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Effect of Current Density, Temperature, and Contact Paste on Flash Sintered 8YSZ

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ABSTRACT

Flash sintering has been investigated as a modern sintering method through examining the effect of processing parameters such as current density, temperature, and contact paste on the flash sintered 8YSZ characteristic. 95% of theoretical density was achieved at 800°C in 30s with a field intensity of $100V.cm^{-1}$ and a current density of $160mA.mm^{-2}$. Such relative density in conventional sintering achieved at 1450°C for 4 hours. Results indicated that the temperature and flash current density have positive effects on the relative density. Contact paste had a significant effect on the relative density. 8YSZ samples with LSM contact paste had a higher relative density in comparison with those flash sintered with Pt contact paste. The positive effect of LSM contact paste was more significant, especially at lower current density.

1. INTRODUCTION

A ceramic body is commonly produced by forming a green body and sintering at high temperatures. The sintering process, especially in ceramics engineering, is carried out at extremely high temperatures (over 1400°C), which leads to high energy consumption as well as high equipment depreciation [1]. As mentioned by the European Commission, producing 1Kg of the ceramic body requires many MJ of energy, most of which are applied for ceramic body sintering [2]. The main challenge in the present decade is using environmentally friendly methods so that they have minimum participation in energy consumption and global warming. Moreover, the high temperature of material sintering leads to some problem such as unwanted reactions and transformations, composition changing, long process time, etc. Therfore, modern sintering techniques such as spark plasma sintering (SPS) [3], microwave sintering [4], resistance sintering [5] that can densify the materials at lower temperatures and shorter times have been highly considered. Flash sintering has been got more interested as a new sintering method since the first report [6]. It occurs when an electrical potential difference is applied across a ceramic powder compact and characterized by an electrical power surge at a specific combination of electric field and temperature accompanied by an extremely rapid densification. Thus far, various ceramics such as oxygen ionic ceramics [6-10], protonic conductors [11] and electronic conductors [12, 13] have been successfully densified using the flash-sintering technique. Flash sintering has several advantages compared to conventional sintering processes. The most obvious one is the huge reduction of time and temperature needed for the ceramic densification, which implies the evident energy saving, less expensive equipment, and more generally, environmental benefits. The consolidation time is typically reduced from some hours for conventional processes to a few seconds/minutes for flash sintering [6-13]. The low temperatures in flash sintering as well as the very short time for sintering can have benefits in simplification of manufacturing processes. Sintering temperatures that lie well below 1000°C can reduce capital costs and the advantages of short sintering times

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can alleviate undesirable reactions [7]. Another advantage of flash sintering arises from the fact that it is an “out of equilibrium” process, which is associated with extremely high heating rates and short processing times. Therefore, it is possible to sinter metastable materials or avoid undesired phase transitions [14, 15]. The main limitation of the flash process is that this process is “autocatalytic” with hot spots [16, 17], which means that the electric current concentration along the preferential paths can be formed in components larger than a few millimeters. For this reason, many types of research have focused on finding technical solutions to avoid hot spot formation [18] during flash sintering. Another limitation of flash sintering is that conductive pastes are usually used to improve the electrical contact between metal electrodes and the samples. The use of such pastes causes local contamination of the component. The development of contactless-flash sintering setup is of actual doubtful interest [19].

Many studies have tried to examine this process and the related phenomena [20, 21], but the precise nature of the process is still not well discovered. So far, a few types of research have been done on the 8YSZ flash sintering, but the optimum conditions have not been reported yet. Cologna et al. [7] performed flash sintering in non-isothermally manner and reached the density of 96%. Steil et al. [22] achieved 89% of theoretical density with an AC field intensity of 190v.cm^{-1} and the current density of 60 mA.mm^{-2} at 800°C. Baraki et al. [23] reached a density of 79% with an AC flash sintering at 1150°C for 3min whose applied field intensity and current density were 40 V.cm^{-1} and 65 mA.mm^{-2}, respectively. Downs et al. [8] reported that full sintering did not occur with a DC field density of 2250V.cm^{-1} at 390°C.

