The Effect of NiO on the Phase Stability and Microstructure of Yttria Stabilized Zirconia

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Abstract

Nickel oxide (NiO) was screen printed onto the surfaces of 3 and 8 mol% yttria stabilised zirconia (YSZ) dense pre-fired substrates and then heat treated at temperatures from 1350 to 1550°C. The effect of NiO was dependent on the yttria content of the substrate. In 3 mol% YSZ it was found to alter the phase composition

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from predominantly tetragonal with a small amount of cubic phase to one consisting of approximately equal amounts of cubic and monoclinic phase. The cubic grains were much larger than the monoclinic ones and contained more nickel. Furthermore, nickel was observed to migrate through the thickness of the tile, a distance of approximately 200 μm . In the 8 mol% YSZ substrates, the phase composition was unaltered, although large grains developed under the printed nickel oxide layer and the nickel migration was confined to the extent of these large grains.

1. Introduction

Yttria stabilised zirconias (YSZs) are used in a range of high temperature applications, including solid electrolytes in solid oxide fuel cells (SOFCs), the active elements in oxygen sensors and thermal barrier coatings in gas turbines. In these applications the zirconia is generally part of a complex system of materials and interdiffusion of elements needs to be considered. For example, in SOFCs the zirconia electrolyte is in contact with a cathode and an anode, both of which usually contain a number of cation species. In common with other SOFC designs, the Rolls-Royce integrated planar solid oxide fuel cell (IP-SOFC) has a nickel oxide – doped zirconia composite anode electrode which is in direct contact with the electrolyte ¹.

Several investigations have found that small additions of NiO help to stabilise the cubic phase in 5 and 6 mol% YSZ at high temperatures ²⁻⁴. However, the prolonged ageing of these samples at 1200°C for 100 hours resulted in the decomposition of part of the cubic phase to produce a cubic and tetragonal phase composition ⁴. Chen *et al.*, ^{3, 5} observed that the solubility limits of NiO in 5 and 10

mol% YSZ were around 3 and 5-10 mol% NiO at 1600°C for 4 hours, respectively. However Kuzjueviics and Linderoth reported that the solubility limit was less than 2 mol% NiO at 1600°C for 12 hours and that it was independent of the yttria content between 6 and 10 mol% ⁶.

All of the previous studies were concerned with the interactions between NiO and YSZ used mixed powders, which were then fired and analysed. Whilst providing useful insights into the degree of reaction and the nature of the reaction products, these studies can give only limited information on the extent of NiO migration. As migration is pertinent to the use of NiO in a SOFC, in the present study the effect of NiO on the microstructure and phase stability of dense pre-fired 3 and 8 mol% YSZ substrates is examined.

2. Experimental procedure

2.1 Sample Preparation

Commercially available pre-fired 3 and 8 mol% YSZ tape-cast tiles (Kerafol, Eschenbach, Germany) were used as substrates in this study. The chemical composition of these tiles was obtained using X-ray fluorescence (XRF), performed by CERAM Research Limited (Stoke-on-Trent, UK) and the results are given Table 1. A window frame-shaped pattern NiO layer was screen printed, using a SMTECH Benchmark 90 screen printer, on one or both sides of the substrates, using a steel square mesh screen (MCI Cambridge Ltd, U.K.). A schematic diagram of the screen printed NiO window frame-shaped pattern is shown in Fig. 1. The NiO inks consisted

of 80 wt% solids loading of nickel (II) oxide powder (Alfa Aesar, Karlsruhe, Germany) mixed with 63/2 Medium, a terpeneol based binder (Johnson Matthey Colour & Coatings Division, Stoke-on-Trent, U.K.).

The samples were all dried at 120°C for 20 minutes before being fired in air. They were fired vertically or horizontally, in the latter case upon either a 3 or 8 mol% YSZ backing tile (i.e. a blank substrate). The firing temperatures ranged from 1350 to 1550°C, with a dwell time of 1 hour, with further samples being fired at 1450°C for 4 hours and 1550°C for 6 hours. Additionally a control (blank) sample for each of the two yttria doped zirconia substrate types was fired at the same time as the printed samples. Low silica containing alumina fibreboard (Tekniform Ltd., Halifax, U.K.) was used to line the furnace (Elite Thermal Systems, Market Harborough, U.K.) and provide a base to support the samples.

