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Improvements to the sintering of yttria-stabilized zirconia by the addition of Ni

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Abstract

We have studied the effect of nickel oxide (NiO) on the sintering of yttria-stabilized zirconia (YSZ) at temperatures from 1100 to 1400 °C. Differences in the densification behaviour were observed between the direct use of NiO powders and Ni metal as precursor. Our results show that with the addition of Ni into YSZ, sintering was completed at 1300 °C instead of 1400 °C, a 100 °C reduction. The addition of Ni also increased the shrinkage rate at 1200 °C from $-0.29\times10^{-6}\,s^{-1}$ to $-0.46\times10^{-6}\,s^{-1}$. Young's modulus of the samples heat treated at 1200 °C measured by microindentation also increased from 26 GPa for YSZ to 65 or 191 GPa for YSZ plus NiO or Ni, respectively. Addition of NiO or Ni also stabilised the cubic phase and promoted grain growth in YSZ during sintering.

Keywords: Yttria-stabilised zirconia; Nickel oxide; Doping; Sintering

1. Introduction

Yttria-stabilised zirconia (YSZ) is used in the production of thermal barrier coatings (TBCs) for the protection of metal substrates in turbine engines [1,2]. Novel TBCs can be prepared by electrophoretic deposition in which the green coatings need to be sintered at high temperatures to consolidate the structure and improve coating/substrate adhesion. In order to avoid deleterious effects on the metal substrate during sintering, the heat treatment needs to be done at temperatures below 1250 °C [1,3]. One of the easiest and cheapest methods to improve the densification, control the microstructure and reduce the sintering temperature is by the addition of sintering aids.

Sintering aids such as cobalt, praseodymium, calcium or copper have been used to improve the properties of zirconia ceramics [4–7]. However, it has been observed that not all elements or concentrations lead to an improvement in densification. For example, the addition of CuO reduced the sintering temperature of YSZ due to the formation of a liquid phase at about 1100 °C [8]. However, at concentrations above 1 wt%, CuO led to the formation of large pores, which were produced by the dissociation of CuO and the subsequent formation of Cu_2O and oxygen [8]. As for the addition of NiO, most of the studies have concentrated on its use in fabrication of anodes (YSZ+NiO mixture) for solid oxide fuel cells [9–11]. The concentrations used in most of these experiments are high (up to 50 mol%), and NiO was no longer considered a dopant. Only a few reports have studied the effect of NiO as sintering aid [12–15]. It has been found that the dissolution of NiO into zirconia stabilised the cubic phase, although in some cases, the metastable tetragonal phase was also stabilized [16–19]. Although NiO addition increased the temperature at which sintering started from 1000 to 1100 °C, NiO–YSZ samples densified faster at temperatures above 1100 °C, promoting shrinkage of the composites [9]. It has been also observed that although NiO can enhance the sintering of YSZ it can also inhibit the full densification of YSZ above 1300 °C [14,15].

In this work, we have studied the effect of NiO on the sintering of YSZ, paying particular attention to its effect on the density, sinterability, phase composition and mechanical properties. Sintering experiments were carried

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out with NiO and Ni metal as the starting material at temperatures from 1100 to 1400 °C. It was found that Ni/NiO addition increased the density of YSZ from 60% up to 90% theoretical density when sintered at 1200 °C, promoted grain growth and stabilized the cubic phase in YSZ.

2. Experimental procedure

2.1. Sample preparation

Samples were prepared by mixing yttria-stabilized zirconia (5 mol% yttrium, MEL® Chemical) with NiO (Sigma-Aldrich, 99% trace metals, < 5 μm size) or Ni metal (Sigma-Aldrich, 99.8% trace metals, < 1 μm size). Powder mixtures with 0, 0.1, 0.5, 1.0 and 2.0 wt% Ni were prepared. Samples were attrition milled (01-HD, Union Process) for 8 h in ethanol, using zirconia media with a rotation speed of 450 rpm. The drying process was carried out overnight by evaporation of the solvent at 78 °C. The dried sample was ground in a mortar and pestle. Powders were uniaxially pressed at 580 MPa in a 12.7 mm diameter die. The green bodies were sintered in air at either 1100, 1200, 1300 or 1400 h with a heating rate of 10 °C. For simplification hereafter Ni concentration will be referred to its precursor, either Ni or NiO.

