Microwave processing: A potential technique for preparing NiO–YSZ composite and Ni–YSZ cermet

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Abstract. In the present study, microwave energy (2.45 GHz) has been used to prepare nickel oxide–yttria stabilized zirconia (NiO–YSZ) composites of composition, $m\text{NiO}-(1-m)\text{Zr}_{0.9}\text{Y}_{0.1}\text{O}_{1.95}$ ($m = 0.2, 0.3, 0.4, 0.5$ and 0.6), from a precursor obtained by mixing NiO, Y_2O_3 and monoclinic ZrO_2 in their stoichiometric ratio. The composites have been prepared by conventional processing also to compare the products with those of microwave processed products. During comparison, it was observed that NiO–YSZ composites of each composition obtained by microwave processing had cubic phase of YSZ while in the conventionally prepared composites of compositions, $m = 0.2$ and 0.3 , monoclinic, tetragonal and cubic phases of zirconia existed instead of its pure cubic phase. The composites were reduced to yield Ni–YSZ.

Keywords. Microwave processing; NiO–YSZ composites; cermet; XRD; SEM.

1. Introduction

An electrical composite is defined as a material comprising of two or more phases of electrical conductors. These conductors may be electronic, inert/insulating or ionic depending upon their charge carrier type. Some unusual electrical properties of composites formed by the mixture of two phases with different charge carrier species have been reported. The properties of a composite may be the average properties of its two constituents or those not seen for any of the constituent phases (Newnham 1986). The possibility of tailoring the properties of composites, particularly electrical properties, by controlling the relative volume fraction of phases has made them of great interest for technological applications (Wu and Liu 1997; Park and Choi 1999; Knauth and Tuller 2002; Kondo *et al* 2003). Nickel oxide yttria-stabilized zirconia (NiO–YSZ) composite is important due to its various technological applications, e.g. it is used as the starting material for the fabrication of Ni–YSZ anodes in solid oxide fuel cells (Minh 1993), in YSZ coatings (Khor and Guy 2000) or bonding to metals and in Ni–zirconia catalyst (Khor and Guy 2000; Qin and Derby 1992). It has been reported that the interactions of NiO and YSZ can occur during preparation of powders, sintering and even during operation (Chen and Shen 1989; Kuzjukevics *et al* 1996).

NiO–YSZ composite, a precursor of anode material, i.e. Ni–YSZ cermet, is usually prepared by mixed oxide

method i.e. by mechanical mixing of commercial NiO and cubic YSZ powders. It is simple, but apt to give rise to a non-uniform distribution of the Ni-phase in the cermets causing poor performance. In order to have uniform distribution of Ni phase in the cermet, various chemical processes have been reported such as sol–gel (Marinsek *et al* 2000; Esposito *et al* 2003), complex formation with chelating agents (Duran *et al* 2003; Shao *et al* 2003), precipitation with buffer-solution of NH_4OH and NH_4HCO_3 (Li *et al* 2001), coat-mix (Simwonis *et al* 1999), liquid condensation process with thermoset polymer (Lee *et al* 2003), combustion synthesis (Aruna *et al* 1998; Marinsek *et al* 2002; Ringuede *et al* 2002), spray pyrolysis of slurry of YSZ in nickel acetate solution (Fukui *et al* 1998) and mechanofusion process (Jiang and Chan 2004). But due to lower processing cost, the mixed oxide method for the preparation of precursor is preferred to other methods.

In the recent past, it has been found that various chemical reactions are accelerated by microwave irradiation of reactants (Meek *et al* 1987; Sutton 1989; Mathis *et al* 1995; Cheng *et al* 1997; Vaidhyanathan *et al* 2001; Thakur *et al* 2002). Excellent reviews have been written to overview the developments in this rapidly growing field of microwave processing (Clark *et al* 1997; Roy *et al* 1997; Agrawal 1998). The major advantages of microwave processing are lower reaction temperatures and shorter processing time as compared to the conventional synthetic procedures. Generally, the majority of the reactions reported using microwave are in solution phases of the reactants. High dielectric loss tangents of the polar solvents are responsible