2.2 Phase Analysis

Small sections, approximately 8 mm × 8 mm in size, were cut from the samples for X-ray diffraction analysis. For the NiO-3 mol% YSZ substrates all the sections were taken from an area which had NiO printed on the surface. The NiO was removed by very lightly rubbing the surface with silicon carbide paper. For the NiO-8 mol% YSZ substrates one section was taken from an area next to the NiO layer. Another section was taken from a distance 5-6 mm away from the NiO layer. The location of the samples removed for X-ray diffraction from the NiO-3 mol% YSZ and NiO-8 mol% YSZ tiles is shown in Fig. 1.

A Phillips X-ray diffractometer (model PW3710, Eindhoven, the Netherlands) with CuK_α radiation was used to analyse the phases present. The measurements were performed at room temperature over three different 2θ ranges. All samples had a full scan over the range $2\theta = 20\text{-}130^\circ$ and a high resolution scan over the range $2\theta = 72\text{-}76^\circ$ to resolve the cubic (400) and tetragonal (400) and (004) peaks. Samples in which the monoclinic phase was present were subjected to another a high resolution scan over the range $2\theta = 17\text{-}36^\circ$ to resolve the cubic and tetragonal (111) and monoclinic (100), (011), (110), (11-1), (111) and (002) peaks. The scans over the range $2\theta = 20\text{-}130^\circ$ used a step size of $\Delta(2\theta) = 0.01^\circ$ with a scan speed of 0.004° 2θ per second. The high resolution scans over the range $2\theta = 72\text{-}76^\circ$ used a step size of $\Delta(2\theta) = 0.04^\circ$ with a scan speed of 0.001° 2θ per second and those over $2\theta = 17\text{-}36^\circ$ used a step size of $\Delta(2\theta) = 0.01^\circ$ with a scan speed of 0.001° 2θ per second.

Estimates of the phase composition were made from the relative intensities of the X-ray peaks. The weight fraction of the monoclinic phase, X_m , was calculated using the following equation ⁷:

$$X_m = \frac{I(111)_{\bar{m}} + I(111)_m}{I(111)_{\bar{m}} + I(111)_m + I(111)_{c,t}} \quad (1)$$

where $I(111)_m$ is the integrated intensity from the monoclinic (111) peak, $I(11-1)_m$ is the integrated intensity from the monoclinic (11-1) peak and $I(111)_{c,t}$ is the integrated intensity from the cubic and/or tetragonal (111) peak. The cubic (400) and tetragonal (400) and (004) peaks were used to calculate the relative amounts of the cubic and tetragonal phases, respectively, as these peaks did not overlap with any from the

monoclinic phase. The weight fraction of the cubic phase, X_c was calculated using equation 2:

$$X_c = \frac{I(400)_c}{I(004)_t + I(400)_t + I(400)_c} \quad (2)$$

where $I(400)_c$ is the integrated intensity from the cubic (400) peak, $I(400)_t$ is the integrated intensity from the tetragonal (400) peak and $I(004)_t$ is the integrated intensity from the tetragonal (004) peak. The lattices parameters of the cubic (c) phase were determined from the measured value of the $(400)_c$ lattice spacing and the $(004)_t$ and $(400)_t$ peaks were used to calculate the tetragonal (t) phase lattice parameters.

2.3. Microstructural Characterisation

Microstructural characterisation was performed using light microscopy (Nikon, Tokyo, Japan) and scanning electron microscopy (SEM, Cambridge Stereoscan 240, Cambridge, U.K.) with an energy dispersive X-ray analyser (EDX, PGT Avalon, Princeton, N.J.) on polished cross sections and surfaces. Cross sections of the samples were prepared and polished down to a 1 μm diamond paste and relief polished with a 0.04 μm colloidal silica solution (Struers, Ballerup, Denmark). To reveal the grain boundaries the polished cross sections were thermally etched for 15 minutes at a temperature 100°C below the firing temperature. Grain size analysis was conducted using a linear intercept technique complying with the British Standard BS EN 623-3:2001 where the number of grains measured per samples was approximately 380.