In the present study, the effect of current density and temperature as well as the role of contact paste are investigated on the relative density of flash sintered 8YSZ .

2. EXPERIMENTAL

TZ-8Y (Tosoh Corporation, Japan) powder with d50=138nm was used as the starting material, whose chemical composition is shown in Table 1. 8YSZ powder was mixed with ethanol (MERCK) and toluene (MERCK) as the solvent, PVB (Sigma Aldrich) as the binder, BBP (Sigma Aldrich) as plasticizer, and terpineol (MERCK) as the dispersant and then, ball-milled for 24 hours. Ball-milling was done by 5mm YSZ balls with the ball to the powder ratio of 1:2 and milling speed of 60RPM. The composition of slurry is shown in Table 2. The prepared slurry was tape cast by a lab cast machine with the thickness of 500μm. As shown in Fig. 1, the dog-bone samples were cut and heated to 800°C in ambient atmosphere with the rate of 1°C.min^{-1} and dewlling time of 1 hour for binder burnout. The sample was cooled with the rate of 5°C.min^{-1}.

TABLE 1. TZ-8Y chemical composition

Y_2O_3 (wt%)	Al_2O_3 (wt %)	SiO_2 (wt %)	Fe_2O_3 (wt %)	Na_2O (wt %)	ZrO_2 (wt%)
13.74	≤ 0.005	≤ 0.002	≤ 0.002	0.007	balance

TABLE 2. Electrolyte slurry composition

Material	Weight percent	Company	role
8YSZ	50	Tosoh	Solid powder
Ethanol	16	MERCK	Solvent
Toluene	22	MERCK	Solvent
Terpineol	0.4	MERCK	Dispersant
Benzyl butyl phthalate (BBP)	5.8	Sigma Aldrich	Plasticizer
Polyvinyl butyral (PVB)	5.8	Sigma Aldrich	Binder

Platinum wires were connected to the dog-bone sample with contact paste and suspended in a vertical tube furnace. The sample was heated up with a rate of 5°C.min^{-1} to the desire temperature and held for 30min for temperature uniformity. The DC field was applied to the sample with a 500W power supply. The voltage and the passing current were monitored by a digital multimeter (GW-INSTEK GDM-397). Each sample was held in flash condition for 30sec. The procedure was recorded using a CCD camera focused on the sample. The schematic of the used flash sintering setup is shown in Fig. 2. As shown in table 3, the flash sintering was done at different temperatures, different flash current densities, and with different contact pastes. The current density and field intensity were chosen according to the values reported in the references [6, 7, 22, 23] as well as power supply limitations.

The relative density of samples was measured in water through the Archimedes method. The fractured cross-section of samples was characterized through the Scanning Electron Microscopy (TESCAN-VEGA II). The Electrochemical Impedance Spectroscopy (Autolab PGSTAT302N with FRA32M) was used to study the catalytic activities of the used paste. Both sides of the 8YSZ disc, which pre-sintered at 800°C, was painted by contact paste and inserted in the EIS setup. The measurements were perfomed at 800°C and the data were analyzed using NOVA software.

