MPa	100 °C/min
S.3.2	3mins; 0MPa	—	3mins; 50MPa	—	100 °C/min
S.3.3	3mins; 0MPa	—	—	7mins; 50MPa	100 °C/min

Specific gravity of as-sintered samples was measured using Archimedes' principle using an electronic balance and deionized water at room temperature. Also, samples were prepared for microstructural analysis. Scanning electron microscope (Tescan Mira3) with Oxford X-Max XEDS detector was used for imaging and chemical analysis. Image analysis (Buehler OmniMet) was used for quantitative measurement of features.

RESULTS AND DISCUSSION

[Figure 1](#) shows the densification curves of the samples sintered at 1300 °C.

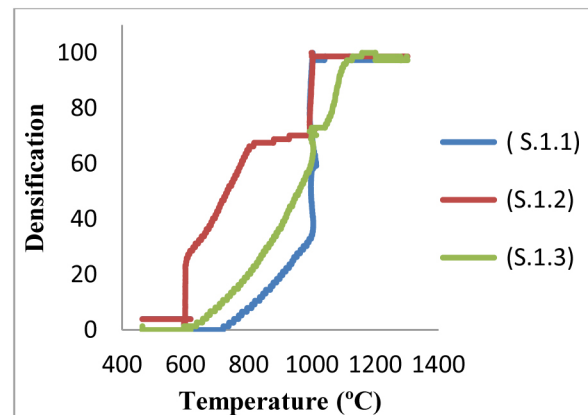


Figure 1. Densification curves for YSZ sintered at 1300 °C.

The densification curves suggest that direct heating of the YSZ powder to the desired sintering temperature of 1300°C (S.1.1) resulted in the slowest densification of the ceramic during heating. In contrast, the runs with intermediate hold at 600°C (S.1.2) or 1000°C (S.1.3) enroute to the sintering temperature of 1300°C densified faster up to ~1000 °C. After this temperature, a rapid increase in densification was observed for all samples. In particular, holding the ceramic for 3 min at 1000 °C during heating was seen to significantly enhance densification. This result is also in agreement with the measurements of specific gravity (relative density) as seen in [Figure 2](#). Overall, the relative density remained relatively high for all specimens. However, sample held at 1000 °C during heating achieved the highest relative density of 99.4%.

Interestingly, only sample S.1.3 remained in one piece and was available for microscopic analysis, while samples S.1.1 and S.1.2. fractured immediately upon ejection from the SPS sintering die, with additional fracturing during sample storage. Thus, the as-sintered YSZ exhibited very brittle behavior. The poor stability of the samples was likely the result of the rapid processing (rapid cooling cycle in particular) of the ceramic during SPS. A possibly remedy to alleviate this problem (likely related to excessive residual stress in the as-sintered sample) would be post-sintering anneal heat treatment or reduced cooling rate after sintering.