A Leo field emission gun SEM (model Leo 1530 VP, Oberkochen, Germany) with an integrated EDAX Pegasus electron back scatter diffraction (EBSD) and EDX system was used to investigate the microstructure and crystallographic phase content of the NiO-3 mol% YSZ substrates fired at 1550°C for 6 hours. The cross sections were prepared by mounting in an electrically conductive cold mounting system (Conducto-Set from MetPrep, Coventry, U.K.) and polishing down to a 1 µm diamond paste followed by relief polishing with a 0.04 µm colloidal silica solution. The samples were sputtered very lightly with palladium-gold to prevent charging. The samples were tilted by 70°, with respect to the base of the vacuum chamber of the SEM and an accelerating voltage of 20 kV with a working distance of 15 mm were used. The Kikuchi patterns were processed and analysed using OIM 4 software, which utilises information from the ICDD diffraction database to identify the cubic and monoclinic zirconia crystal phases. The EBSD orientation and EDX element maps were produced using a scan step size of 0.1 µm.

3. Results

3.1 General Observations

The NiO-3 mol% YSZ substrates were found to warp or fracture significantly when fired. The firing orientation had an effect; those samples that were fired horizontally tended to bond to the backing tile and fracture, presumably due to being constrained, and those fired vertically warped significantly. Examination of these vertically-fired samples revealed that numerous cracks had formed around the areas at

the edge of the region where the NiO had been printed. Furthermore, the samples were found to be fragile, due to the presence of numerous cracks. The NiO-8 mol% YSZ substrates, by contrast, were not found to crack or distort during firing.

When either a 3 or 8 mol% YSZ tile was used as a backing tile, the areas that had been in contact with a NiO layer printed on the bottom of the substrate above turned orange as shown in Fig. 2a. EDX analysis of the backing tiles indicated that a small amount of NiO was present in the orange areas (approximately 0.3-0.8 mol% [†]) but no trace of NiO was found in the white areas. Previous studies have reported similar color changes from white to light red ⁸ or light brown ⁹ when zirconia is calcined with NiO.

When a 3 mol% YSZ backing tile was used, a blue projection of the printed NiO pattern was observed on the furnace furniture below, as shown in Fig. 2b. A very faint blue projection was found when the samples were fired to 1450°C for 4 hours and the color of the blue phase became more intense with increasing firing temperature. Examination of this blue phase by EDX and X-ray diffraction revealed it to be nickel aluminate spinel, indicating that nickel had migrated through the thickness of the backing tile i.e. a distance of approximately 200 μm . No such nickel migration was observed when an 8 mol% YSZ backing tile was used.

[†] All the compositions of nickel and yttrium measured by EDX were converted to mol% assuming stoichiometric compositions for NiO and Y₂O₃.

3.2 XRD Phase Analysis

Fig. 3. shows the X-ray diffraction patterns for the 3 mol% YSZ control samples and the NiO-3 mol% YSZ substrates; the qualitative estimates of the phase compositions are shown in Table 2. The control samples were found to consist of approximately 90 wt% tetragonal phase, and 10 wt% cubic phase over all of the firing temperatures and times. Trace amounts of the monoclinic phase could just be resolved for the samples fired at 1550°C for 1 hour or longer, but there was insufficient to quantify. In the NiO-3 mol% YSZ substrates the amounts of the cubic and monoclinic phases were found to increase, at the expense of the tetragonal phase, with increasing firing temperature and time. After firing at 1550°C for 6 hours the sample was found to contain equal amounts of the cubic and monoclinic phases without any of the tetragonal phase being present.

The lattice parameters of the cubic and tetragonal phases calculated from the X-ray diffraction patterns are plotted alongside those reported by Scott¹⁰ in Fig. 4. The lattice parameters of the control samples did not change significantly and correspond to yttria contents of approximately 5 mol% and 2-3 mol% for the cubic and tetragonal phases, respectively. The cubic and tetragonal lattice parameters for the NiO-3 mol% YSZ substrates were found to decrease with increasing firing temperature and time. It is well known that the cubic lattice parameter of YSZ decreases with increasing NiO content^{3, 5, 9}. As the cubic and tetragonal phases in YSZ are very similar it would not be unreasonable to expect that the tetragonal lattice parameters would experience the same effect. In both sets of samples the c/a ratio was found to be around 1.016, which corresponds to a 2-3 mol% yttria content^{10, 11}. The lattice parameters for the monoclinic phase were calculated from the (110)_m, (002)_m

and $(011)_m$ spacings, using $\beta = 99.2^\circ$ ¹². There is a high level of uncertainty in the values of the monoclinic lattice parameters, but they were comparable to those reported for single crystal zirconia¹² and 2 to 3 mol% YSZ polycrystalline samples¹³.