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for their effective coupling with the microwave field. Relatively, a few reports are available on the solid state synthesis of complex oxides using microwave. In the synthesis of BaTiO₃ (Agrawal *et al* 1998), it has been observed that non-stoichiometry of TiO₂ is responsible for the enhanced coupling of microwave. Also, in the synthesis of PZT, it has been reported that the use of stabilized zirconia and reduced TiO₂ not only enhances the kinetics of formation of PZT, but changes the mechanism also (Vaidhyanathan *et al* 2001). Further, during the formation of fully cubic calcium stabilized zirconia, the higher diffusion of participating cations has been reported (Singh *et al* 2007). The reduction in the processing time and temperature is believed to be due to the higher diffusion rates induced by microwave field.

In most of the studies for the preparation of NiO–YSZ composites, the fully cubic stabilized YSZ has been used as the starting material and is mixed with NiO, thereafter the mixture is calcined and sintered. In the present investigation, the microwave energy has been used for the first time to prepare NiO–YSZ composites of composition, $m\text{NiO}-(1-m)\text{Y}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$ ($m = 0.2, 0.3, 0.4, 0.5$ and 0.6), from the mixture of NiO, Y₂O₃ and monoclinic ZrO₂. The stoichiometry of ZrO₂ and Y₂O₃ is maintained such that it results in YSZ phase of composition, Y_{0.1}Zr_{0.9}O_{1.95}, in each of the composites mentioned above. The composites of the same compositions as mentioned above have been prepared by conventional heating also. The composites, $m\text{NiO}-(1-m)\text{Y}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$, obtained by the microwave as well as the conventional heating processes have been reduced in the hydrogen atmosphere to convert them into Ni–YSZ cermets of respective compositions. The characteristics of microwave processed products have been compared with those of the conventionally processed products in order to investigate the potentiality of microwave energy in the fabrication of NiO–YSZ composites and Ni–YSZ cermets.

2. Experimental

90 Mol% of monoclinic ZrO₂ and 10 mol% of YO_{3/2} were taken and mixed for 6 h by ball milling using zirconia ball and acetone as the grinding medium resulting in a powder of composition, Zr_{0.9}Y_{0.1}O_{1.95}, now hereafter termed as YSZ. Precursors of five compositions for NiO–YSZ composites i.e. $m\text{NiO}-(1-m)\text{Y}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$ ($m = 0.2, 0.3, 0.4, 0.5$ and 0.6) were prepared by mixing NiO with the already prepared YSZ. The stoichiometry of NiO and YSZ mixture were taken for the composition of $m\text{NiO}-(1-m)\text{Y}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$ ($m = 0.2, 0.3, 0.4, 0.5$ and 0.6) and again ball milled for 6 h using zirconia ball and acetone as the grinding medium. After drying, the powders were mixed with 4% poly vinyl alcohol (PVA) solution and were consolidated in the cylindrical green pellets at 200 MPa by uniaxial pressing. The PVA from the green

pellets was removed by heating them at 500°C for 6 h before sintering. The green pellets, five pellets of each composition, were taken in alumina crucible and were covered with 8% PVA solution. The PVA solution acts as a susceptor (Singh *et al* 2007) to preheat the samples so that they could absorb microwave energy. They were fired at 1400°C for 15 min with microwave energy of 2.45 GHz. In this study, platinum shielded S-type Pt–10%Rh/Pt thermocouple was used to measure temperature. The thermocouple was properly shielded and grounded to avoid the microwave interference with the thermocouple and to get reliable temperature readings. The thermocouple was fitted in the microwave so that the tip of the thermocouple was 1 mm away from the work piece in the sintering packet. A voltage system consisting of two variacs was added to the power supply of the magnetron to control the heating rate and to achieve the required temperature for desired exposure time. The temperature of the sample was measured with an accuracy of $\pm 1^\circ\text{C}$ during processing.