2.2. Sample characterisation

Densities were measured by the Archimedes method in water. The densification of the samples (6 mm length, 6 mm diameter) was characterised by dilatometric measurements (Built-in-House Equipment, Manchester Materials Science Centre, UK) at a heating rate of 10 °C/min from 20 to 1400 °C. Thermal analysis was carried out in air by thermogravimetric analysis (TG; NETZSCH STA 449C, Germany) at a heating rate of 10 °C/min. The phase composition was determined by X-ray diffraction (XRD; Cu $K_{\alpha 1}$ radiation; Philips PW 1830). The microstructure was characterised using scanning electron microscopy (Philips XL30 FEG-SEM). SEM specimens were prepared by grinding with successive grades of SiC paper, and polished with 3 and 1 μm grit diamond paste. Finally, the samples were thermally etched at 50 °C below the sintering temperature for 30 min for observation of grains and grain boundaries. ImageJ software was used to measure grain size using a minimum of 188 grain intercepts. Microindentation was performed using an instrumented microindenter (CSM MHTX; Switzerland) with an indentation load of 1 N for all indents.

3. Results and discussion

Figs. 1 and 2 show the effect of sintering temperature and Ni and NiO concentrations on the density of YSZ. Thermogravimetric analysis showed that Ni oxidised into NiO between 400 and 600 °C (not shown). Fig. 1 shows

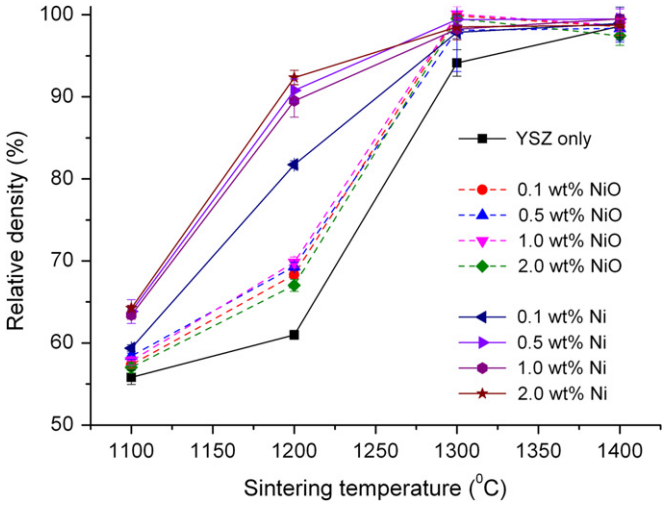

Fig. 1. Effect of sintering temperature and Ni and NiO addition on the density of YSZ.

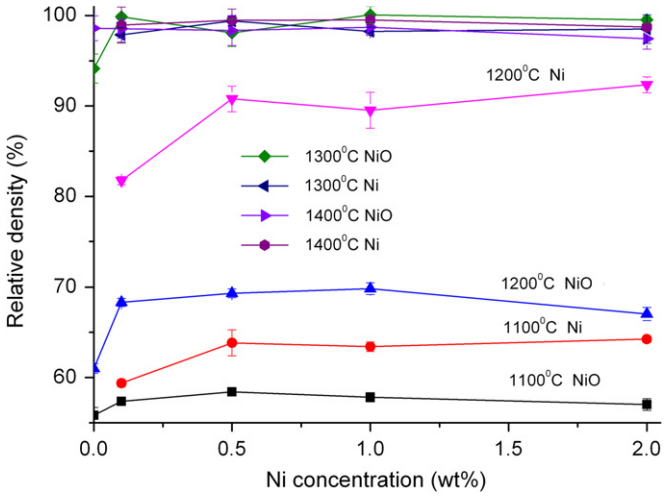

Fig. 2. Effect of Ni concentration on the density of YSZ.