In contrast the 8 mol% YSZ substrates were found only to contain the cubic zirconia phase whether NiO was present or not. Table 3 shows the measured lattice parameters of 8 mol% YSZ control samples and the NiO-8 mol% YSZ substrates all fired to 1550°C for 6 hours. The cubic lattice parameters in the NiO-8 mol% YSZ substrate in areas away from the NiO layer, were found to be the same as the thermal control sample and are in agreement with those reported for 8 mol% YSZ^{10, 14}. However the cubic lattice parameter in the NiO-8 mol% YSZ substrate nearer to the NiO was smaller. As mentioned earlier, it is well known that the lattice parameter of cubic YSZ decreases with increasing NiO content^{3, 5, 9}.

3.2 Microstructural Changes

The starting microstructures of the 3 and 8 mol% YSZ tape-cast tiles were both mono-modal with mean grain sizes of 0.3 and 2.2 μm , respectively. The microstructure of the backing tiles in the orange and white areas was dependent on the yttria content. With the 3 mol% YSZ backing tiles, a bimodal grain size distribution was observed in the orange areas and this microstructure extended through the thickness of the tile, i.e approximately 200 μm . The white areas were found to exhibit a mono-modal grain size distribution, similar to the starting microstructure. In the NiO-3 mol% YSZ substrates the microstructure under the printed NiO layer exhibited the same bimodal grain size distribution as found in the orange area of the 3 mol%

YSZ backing tiles. Fig. 5 shows the bimodal grain size microstructure found through the thickness of the NiO-3 mol% YSZ substrates below the NiO layer. The microstructure of the NiO-3 mol% YSZ substrates away from the NiO layer exhibited the same mono-modal grain size distribution as found in the white areas of the 3 mol% YSZ backing tiles.

In contrast, the grain size of the 8 mol% YSZ backing tiles in both the orange and white areas was mono-modal, but the mean grain size in the orange areas was significantly larger than in the white areas. Furthermore, unlike the 3 mol% YSZ backing tiles, these large grains were not found to extend through the thickness of the tiles. On the reverse side of the backing tile the microstructure consisted of smaller grains, similar in size to those found in the white areas and on the corresponding control samples. A very similar microstructure was found in the NiO-8 mol% YSZ substrates, where large grains were observed on the surface just below the NiO layer, but these did not extend beyond one to two grain depths, as shown in Fig. 6. As it was difficult to accurately measure the nickel concentration using EDX due to its low levels, the lattice parameter can be used to provide an independent estimate of the nickel concentration in the zirconia substrate near the NiO layer. Using the cubic lattice parameter for 8 mol% YSZ as a function of NiO⁹, it is estimated that the NiO concentration in the edge of the NiO-8 mol% YSZ substrate is approximately 1.3 mol%. This value is in good agreement with that measured near the edge of the NiO layer using EDX, at approximately 1.1 mol%, increasing confidence in the hypothesis that there was a solid solution of NiO in the zirconia where the grains were found to be largest.

Further analysis of the size of the grains in the orange and white areas of the 3 mol% YSZ backing tiles revealed that not only had the microstructure changed from a mono-modal to a bimodal grain size distribution, but the actual size of the smaller grains was larger in the orange areas compared with the white areas. Fig. 7 shows the surface grain size of the small grains in the orange and white areas for samples fired at increasing temperatures. The difference in the grain size of the small grains in the white and orange areas was found to increase with increasing firing temperature and time. The grain sizes in the white area were observed to be comparable with those measured on the surface of the thermally aged control samples.

The chemical compositions of the large and small grains were acquired using the EDX point analysis mode with an accelerating voltage of 20 kV. Using polished and thermally etched cross sections, five large and five small grains were measured in the orange area of the 3 mol% YSZ backing tile and in the area immediately under the printed NiO layer in the NiO-3 mol% YSZ substrates. The yttria content for the small grains was found to be around 1.5 to 2.5 mol%; it was around 4 to 5 mol% in the large grains.