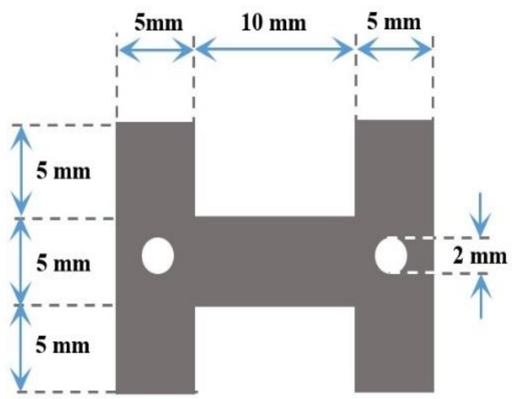


Figure 1. Schematic design of the Dog-bone for flash sintering

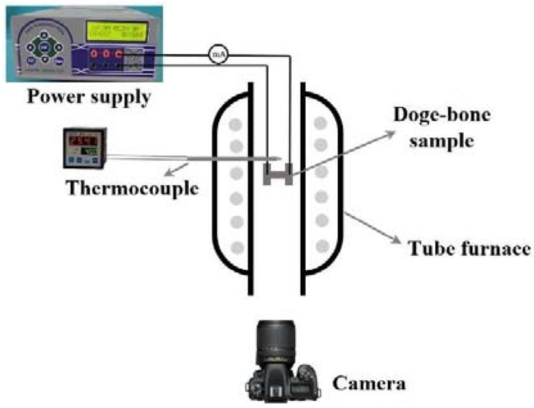


Figure 2. Schematic of used flash sintering set-up

TABLE 3. Experimental conditions for flash sintering of 8YSZ samples

sample	Field intensity (V/cm)	Temperature (°C)	Current density (mA/mm^2)	Contact paste
100V-60mA-800	100	800	60	Pt
100V-160mA-800	100	800	160	Pt
100V-110mA-800	100	800	110	Pt
100V-110mA-900	100	900	110	Pt
100V-110mA-700	100	700	110	Pt
100V-110mA-800-LSM	100	800	110	LSM
100V-110mA-800-LSM	100	800	110	LSM

3. RESULTS AND DISCUSSION

Connecing the sample to the power supply, the current passing the sample started to increase, the field intensity dropped, and an intensely bright light was emitted by sample (Fig. 3), which was accompanied by an obvious shrinkage (Fig. 4). Then, a constant current equal to the current limit, which was set on power supply, passed the sample.

Results showed that achieving 95% of density at 800°C in 30 seconds is possible by flash sintering, whereas 8YSZ needs to be sintered for 4 hours at 1450°C by conventional sintering as proposed by Tosoh Company.

As shown in Fig. 5, increasing furnace temperature leads to higher relative density in a certain current density. The increase rate of relative density is higher at high temperatures. 8YSZ resistance drops at high temperatures and therefore, more heat is generated in the sample according to Joule heating relation (Q=V2/R). Moreover, the results showed that the higher current density leads to higher relative density in a certain temperature (Fig. 6). Here, more heat is generated at higher current density as well based on Joule heating relation (Q=RI2).

Pt and LSM (Lanthanum strontium manganite) used as contact paste to investigate the effect of the contact paste on flash sintered 8YSZ. As shown in Fig. 7, LSM contact paste has led to a higher relative density in comparison with Pt contact paste for both samples in which the flash sintered with the current density of 110mA.mm-2 and 160mA.mm-2. Nyquist plots of EIS spectra of Pt and LSM are shown in Fig. 8 with the corresponding equivalent circuit. LSM showed less resistance against oxygen reduction in compare with Pt (R2 in Table 4). A portion of the current passed through the sample by oxygen ions and more oxygen ion led to more current passing the sample. Especially, higher activity of LSM for oxygen reduction is more prominent in low current density in which the number of electrons is more limited. Therefore, more oxygen ion would be generated using LSM, which pass the sample and result in more densification.

The microstructure analysis of samples by SEM also revealed that the samples were well densified despite the low temperature and the short duration of the flash sintering process (Fig. 9). The XRD pattern of starting powders and the flash sintered sample are shown in Fig. 10. There was no evidence of amorphization in the flash sintered 8YSZ. The comparison of the results of the present study with other methods reported in references (Table 5) indicated that the flash sintering can densify 8YSZ at much lower temperatures and much shorter times respect to other modern sintering methods.