that the addition of both Ni or NiO successfully increased the density of YSZ. The use of Ni as the initial powder was more efficient in increasing the density of YSZ at temperatures below 1300 °C. For example, at 1200 °C YSZ and YSZ+NiO reached densities of only around 61% and 69%, respectively, whereas YSZ+Ni had a maximum density of 90%. Furthermore, Fig. 2 shows that in general an increment in Ni or NiO concentration above 0.5 wt% up to 2 wt% had little effect on the density of YSZ; for instance the density of YSZ with addition of different levels of NiO had a density between 68% and 70% at 1200 °C. Conversely, the density increased from 82% to 90% as Ni metal concentration was increased from 0.1 to 0.5 wt% Ni. At 1300 °C, the samples with addition of 0.1 wt% NiO reached the highest densities of around 99% in comparison to 94% of YSZ. On the other hand, the density of the mixture YSZ+Ni increased up to 98% for 0.5 wt% Ni, but then decreased to 94% for the sample containing 2 wt%. At 1400 °C most of the samples

Table 1
Mechanical properties of YSZ with and without the addition of NiO.

Ni content (wt%)	Sintering temperature (°C)	Young's modulus (GPa)	Hardness (GPa)
0	1200	26.18 ± 0.47	1.13 ± 0.03
0.5 NiO	1200	65.13 ± 1.31	3.11 ± 0.11
0.5 Ni	1200	190.86 ± 4.42	14.4 ± 0.48
0	1400	207.46 ± 2.73	15.71 ± 0.41
0.5 NiO	1400	206.52 ± 3.63	15.27 ± 0.30
0.5 Ni	1400	208.87 ± 2.90	15.57 ± 0.39

containing either Ni or NiO had lower densities than that of YSZ. For example, the samples containing 2 wt% Ni as NiO or Ni had a density of ~97% in comparison to ~99% for only YSZ.

The differences in density were also reflected in changes of the mechanical properties (Table 1). Young's modulus of YSZ at 1400 °C was very similar for samples with and without 0.5 wt% Ni with values around 207 GPa. At 1200 °C the sample containing 0.5 wt% Ni had a Young's modulus of 191 GPa, considerably higher than the value obtained for the sample with NiO (65 GPa) and seven times higher than for only YSZ (26 GPa). Likewise, hardness changed from 13 to 3 and 1 GPa for samples containing 0.5 wt% Ni, NiO and YSZ only, respectively.

The samples containing Ni as the initial powder were also studied by dilatometry up to 1400 °C (Fig. 3). Dilatometry shows a volume expansion above 400 °C corresponding to Ni oxidation. The initial sintering start temperature of YSZ without any additive was around 890 °C. As Ni was added, the initial sintering temperature was reduced to ~870 °C for 0.5 wt% Ni. Furthermore, Fig. 3b shows that Ni addition shifted the maximum shrinkage rate to lower temperatures, from around 1320 °C (without any Ni) to 1250 °C with 0.5 wt% Ni. The improvement in shrinkage rate was evident at 1200 °C with an increase from $-0.29 \times 10^{-6}\,s^{-1}$ to $-0.46 \times 10^{-6}\,s^{-1}$. In general it can be said that 0.5 wt% Ni was the most effective concentration to promote the densification of YSZ.

Fig. 4 shows the XRD of YSZ with 2 wt% Ni after sintering at different temperatures. The initial powder contained a combination of monoclinic and cubic/tetragonal phases (cubic and tetragonal signals appear overlapped as evident in the signal between 72 and 76° in Fig. 5 and described below). The monoclinic phase disappeared after sintering at 1100 °C and the NiO phase was detected after oxidation of Ni. The relative intensities of the XRD peaks at 72–76°, corresponding to the tetragonal and cubic phases (Fig. 5), were used to calculate the content of cubic phase in YSZ according to [20,21]

$$V_c = I(400)_c / [I(004)_t + I(400)_t + I(400)_c] \quad (1)$$

where $I(hkl)$ are the integrated intensities of reflections of the cubic (c) and tetragonal (t) phases (Fig. 5). Figs. 5 and 6 show the effect of sintering temperature and NiO concentration on the content of cubic phase, respectively.