Although it was quite difficult to measure the nickel concentration, as the levels were low and close to the detection limit for EDX, there did seem to be a positive correlation between the nickel content and the grain size. The relationship between the yttria concentration of the grains and their nickel concentration highlighted two groupings, one for the small grains and the other for the large grains, as shown in Fig. 8. The small grains had a tighter grouping and were located in the area between 2 to 3 mol% yttria and 0.1 to 0.2 mol% NiO. There was a much looser

grouping for the larger grains, located in the area between 3 and 5 mol% yttria and 0.3 and 0.4 mol% NiO. Unlike the small grains, there appeared to be a trend of increasing grain size and yttria content with increasing firing temperature and time. Additionally, the large grains in the orange areas of the backing tiles had lower NiO concentrations than those under the printed NiO layer in the NiO-3 mol% YSZ samples. The compositions of the larger grains have larger errors associated with them. This is likely to arise from sampling effects. A large grain is surrounded by many small grains so the electron interaction volume may well include both types of grain when a nominally large grain is being analysed, especially when sectioning effects are taken into account.

The phase map created from analysis of the Kikuchi line patterns using EBSD for the cubic and monoclinic zirconia phases, together with an EDX map for yttria over the same area in the NiO-3 mol% YSZ substrate fired to 1550°C for 6 hours are shown in Fig. 9. It was clearly evident from the EBSD phase map that the large grains are the cubic phase and that there is an approximately equal volume fraction of the cubic and monoclinic phases. The densities of the monoclinic and cubic phases calculated from the measured lattice parameters from the NiO-3 mol% YSZ substrate fired at 1550°C for 6 hours were similar at 5.77 and 6.08 g cm⁻³, respectively. Thus, the volume fraction is approximately equal to the weight fraction, meaning that the estimated amounts of the two phases results measured here are in close agreement with those from the X-ray diffraction results. However, as XRD and EBSD are not able to detect small quantities of a given phase, only the predominate phases could be determined. For example, the presence of minor tetragonal precipitates in the cubic

grains could have been overlooked. Consequently a transmission electron microscopy study is underway to characterise the microstructure further.

4 Discussion

4.1 Phase Stability

The 3 mol% YSZ composition is just inside the cubic and tetragonal two phase field between 1350 and 1550 °C¹¹. Under equilibrium conditions the tetragonal phase should be the major phase with only a small amount of the cubic phase forming. The composition of the tetragonal and cubic phases should correspond to 1-3 mol% and 5.5-7.5 mol% yttria, respectively.

When the firing temperature was 1500°C or higher, increasing amounts of cubic and monoclinic phases were observed when NiO was present; the phase compositions of the control samples remained unchanged. The increase in the amount of the cubic phase was accounted for by the growth of the original cubic grains rather than by the formation of new ones. The cubic phase was estimated to have a composition of 0.3-0.5 mol% NiO and 4-5 mol% yttria. The yttria content needed to stabilise the cubic phase is lower than predicted from the phase diagram, suggesting that the nickel is having a stabilising effect in addition to the yttria. Similar observations have been seen with small amounts of NiO in 5 mol% YSZ³ and 6 mol% YSZ⁴ and MgO in 3 mol% YSZ¹⁵ where a greater quantity of the cubic phase was stabilised than that predicted from the equilibrium phase diagram.

The cubic lattice parameter in both the 3 and 8 mol% YSZ was found to decrease with increasing firing temperature and time in the samples with NiO present. Similar results have previously been observed in 5, 8 and 10 mol% yttria doped zirconia^{3, 5, 9}. Examining the likely effect that the substitution of NiO would have on zirconia, using Kroger-Vink notation, gives:

where O_O^x is an oxygen neutral atom on an oxygen lattice site, Ni_{Zr}'' is a Ni^{2+} ion on a zirconium lattice site and $V_O^{\bullet\bullet}$ is a double positively charged oxygen vacancy. This can be compared with the substitution of yttria into zirconia:

where O_O^x is an oxygen neutral atom on an oxygen lattice site, Y_{Zr}' is a Y^{3+} ion on a zirconium lattice site and $V_O^{\bullet\bullet}$ is a double positively charged oxygen vacancy. Thus, twice as many oxygen vacancies per cation can be created when nickel is substituted instead of yttrium. The effect of this increase in oxygen vacancies would be to decrease the lattice parameters, hence destabilising the tetragonal phase, and stabilising the cubic phase.

It is well known that both the stabiliser content and the grain size have a profound effect on the retention of tetragonal grains at room temperature. Once the

tetragonal grain exceeds a critical size it will spontaneously transform to a monoclinic grain during cooling^{16, 17}. As the small tetragonal grains are observed to grow faster when NiO is present it is reasoned that they will exceed the critical grain size sooner than those in the control samples. Hence, more of the tetragonal grains would be found to transform to the monoclinic structure, explaining the increases in the amounts of the monoclinic phase at the expense of the tetragonal phase in the samples containing NiO.