Another set of green pellets, five pellets of each composition, were fired at 1400°C for 4 h by the conventional heating also for comparison purpose. The fired products obtained after microwave processing and conventional processing were reduced in the presence of mixture of 5% H₂ and 95% Ar at 800°C for 4 h to convert NiO–YSZ composites to Ni–YSZ cermets. Thus, four types of samples, each having five compositions corresponding to $m = 0.2, 0.3, 0.4, 0.5$ and 0.6 , were prepared in all. These types of samples were designated as $m\text{NiO}–\text{YSZ MW}$ for composites obtained from microwave processed $m\text{NiO}-(1-m)\text{Y}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$ precursors, $m\text{NiO}–\text{YSZ CON}$ for composites obtained from conventionally processed $m\text{NiO}-(1-m)\text{Y}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$ precursors, $m\text{Ni}–\text{YSZ MW}$ for reduced $m\text{NiO}–\text{YSZ MW}$ and $m\text{Ni}–\text{YSZ CON}$ for reduced $m\text{NiO}–\text{YSZ CON}$. The phase changes in the samples obtained after microwave processing and conventional processing, and their reduced products were investigated by X-ray diffraction technique (X-ray Diffractometer, Model: Bruker AXS, D-8 Advance, Switzerland). The pellets were polished with diamond paste and their microstructures were studied by SEM (Scanning Electron Microscope, Model: LEO 435 VP, Cambridge, UK). The energy dispersive X-ray (EDAX) analysis was done by taking FESEM (FEI, Model Quanta 200F, The Netherlands) which was used to study distribution of alloying elements in NiO–YSZ composites.

3. Results and discussion

The precursors of $m\text{NiO}-(1-m)\text{Y}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$ ($m = 0.2, 0.3, 0.4, 0.5$ and 0.6) composites prepared by ball milling were black in colour. The sintered pellets of each composition obtained after microwave firing at 1400°C for 15 min as well as conventional firing at 1400°C for 4 h were found

to be green in colour. The Ni-YSZ cermets obtained after reduction of microwave and conventionally processed NiO-YSZ composites were black in colour.

Figure 1 shows XRD patterns of microwave processed $\text{Y}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$ along with the microwave processed composites ($m\text{NiO-YSZ MW}$). Figure 2 shows XRD patterns of conventionally processed $\text{Y}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$ along with conventionally processed composites ($m\text{NiO-YSZ CON}$). The XRD patterns of cermet $m\text{Ni-YSZ MW}$ and cermet $m\text{Ni-YSZ CON}$ are shown in figures 3 and 4, respectively. Different phases of zirconia (monoclinic, tetragonal and cubic) and phases of NiO and Ni have been identified in the XRD patterns.

In figures 1 and 2, the presence of cubic phase of zirconia and NiO cubic phase have been identified from the (111) peak and (200) peak, respectively whereas the presence of monoclinic phase of zirconia has been identified by (11 $\bar{1}$) peak. Since the 2θ for (111) peak of tetragonal

and cubic phase is almost same, therefore, the tetragonal phase has been distinguished from cubic phase by separation of (002) and (200) peaks of the tetragonal structure. In the Ni-YSZ cermets, the presence of Ni phase has been identified from (200) peak in figures 3 and 4 while cubic and monoclinic phases of zirconia were identified by (111) peak and (11 $\bar{1}$) peak, respectively.

The XRD pattern of microwave processed $\text{Zr}_{0.9}\text{Y}_{0.1}\text{O}_{1.95}$ in figure 1a shows the (11 $\bar{1}$) peak of monoclinic phase and (111) peak of tetragonal and cubic phases of zirconia. The existence of tetragonal phase could be distinguished from cubic phase by the presence of (002) and (200) peaks of the tetragonal structure. The XRD patterns of composites, $m\text{NiO-YSZ MW}$ ($m = 0.2, 0.3, 0.4, 0.5$ and 0.6), in figure 1(b-f) show the peaks due to the presence of cubic zirconia and NiO only. The presence of tetragonal zirconia in composites of all compositions is ruled out as no corresponding peaks appear in the XRD patterns. It shows that the zirconia component is fully cubic in $m\text{NiO-}$

Figure 1. XRD patterns of microwave processed (a) $\text{Zr}_{0.9}\text{Y}_{0.1}\text{O}_{1.95}$, (b) 0.2NiO-YSZ MW, (c) 0.3NiO-YSZ MW, (d) 0.4NiO-YSZ MW, (e) 0.5NiO-YSZ MW and (f) 0.6NiO-YSZ MW.