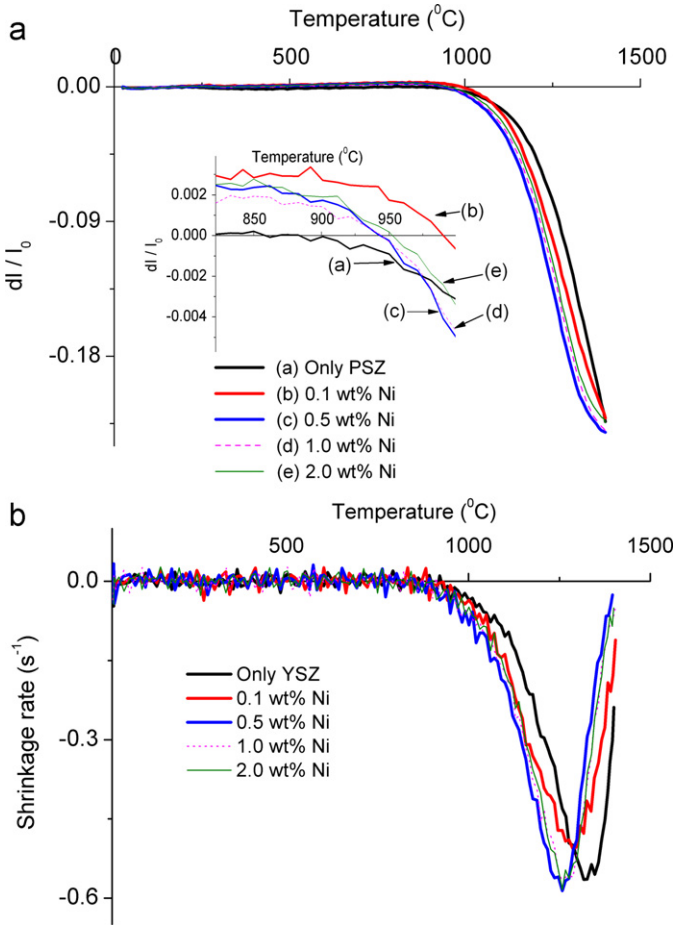

Fig. 3. Effect of Ni on the shrinkage behaviour of YSZ as measured by dilatometry.

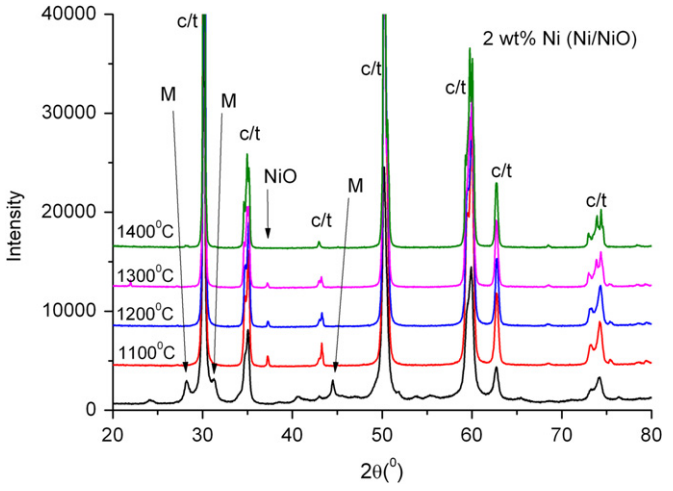

Fig. 4. Effect of sintering temperature on the phase composition of YSZ plus 2 wt% Ni; m, c and t refer to monoclinic, cubic and tetragonal phase, respectively. Bottom XRD spectrum is before sintering.