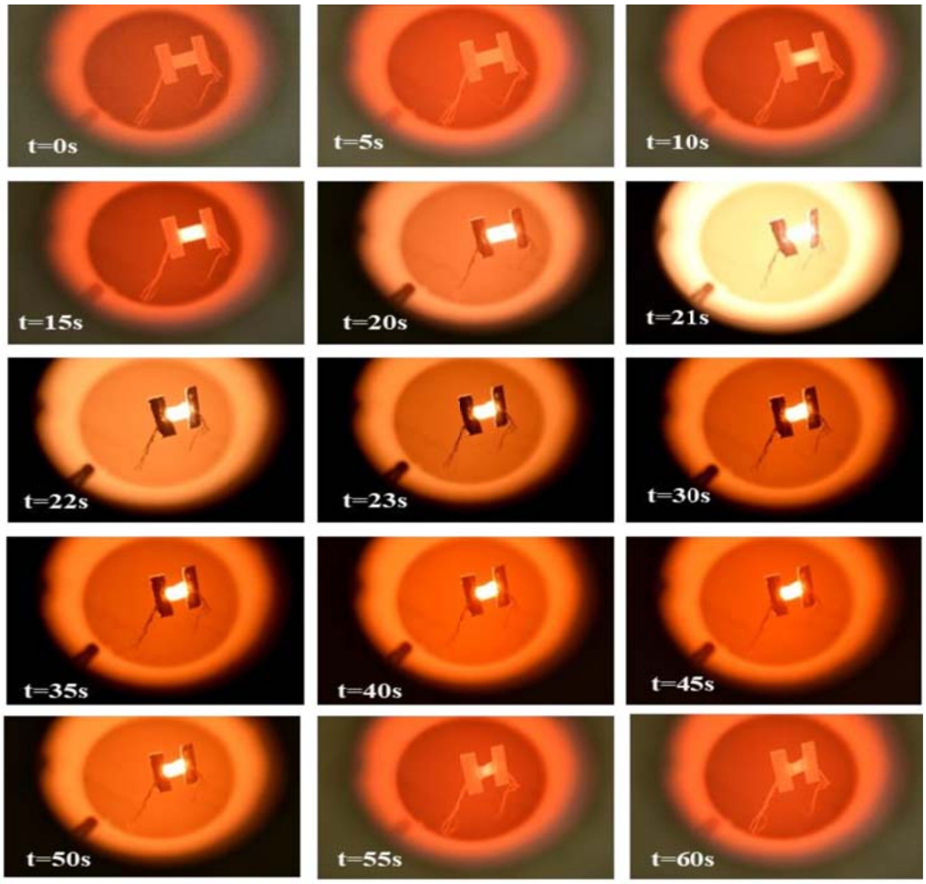


Figure 3. 8YSZ sample under flash sintering. t=5s voltage is applied to the sample. t=20s flash is beginning, t=50s current is cut off.

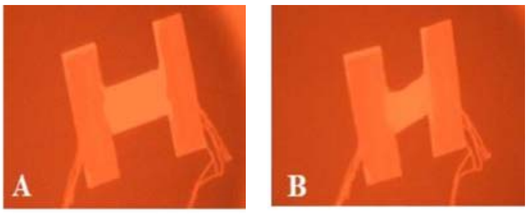


Figure 4. 8YSZ sample A) before and B) after flash sintering

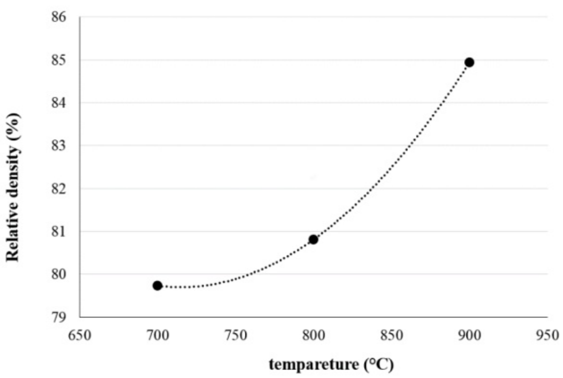


Figure 5. The effect of temperature on the relative density of flash sintered 8YSZ at E=100v.cm^{-1}, J=110mA.mm^{-2} with Pt contact paste