Figure 2. XRD patterns of conventionally processed (a) $\text{Zr}_{0.9}\text{Y}_{0.1}\text{O}_{1.95}$, (b) 0.2NiO-YSZ CON, (c) 0.3NiO-YSZ CON, (d) 0.4NiO-YSZ CON, (e) 0.5NiO-YSZ CON and (f) 0.6NiO-YSZ CON.

Figure 3. XRD patterns of cermets obtained from microwave processed composites, $m\text{NiO-(1-m)YSZ}$: (a) 0.2Ni-YSZ MW, (b) 0.3Ni-YSZ MW, (c) 0.4Ni-YSZ MW, (d) 0.5Ni-YSZ MW and (e) 0.6Ni-YSZ MW.

Figure 4. XRD patterns of cermets obtained from conventionally processed composites, $m\text{NiO-(1-m)YSZ}$: (a) 0.2Ni-YSZ CON, (b) 0.3Ni-YSZ CON, (c) 0.4Ni-YSZ CON, (d) 0.5Ni-YSZ CON and (e) 0.6Ni-YSZ CON.

Table 1. Lattice parameters of $m\text{NiO-YSZ MW}$ and $m\text{NiO-YSZ CON}$.

Microwave processed		Conventionally processed	
Sample	Lattice parameter (nm)	Sample	Lattice parameter (nm)
20NiO-YSZ MW	0.5132	20NiO-YSZ CON	0.5132
30NiO-YSZ MW	0.5133	30NiO-YSZ CON	0.5133
40NiO-YSZ MW	0.5133	40NiO-YSZ CON	0.5132
50NiO-YSZ MW	0.5133	50NiO-YSZ CON	0.5134
60NiO-YSZ MW	0.5132	60NiO-YSZ MW	0.5132

Figure 5. Scanning electron micrographs of microwave processed composites, $m\text{NiO}-(1-m)\text{YSZ}$: (a) 0.2NiO-YSZ MW, (b) 0.3NiO-YSZ MW, (c) 0.4NiO-YSZ MW and (d) 0.5NiO-YSZ MW.

(1 - m) YSZ MW composites of all compositions prepared by microwave processing.

The XRD patterns of conventionally processed $\text{Zr}_{0.90}\text{Y}_{0.10}\text{O}_{1.94}$, 0.2NiO-YSZ CON and 0.3NiO-YSZ CON in figures 2a, b and c, respectively show presence of monoclinic phase, tetragonal phase and cubic phase of zirconia. The cubic and tetragonal phases of zirconia cannot be

distinguished by their (111) peak. However, 002 and 200 peaks of tetragonal phases are visible in figures 2a, b and c. The amount of monoclinic phase decreases as the concentration of NiO increases and disappears in the composition of 0.4NiO-YSZ CON and other composition of higher NiO content. The coexistence of tetragonal and cubic phases cannot be ruled out in 0.4NiO-YSZ CON, 0.5NiO-

Figure 6. Scanning electron micrographs of conventionally processed composites, $m\text{NiO}-(1-m)\text{YSZ}$: (a) 20NiO-YSZ CON, (b) 30NiO-YSZ CON, (c) 40NiO-YSZ CON and (d) 50NiO-YSZ CON.

YSZ CON and 0.6NiO-YSZ CON as the peak between $2\theta = 34$ and 36 is broad which may be due to the presence of the tetragonal phase.

Table 1 shows the lattice parameter of $m\text{NiO}-(1-m)\text{YSZMW}$ and $m\text{NiO}-(1-m)\text{YSZ CON}$ calculated from (111) peak of each sample.