Our results show that the cubic phase in YSZ increases with sintering temperature and NiO concentration. The stabilisation of the cubic phase in YSZ is related to the increase of the amount of oxygen vacancies [22,23], which

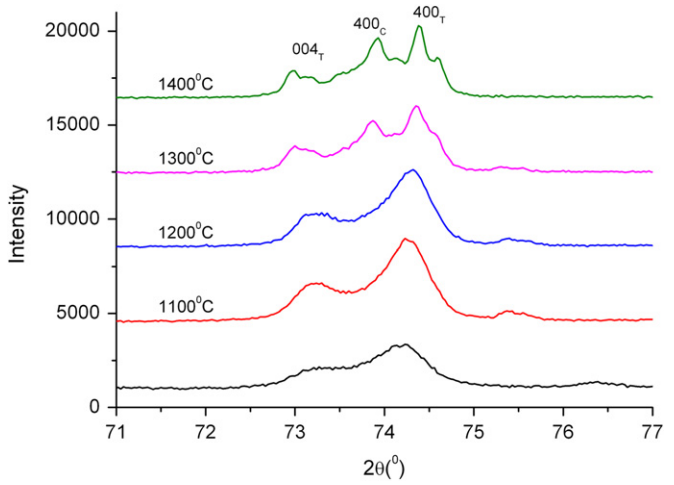

Fig. 5. Details of the XRD pattern showing the effect of sintering temperature on the cubic phase content in YSZ with 2 wt% Ni.

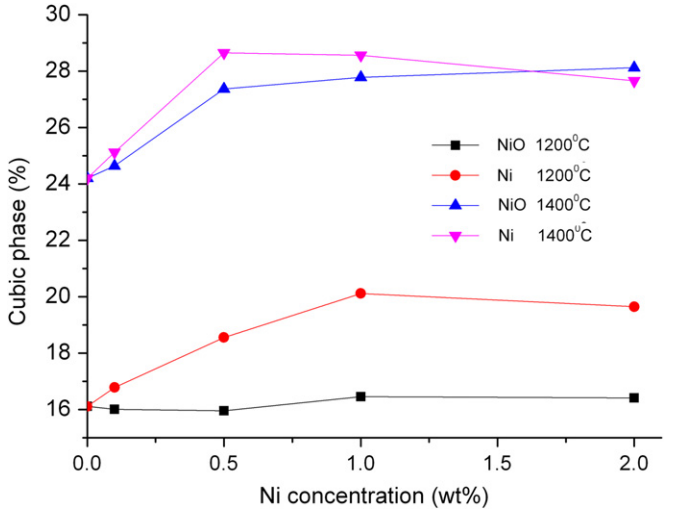

Fig. 6. Increase of cubic phase in YSZ by the addition of NiO and Ni/NiO at 1200 and 1400 °C.

as suggested is formed by the dissolution of NiO into YSZ. Therefore, in general higher NiO concentration should produce an increase in the amount of cubic phase in YSZ. However, Fig. 6 shows that when the samples were sintered at 1200 °C the amount of cubic phase was higher for the compacts containing Ni than NiO . However, such differences disappear with sintering at 1400 °C.

Figs. 7 and 8 show SEM images of YSZ sintered at 1200 and 1400 °C with and without the addition of Ni and NiO. Fig. 7 also shows a denser microstructure with the addition of NiO and Ni when sintered at 1200 °C. Comparing Fig. 7, it was observed that the addition of Ni already produced a small but consistent increase of grain size from 0.3 μm for YSZ to 0.32 and 0.36 μm for 0.5 wt% NiO and Ni, respectively. Furthermore, the sample containing 0.5 wt% Ni (Fig. 7c) already started to show the development of a bimodal particle size distribution, suggesting abnormal grain growth. When samples were sintered at 1400 °C (Fig. 8), NiO and Ni alike promoted grain growth. Nonetheless, the use of NiO produced larger grains than those of Ni (Fig. 8b and c). The grain size increased from 0.79 μm for YSZ to 0.94 and 1.52 μm for 0.5 wt% Ni and NiO, respectively. Furthermore, the addition of 0.5 wt% NiO produced grains as large as 3 μm (Fig. 8c), whereas similar microstructure was observed only for concentrations of 2 wt% Ni (Fig. 8d).