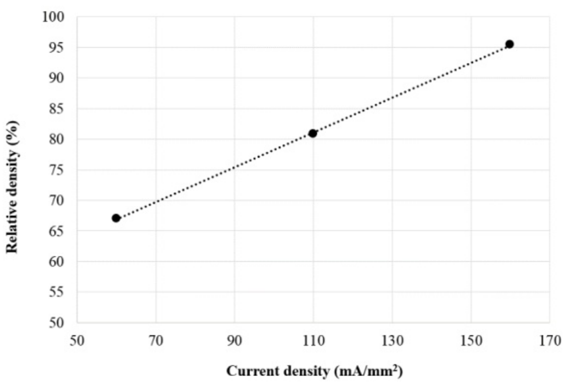


Figure 6. The effect of current density on the relative density of flash sintered 8YSZ at E=100v.cm^{-1} and T=800°C with Pt contact paste

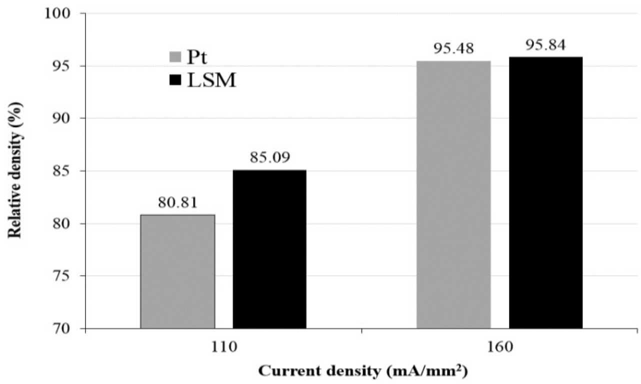
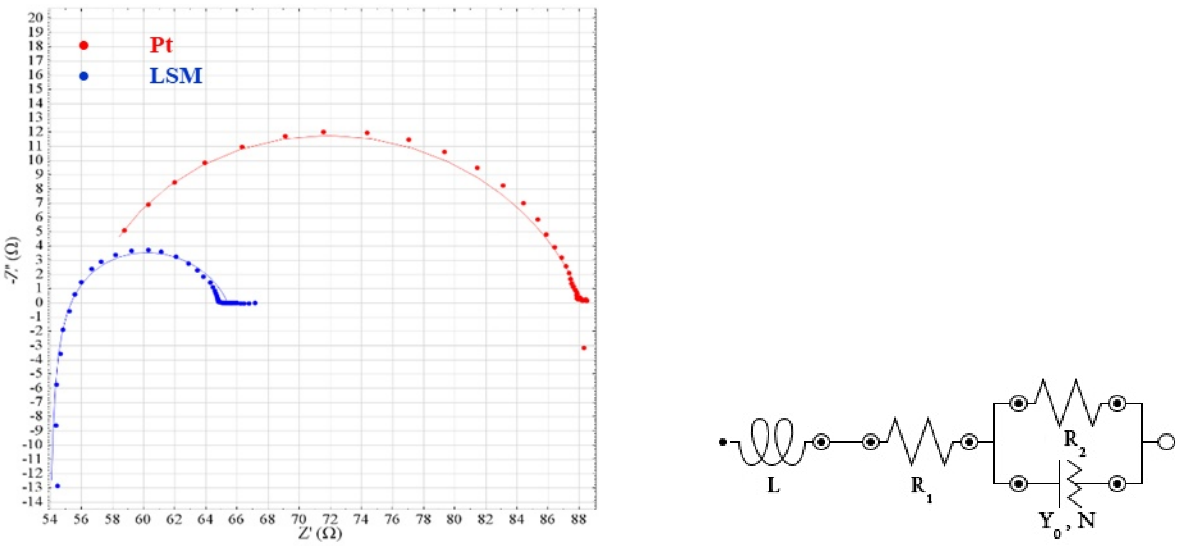