The XRD patterns of cermet $m\text{Ni-YSZ MW}$ in figure 3(a-e) shows that all the peaks due to NiO have disappeared after the reduction and only the peaks corresponding to Ni and cubic YSZ are present. This means that all the $m\text{NiO-YSZ MW}$ composite particles were transformed successfully to $m\text{Ni-YSZ MW}$ cermet under reducing condition. The crystal structure of zirconia remains to be cubic in cermet $m\text{Ni-YSZ MW}$ for all compositions. The XRD patterns of $m\text{Ni-YSZ CON}$ in figure 4 (a-e) shows that NiO of $m\text{NiO-YSZ CON}$ composites has reduced to Ni in all compositions of cermet $m\text{Ni-YSZ CON}$. The monoclinic phase of zirconia persists in 0.2Ni-YSZ CON

and 0.3 Ni-YSZ CON which is present in their respective composites also. The monoclinic phase of zirconia also precipitates in cermet 0.4Ni-YSZ CON unlike in its corresponding composite, 0.4NiO-YSZ CON. In the $m\text{Ni-YSZ}$ for $m = 0.5$ and 0.6 , the crystal structure of zirconia remains to be cubic.

The scanning electron micrographs of microwave processed composites, $m\text{NiO-YSZ MW}$ for $m = 0.2, 0.3, 0.4$ and 0.5 , are shown in figure 5(a-d). In the SEM of figure 5(a-d), the NiO phase is identified by its stripped surface (Parks and Choi 1999). Figure 5a shows the uniform distribution of YSZ and particles of NiO are also seen. It appears from the SEM (figure 5b) of 0.3NiO-YSZ MW that the grain growth of YSZ has increased and at the same time agglomeration of NiO particles is also seen. The grains of YSZ and NiO are of nearly same size at 40 mol% ($m = 0.4$) of NiO in YSZ. Further, in this sample the stripped surface of NiO is quite distinct and particles of

Figure 7. FESEM and EDAX of (a) 0.2NiO-YSZ MW and (b) 0.3NiO-YSZ MW.

YSZ and NiO are uniformly distributed similar to the result reported by Park and Choi (1999). However, the agglomeration of NiO has also increased as the content of NiO is increased in YSZ.

The scanning electron micrographs of conventionally sintered composites, m NiO-YSZ CON for $m = 0.2, 0.3, 0.4$ and 0.5 , are shown in figure 6(a-d). The SEM of conventionally sintered composites, m NiO-YSZ CON, as shown in figure 6 reveals that the agglomeration of NiO is more even in the 0.2NiO-YSZ CON composite unlike in microwave sintered 0.2NiO-YSZ MW composite in which the distribution of NiO and YSZ is uniform. Also, the grain growth of YSZ in this conventionally sintered composite is low as compared to that of 0.2NiO-YSZ MW microwave sintered composite. In the 0.3NiO-YSZ CON, the grain growth of YSZ has initiated and also the agglomeration of NiO can be seen there. The XRD patterns of 0.2NiO-YSZ CON and 0.3NiO-YSZ CON show the presence of monoclinic phase as shown in figures 2a and b. The presence of monoclinic phase, as observed in XRD pattern of these samples, causes poor densification of the samples, which is evident in the SEM of conventionally

sintered composites of 0.2NiO-YSZ CON and 0.3NiO-YSZ CON shown in figures 6a and b.

The dissolution of NiO and Y_2O_3 in zirconia in samples 0.2NiO-YSZ MW, 0.3NiO-YSZ MW, 0.2NiO-YSZ CON and 0.3NiO-YSZ CON was estimated by EDAX and compared. The amount of Y_2O_3 dissolved in ZrO_2 could not be ascertained in any of the above samples as the peaks of zirconium and yttrium overlap because their atomic numbers are close to each other. However, yttrium is present in grains of zirconium of each sample as shown in figures 7 and 8. The dissolution of NiO in 0.2NiO-YSZ MW and 0.3NiO-YSZ MW is higher as compared to those of 0.2NiO-YSZ CON and 0.3NiO-YSZ CON as shown in figures 7(a, b) and 8(a, b).