The promotion of densification when Ni and NiO additions are made to YSZ is expected as NiO has some solubility in YSZ [13]. This improvement of the sintering of YSZ could be related to an increase in the oxygen vacancy concentration, or due to the differences in ionic radii, or a combination of both that would increase the rate of cation diffusion and promote sintering [7,13]. Whilst both Ni and NiO promote sintering, the use of Ni metal as the starting material caused a sudden increase in density at 1200 °C which was not observed at this temperature with the direct use of NiO. The difference between Ni and NiO is difficult to explain as thermogravimetric analysis indicates that Ni oxidises into NiO below 600 °C, which is below the temperature at which sintering of YSZ starts. It might be considered that the volume expansion associated with the oxidation of Ni into NiO would cause a beneficial increase in density, in addition to use of different size powders; however the strength of such a mechanism would be vanishingly weak for an addition of 0.5 wt% Ni. The purity of the powders is similar; however their different chemical and mechanical behaviours during milling may lead to changes in the nature of the green bodies. One simple difference between the two would be that due to a five-fold difference in size between the starting powders there could be a 125-fold difference in number concentration of dopant particles in the green body. Furthermore, in the case of a metallic addition deformation during milling may further distribute the dopant. More even distribution such as this may improve early stage sintering.

Moreover, the increase in grain size agrees with the idea proposed by Allemann et al. [7], who suggested that dopants with smaller atomic radii than that of the host material would facilitate grain boundary mobility by reducing lattice misfits between the grains. It has also been suggested that the dissolution of NiO could result in the appearance of concentration stresses due to the size mismatch between the dopant and the host ion (Zr^{4+}—0.84 Å, Ni^{2+}—0.72 Å) [24–26]. Depending on the type of concentration stresses, such effects might reduce the lattice misfits between adjacent grains, thus facilitating grain boundary mobility. Additionally, before the grain boundary moves, yttria needs to diffuse from the tetragonal to the cubic grains (phase partitioning); however since the addition of NiO stabilises the cubic phase, less yttria will need to diffuse before the grain boundary moves. This acceleration in phase partitioning also eases grain boundary mobility, thus promoting grain growth [20]. The details for the improvement of densification of YSZ by the addition of NiO are still unknown. A more detailed study on the origin of the differences between Ni and NiO is currently underway and will be reported in a subsequent publication.