4.2 Grain Growth

In the 3 mol% YSZ control samples the grain size was found to be monomodal with a mean grain size that increased slowly with increasing firing temperature and time. When NiO was present, a bimodal grain size distribution was observed, when the firing temperature was above 1500°C. Both these large and small grains were observed to grow at a fast rate. The large cubic grains grew to be 8 to 10 times larger than the surrounding small grains and the smaller grains were found to grow faster in the presence of NiO, as shown in Fig. 7. From this it can be concluded that NiO is affecting the grain boundary mobilities of the zirconia phases.

It has been observed previously that the grain growth of single phase zirconia microstructures is faster than in two phase microstructures and that the grain growth is faster for cubic structures than other phases¹⁸⁻²². The slower grain growth in two phase zirconia microstructures is attributed to the phase partitioning, i.e. the yttria needs to first diffuse from the tetragonal grain to the cubic grains, allowing the equilibrium concentrations to be reached, before the grain boundaries can move. If it is assumed that NiO helps stabilise the cubic phase with lower yttria contents than

predicted from the phase diagram, as argued in the previous section, then the amount of yttria that would need to be expelled from the tetragonal grains and consumed by the cubic grains would decrease. This in turn would enable the phase partitioning to occur sooner and thus grain growth to begin earlier, resulting in larger grains compared with the control samples.

4.3 NiO Migration

All previous studies into the effect of NiO on YSZ were performed by analysing calcined mixed powders, and thus provided only limited information on the extent of NiO migration through polycrystalline 3 mol% YSZ. In this study NiO was applied to the surface of dense pre-fired YSZ substrates and therefore, this migration phenomenon was observed directly.

The diffusion profile of nickel through a zirconia substrate can be estimated using the semi-infinite source boundary condition solution to Fick's second law of diffusion ²³:

$$\frac{C_{(x,t)} - C_o}{C_s - C_o} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (5)$$

where D is the diffusion coefficient, $\operatorname{erf}(x/2\sqrt{Dt})$ is the error function of $x/2\sqrt{Dt}$, C_s is the surface concentration, C_o is the initial concentration and $C_{(x,t)}$ is concentration at distance x , at time, t . Using the bulk diffusion coefficients for nickel in 9.5 mol%

YSZ²⁴, the depth at which the concentration reaches 1 mol% nickel after 6 hours at 1550°C can be calculated to be of the order of 10 micrometres. Although grain boundary diffusion of nickel may be faster than bulk diffusion, the estimated diffusion depth would still be of the order of tens of micrometres. This could account for the extent of the grain growth in the 8 mol% YSZ backing tiles which were observed to be limited to depths of tens of μm , but it cannot explain the migration of nickel through a 200 μm thick 3 mol% YSZ tile. Although it has been established that the migration of nickel in 3 mol% YSZ is more extensive than in 8 mol% YSZ, further work to elucidate the mechanism for this is required.

5. Conclusions

A combination of EBSD, EDX and X-ray diffraction analysis has established that the phase composition and microstructure of dense pre-fired YSZ substrates is affected by the presence of NiO. Additionally the effect of NiO was dependent on the yttria content of the substrate. With 3 mol% YSZ, NiO was found to promote the formation of large cubic phase grains with lower yttria concentrations than normally found for cubic grains doped with only yttria. The grain growth of both the cubic and tetragonal grains increased, and resulted in greater numbers of the tetragonal grains exceeding the critical size, resulting in their transformation to the monoclinic phase during cooling. Additionally, nickel was found to migrate through the thickness of the tiles, a distance of approximately 200 μm . With 8 mol% YSZ the phase composition remained unaltered, although large grains formed beneath the printed NiO layer. The nickel migration was confined to the depth of these large grains.