Kuzjukevics and Linderroth (1997) prepared NiO-YSZ composites from oxides of NiO, Y_2O_3 and ZrO_2 by plasma synthesis. It has been inferred that NiO promotes the formation of cubic zirconia by dissolving NiO in ZrO_2 , as the dissolution of NiO in YSZ significantly decreases the lattice parameter of cubic zirconia due to smaller ionic radius of Ni^{2+} in comparison to both the Zr^{4+} and Y^{3+} . Further, the decrease in the lattice parameter of

Figure 8. FESEM and EDAX of (a) 0.2NiO–YSZ CON and (b) 0.3NiO–YSZ CON.

YSZ is a function of NiO concentration and the maximum limit of dissolution of NiO in YSZ is ≤ 5 mol% (Chen *et al* 1992). In the present work, the lattice parameter value of composites were found to be lower than the previously reported data of fully cubic YSZ of composition, $\text{Zr}_{0.9}\text{Y}_{0.1}\text{O}_{1.95}$ (Ingel and Lewis 1986), however, the value of lattice parameter remained almost constant with the increase in NiO content (table 1) for microwave processed composites. Since zirconia is a mixture of its tetragonal, cubic and monoclinic phases in the samples, 0.2NiO–YSZ CON and 0.3NiO–YSZ CON, whereas in the tetragonal and cubic phases in 0.4NiO–YSZ CON, 0.5NiO–YSZ CON and 0.6NiO–YSZ CON, the value of the lattice parameter observed could not be interpreted which may be due to the compositional fluctuations. These results suggest that the dissolution of NiO occurs during microwave processing, but the solubility of NiO does not increase with the increase in NiO concentration.

From figures 1a and b, it is evident that the dissolution of 10 mol% of $\text{YO}_{1.5}$ is not sufficient to stabilize cubic phase of YSZ by microwave processing as well as conventional processing, but gives partially stabilized zirconia

phase of YSZ (Y–PSZ). Also, the percentage of monoclinic phase in partially stabilized zirconia obtained by conventional processing is 47% while in that obtained by microwave processing is 17% (Singh *et al* 2008). This shows that the dissolution of Y_2O_3 in ZrO_2 is less during conventional processing than that of microwave processing (Singh *et al* 2008).

In the present study of the conventional processing, the formation of almost cubic phase of YSZ was observed only in composites, $m\text{NiO}$ –YSZ CON with $m > 0.3$. This suggests that the introduction of NiO in sufficient amount ($m > 0.3$) enhances the stabilization of zirconia in YSZ even at lower Y_2O_3 concentration by promoting Y_2O_3 diffusion along with NiO on lattice site of ZrO_2 . This observation has already been reported by Kuzjuevics and Linderroth (1997) and Chen *et al* (1994). However, NiO alone is not a stabilizer of cubic zirconia (Chen and Shen 1989). In case of the microwave processing, the cubic phase of YSZ formed even with 20 mol% ($m \geq 0.2$) of NiO. It appears that the presence of microwave field increases the probability of diffusion of Y_2O_3 along with NiO on lattice site of ZrO_2 . It suggests that the diffusion of ions

in the microwave processing is controlled by some additional factors also other than the thermal diffusion (Singh et al 2007).

In this work, the firing in either microwave processing or conventional processing involves solid state reaction between NiO, Y_2O_3 and ZrO_2 resulting in chemical homogenization accompanied by sintering. Chemical homogenization influences the microstructure of the product. It is evident from XRDs in figure 1 that microwave processing has led to the formation of two-phase composite that includes cubic YSZ and NiO i.e. $mNiO-(1-m)YSZ$ MW composite ($m = 0.2, 0.3, 0.4, 0.5$ and 0.6). Therefore, their SEM in figure 5 (a–d) shows very clear grain boundaries. In the composites, $mNiO-(1-m)YSZ$ CON, having compositions $m = 0.2$ and 0.3 , the solid solution forma-

tion of YSZ is not complete. The compositional inhomogeneity is evident from their respective SEMs in figures 6a and b due to presence of the monoclinic phase of zirconia which are only partially sintered with a loose particle cloud. It is evident from above discussion that NiO behaves in different ways during microwave processing, since the presence of microwave facilitates the formation of solid solution of Y_2O_3 and ZrO_2 to have cubic YSZ. In the conventional processing, cubic YSZ does not form for $m = 0.2$ and 0.3 .