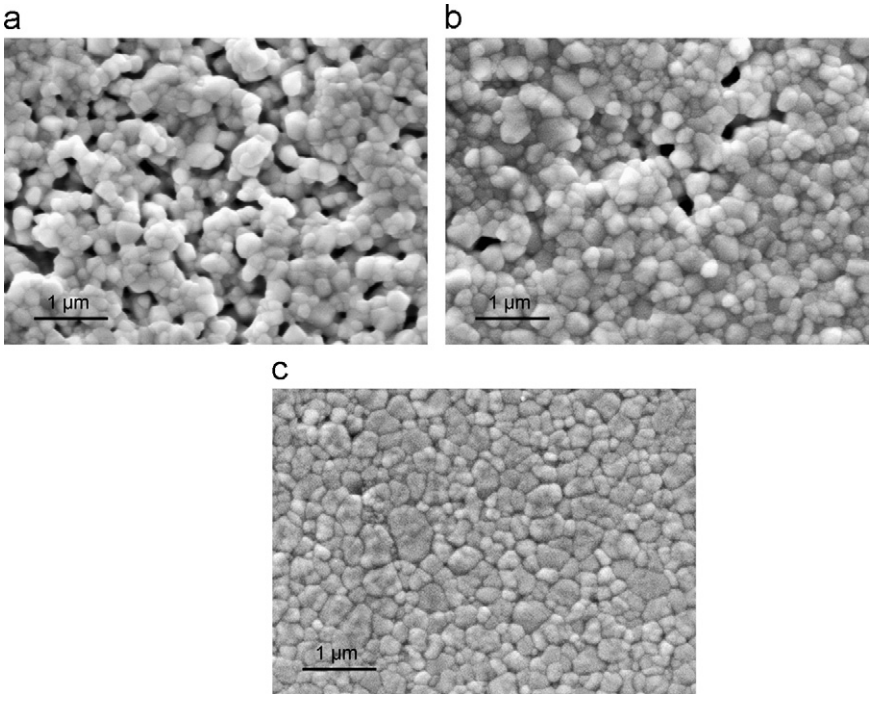

Fig. 7. YSZ samples sintered at 1200 °C: (a) YSZ only; (b) YSZ+0.5 wt% NiO; and (c) YSZ+0.5 wt% Ni.

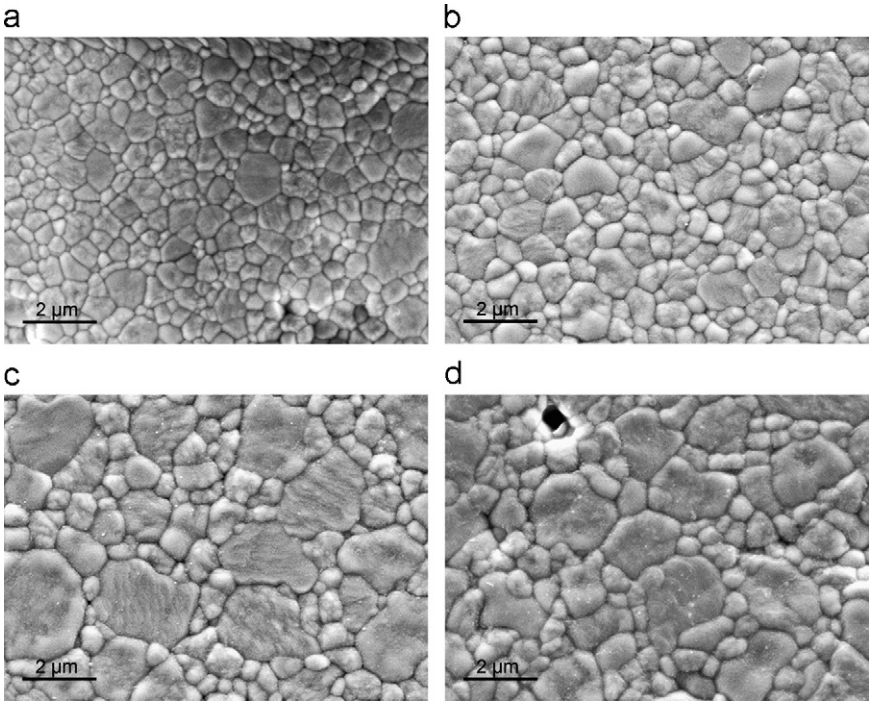

Fig. 8. Effect of NiO on the microstructure of YSZ sintered at 1400 °C: (a) YSZ only; (b) 0.5 wt% Ni; (c) 0.5 wt% NiO; and (d) 2 wt% Ni.

4. Conclusions

Our experiments have shown that NiO can successfully increase the density and mechanical properties of YSZ but more importantly that the initial use of Ni metal as precursor can have a much higher impact than the direct use of NiO. Although the origin of this difference is still unclear, the use of Ni metal can reduce the sintering temperature from 1400 to 1300 °C. Similarly, Young's modulus and hardness were considerably higher and changed from 26 and 1.3 GPa to 191 and 14 GPa, respectively. Dilatometry results show that the temperature at which maximum shrinkage occurred dropped from 1320 °C to 1250 °C with the addition of 0.5 wt% Ni and

that the shrinkage rate increased considerably from $-0.29\times10^{-6}\,s^{-1}$ to $-0.46\times10^{-6}\,s^{-1}$ at 1200 °C. The current results are encouraging for the use of NiO (from Ni metal) as an additive for the production of thermal barrier coatings, although further work will be needed to ensure that the excessive shrinkage will not degrade coating integrity.

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