Figure 7. The effect of contact paste on the relative density of flash sintered 8YSZ under various current densities



(A)

(B)

Figure 8. A) Nyquist plots of contact paste at 800°C and B) Corresponding equivalent circuit

TABLE 4. The values of the equivalent circuit components

Contact paste	L (µH)	R_1 (Ω)	R_2 (Ω)	Y_0 (µMho)	N
LSM	4.19	53.7	11.7	16.4	0.749
Pt	4.19	53.7	34.5	2.8	0.787

TABLE 5. Comparison between flash sintering (the present study) and other sintering methods

Sintering method	Sintering condition	Sintering Temperature (°C)	Sintering time	Relative density (%)	reference
Flash sintering	E=100v/cm J=160mA/mm^2	800	30 sec	95.8	-
Conventional sintering	-	1500	12 hours	97.4	24
Hot press	P=25MPa	1250	3 hours	97	24
SPS	P=70MPa	1200	5 min	97.3	24
Microwave sintering	1kw, 2.5GHz	1200	5 min	95.8	25

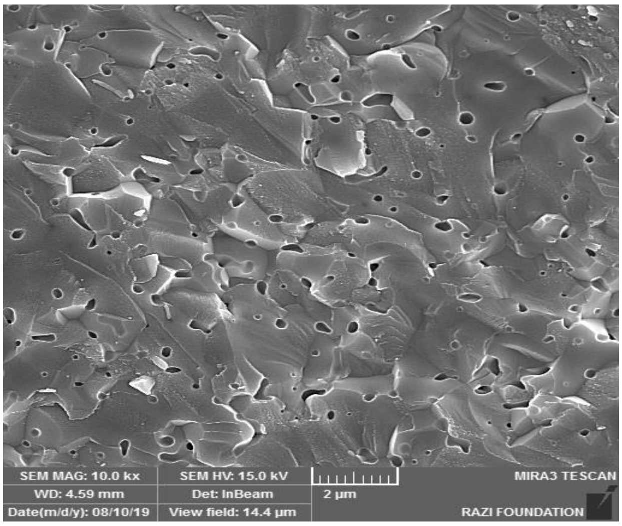


Figure 9. SEM micrograph of flash sintered 8YSZ

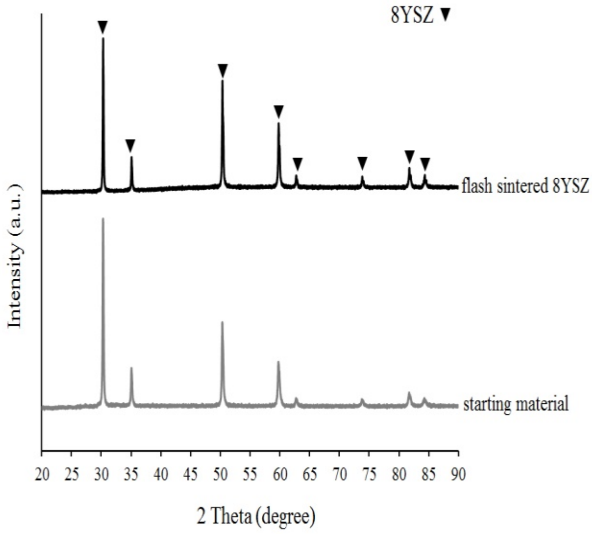


Figure 10. XRD spectra of starting materials and flash sintered 8YSZ sample

4. CONCLUSION

Flash sintering method is a promising method for 8YSZ sintering at 800°C in 30sec, whereas the conventional sintering methods require much more temperatures and times. The results revealed that both furnace temperature and current density have a positive effect on the relative density. The effect of LSM as contact paste is more significant on the relative density, especially at lower current densities. The lower resistance of LSM for oxygen reduction promotes the oxygen reduction and facilitates current passing through the sample and results in more densification.

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