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Tables

Table 1

X-ray Fluorescence Analysis of 3 and 8 mol% Yttria-Stabilized Zirconia (YSZ) Sample Tiles

		Composition (wt%)	
		3 mol% YSZ	8 mol% YSZ
Zirconia	(ZrO ₂)	92.51	83.74
Yttria	(Y ₂ O ₃)	5.39	14.36
Hafnia	(HfO ₂)	1.95	1.80
Silica	(SiO ₂)	0.03	0.05
Alumina	(Al ₂ O ₃)	0.03	<0.02
Uranium Oxide	(UO ₂)	0.01	0.03
Ferric Oxide	(Fe ₂ O ₃)	0.01	<0.01
Soda	(Na ₂ O)	<0.1	<0.1
Magnesia	(MgO)	<0.05	<0.05
Titania	(TiO ₂)	<0.01	<0.01
Lime	(CaO)	<0.01	<0.01
Nickel Oxide	(NiO)	<0.01	<0.01
Loss on Ignition at 1025°C		0.07	0.02

Table 2

The Phase Content of the 3 mol% Ytria-Stabilized Zirconia (YSZ) Samples, With and Without NiO

	Temperature (°C)	Time (hours)	Phase Content (wt%)		
			Cubic	Tetragonal	Monoclinic
NiO-YSZ	1350	1	8	92	0
	1500	1	10	81	9
	1550	1	15	43	42
	1550	6	50	0	50
Controls	1350	1	8	92	0
	1500	1	9	91	0
	1550	1	8	92	0 [†]
	1550	6	10	90	0 [†]

[†] Trace amounts of the monoclinic phase were resolved, but not enough to quantify.

Table 3
Cubic Lattice Parameters from the 8 mol% Yttria-Stabilized Zirconia (YSZ)
Substrates Fired to 1550°C for 6 hours

Sample	Lattice Parameter (Å)
RT Control	5.1416
Thermal Control	5.1407
Away from the NiO	5.1407
Near the NiO	5.1373

Figure Captions

Fig. 1.

A schematic diagram of the sample printed with a nickel oxide (NiO) window pattern, showing the dimensions. The dashed squares represent the areas removed for X-ray diffraction of (a) NiO-3 mol% yttria-stabilized (YSZ) samples, (b) NiO-8 mol% YSZ near the NiO layer, and (c) NiO-8 mol% YSZ sample away from the NiO layer.

Fig.2.

A photograph of (a) the 3 mol% yttria-stabilized zirconia substrate with nickel oxide (NiO) pattern printed on both side, which was fired horizontally upon a 3mol% yttria doped zirconia backing tile at 1550°C for 6 hours and (b) the blue projection of the printed NiO pattern on the furnace furniture underneath the backing tile.

Fig. 3.

X-ray diffraction patterns for the (a) 3 mol% YSZ controls, (b) high resolution traces of the {400} peaks from the 3 mol% YSZ controls, (c) NiO-3 mol% YSZ under the NiO layer and (d) high resolution traces of the {400} peaks from the NiO-3 mol% YSZ under the NiO layer.

Fig. 4.

(a) The measured cubic and tetragonal zirconia lattice parameters. The solid lines and solid points are for the NiO-3 mol% YSZ samples. The dashed lines and open points are for the control samples. The triangular and square points are for the samples fired for 1 and 6 hours, respectively. (b) The cubic and tetragonal zirconia lattice parameters as a function of yttria, (data from Scott ¹⁰).

Fig 5

Scanning electron micrograph of a thermally etched polished cross section of NiO-3 mol% YSZ fired to 1550°C for 1 hour, taken from an area under the NiO layer and showing a bimodal grain size.

Fig. 6.

A light micrograph of a cross-section of a NiO-8 mol% YSZ substrate with NiO printed on both sides and fired to 1550°C for 6 hours, showing that grains immediately under the NiO are larger than those in the middle.

Fig. 7.

The surface grain size of the small grains in the white and orange areas of the 3 mol% yttria –stabilized zirconia backing tiles. The solid and open points represent the samples fired for 1 and 6 hours, respectively. The error bars represent one standard deviation from the mean.

Fig. 8.

The relationship between the yttria concentration and the nickel oxide (NiO) concentration of the grains in the NiO-3 mol% yttria-stabilized zirconia (YSZ) samples. The error bars represent the standard error.

Fig. 9.

(a) EBSD phase map from the NiO-3 mol% YSZ sample fired to 1550°C for 6 hours, showing the cubic phase as blue and the monoclinic phase as yellow and (b) EDX map for yttrium over the same area, where the darker blue represents higher yttrium concentration.

Figure Images

Fig 1.

Fig 2.

Fig. 3.

Fig. 4.

Fig 5

Fig. 6.

Fig. 7.

Fig. 8

Fig. 9.