The solid state reactions in conventional furnaces generally take place under isothermal conditions where the transfer of heat occurs from the heating elements of the furnace to the sample. The individual phases in a multi-phase sample is heated more or less to the same temperature

Figure 9. Scanning electron micrographs of cermet: (a) 0.3Ni-YSZ MW, (b) 0.3Ni-YSZ CON, (c) 0.4Ni-YSZ MW and (d) 0.4Ni-YSZ CON.

as that of the furnace, a situation known as isothermal heating. However, in the case of microwave heating, due to differences in the microwave absorption, the individual phase is heated up to different temperatures at different rates creating a unique situation which is referred to as 'anisothermal heating' (Peelamedu *et al* 2003; Yadoji *et al* 2003). The species which achieves higher temperature works as micro heat sources and species having lower temperature works as micro heat sinks. A large temperature difference between the constituent phases leads to a reaction path and diffusion mechanisms different from those of conventional isothermal heating. The model experiment of Roy and co-workers (Peelamedu *et al* 2001) has established that the anisothermal reactions in the Y_2O_3 - Fe_3O_4 system involve a predominant one-directional diffusion of Fe_3O_4 (Fe_3O_4 is a microwave susceptor) towards Y_2O_3 as compared to a mutual diffusion that generally takes place in the conventional, isothermal reactions. Given the fact that the NiO being a magnetic material, is a microwave susceptor (Meek *et al* 1987) and works as heat source and other constituent as heat sink. This will lead to anisothermal behaviour of NiO in NiO- Y_2O_3 - ZrO_2 system leading to higher and faster diffusion of NiO along with Y_2O_3 in ZrO_2 . The group has already prepared fully calcium stabilized zirconia by microwave processing within five minutes at 1100°C (Singh *et al* 2007). The reaction between NiO and Y_2O_3 by the microwave energy has not been studied in this work.

Figure 9 shows SEM of 0.3Ni-YSZ MW (figure 9a), 0.3Ni-YSZ CON (figure 9b), 0.4Ni-YSZ MW (figure 9c) and 0.4Ni-YSZ CON (figure 9d). From comparison of figures 9a and b, it is observed that the grains of ZrO_2 has grown uniformly in the microwave processed 0.3Ni-YSZ MW and the distribution of holes are uniform whereas in case of conventionally processed 0.3Ni-YSZ CON, the formation of segregated holes due to inhomogeneous distribution of NiO is observed. Similarly, the SEM of 0.4Ni-YSZ MW (figure 9c) shows more uniform grain growth as compared to the sample, 0.4Ni-YSZ CON (figure 9d). Uniform distribution of Ni in YSZ matrix is one of the important factors which improves the property of Ni-YSZ cermet in terms of conductivity and reduces thermal mismatch with YSZ. The Ni distribution is more uniform in 0.3Ni-YSZ MW and 0.4Ni-YSZ MW as compared to the corresponding cermets derived from their composites obtained by conventional processing. This suggests that the microwave processing may be used to fabricate composite, NiO-YSZ, even from mixtures of NiO, Y_2O_3 and ZrO_2 . The electrical properties of composites and cermets prepared are yet to be investigated.

4. Conclusions

(I) Microwave processing leads to the formation of $mNiO$ -($1-m$)YSZ composite of compositions ($m = 0.2, 0.3, 0.4, 0.5$ and 0.6) having single cubic phase YSZ. Solid solu-

tion of YSZ does not form during the conventional processing of $mNiO$ -($1-m$) $Zr_{0.9}Y_{0.1}O_{1.95}$ for $m = 0.2$ and 0.3 . It suggests that during microwave processing an additional driving force works which leads to the faster diffusion of ions resulting in the formation of solid solution.

(II) The cermets obtained from reduction of microwave processed composites have more uniform grain growth as compared to that obtained from conventionally processed composites.

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