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Nanosize NiO/YSZ Powders Produced by ICP Technique

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Abstract

The plasma synthesis of nanosize NiO/ZrO_2 *and NiO/YSZ powders has been developed by introducing a mixture of coarse-grained zirconia, yttria and nickel oxide into an inductively coupled plasma flame. The average particle size of the prepared powder is in the range of 16–55 nm and specific surface area is 15–35* $m^2\ g^{-1}$*. The phase and granulometric composition of the powders produced depend on reagent concentration in the plasma flame and cooling rate, on the content of* Y_2O_3 *and NiO. In the* NiO/ZrO_2 *system NiO increases the fraction of the metastable tetragonal phase of* ZrO_2 *but in the NiO/YSZ system promotes formation of non-transformable t′-phase and cubic* ZrO_2*. © 1997 Elsevier Science Limited.*

Es wurde ein Herstellungsverfahren von feinen, kugelförmigen NiO/ZrO_2 *und NiO/YSZ Teilchen durch verdampfen der Yttriumoxyd, Nickel (II)-oxyd und Zirkoniumdioxyd Mischung in Induktionsplasmastrohm ausgearbeitet. Die Korngröße des Nanopulvers beträgt 16–55 nm, die spezifische Oberfläche 15–35* $m^2\ g^{-1}$*. Die Reagentienkonzentrationen in Plasmastrohm, Kühlungsgeschhwindigkeit und Verhältnisse zwischen Ausgangsstoffen bestimmen die granulometrische und Phasenzusammenstzung des Produkts. Durch NiO wird der Auteil des metastabillen tetragonallen* ZrO_2 *im System* NiO/ZrO_2 *vergrößert. Im System NiO/YSZ stimuliert NiO die Bildung von t′-*ZrO_2 *und c-*ZrO_2*.*

1 Introduction

Yttria-stabilized zirconia (YSZ) with nickel is one of the most commonly used materials for solid oxide fuel cells (SOFC) anodes. Characteristics of the anode are determined by structure, nickel content and distribution of particles. It is expected that the performance of an SOFC anode could be improved by increasing the three-phase boundary region formed by electrolyte, gas and electrode[1] which is influenced by the method of manufacturing of the precursor powder of Ni(NiO)/YSZ and the anode. In this connection several novel methods such as drip-pyrolysis,[2] nitrate pyrolysis,[3] chemical and electrochemical vapour deposition[1] for preparation of Ni(NiO)/YSZ powder or anode with fine and uniformly distributed particles of components have been investigated. However, little is known about the synthesis of nanosized NiO/YSZ powder using thermal plasma technique although this technique is successfully used for manufacture of ultrafine composite powders of refractory compounds[4] and ZrO_2.[5]

The present work was aimed at extending the thermal plasma technique to the synthesis of nanosize NiO/YSZ powder with various contents of components and obtaining information about the interaction of NiO and zirconia at high temperature.

2 Experimental Procedure

2.1 Powder preparation

The nanocrystalline NiO/YSZ powders were prepared by introduction and evaporation of coarse-grained commercially available zirconia, yttria and nickel oxide powders into a high-temperature, radio frequency inductively coupled air plasma (ICP). The experimental apparatus, developed for producing ultrafine powders of refractory compounds,[4] consists of a radio frequency (5·28 MHz) oscillator with maximum power 100 kW, a quartz discharge tube (65 mm diameter) with an induction coil, raw powder and gas supply systems, water-cooled stainless steel reactor and heat exchanger, and cloth filter for collecting powder (Fig. 1). The commercially available raw powders of zirconia (99·8%), yttria (99·9%) and nickel oxide (99·9%) with particle size of 10–40, 10–40 and 40–60 μm respectively were premixed and introduced into the air plasma flame radially

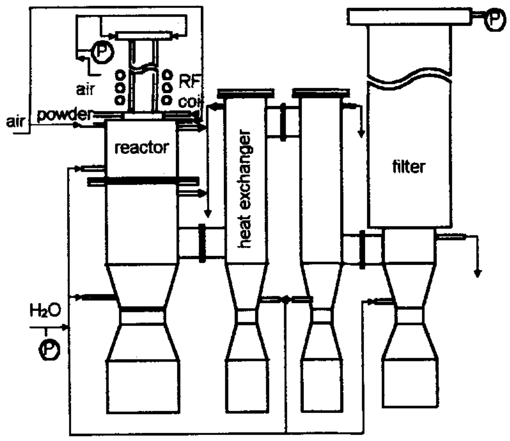

Fig. 1. Schematic view of a plasma apparatus.

through four tubes (3 mm diameter) welded into a water-cooled flange with inner diameter of 40 mm by transporting gas. Condensation and the subsequent growth process of NiO/YSZ particles was controlled by introducing cold air (3·0–6·0 m^3 h^{-1}) into the reaction chamber. Under typical synthesis conditions the flow rate of plasma-forming gas was 7·6 m^3 h^{-1} and feed rate of raw powder 0·3–1·4 kg h^{-1}.

In order to clarify the influence of NiO on the phase composition of ZrO_2 and YSZ at high temperature, besides NiO/YSZ powders samples of single components and of NiO/ZrO_2 powders as well as a mechanical mixture of nanosized NiO/ZrO_2 and NiO/YSZ powders were prepared.

2.2 Powder characterization

The prepared powders were characterized by conventional chemical analysis and X-ray powder diffraction studies using K_α radiation. The content of monoclinic phase of ZrO_2 was calculated from ratio of integrated intensities of diffraction maxima.[6] The specific surface area of powders was determined by BET argon adsorption-desorption method. The average particle size was calculated from the specific surface area of powder. The shape of particles was determined by transmission electron microscopy (TEM). Presence of coarse particles was controlled by sedimentation. A weighed amount of an as-prepared powder (300 mg) was dispersed in pure ethanol (300 ml) by ultrasonic agitation (44 kHz) for 20 min. Afterwards the suspension was allowed to settle for 20 min and the suspension of the fine particle fraction in ethanol was separated from the sediment.

To study the effect of heat treatment on the specific surface area and phase composition of powders samples were annealed at temperatures up to 1300 °C for 2 h, followed by furnace cooling. To study the stress-induced phase transformation various samples were dry pressed up to 10^3 MPa.

3 Results and Discussion

3.1 Dispersity and particle shape

The characteristics of some powders prepared under typical synthesis conditions are listed in Table 1. From the data, the average particle size of prepared powders varies from 34 to 52 nm depending on the chemical composition of the samples. Sedimentation analysis showed that the amount of coarse particles with size about 1 μm were less than 0·1 wt%, which means that the conditions of synthesis ensure the evaporation of raw materials.

Similarly to other plasma processes, the specific surface area and the average particle size as well as the amount of coarse particles of produced powders depend on the feed rate of raw powder and flow rate of cooling gas (Fig. 2), that is, on the cooling rate of particles. Increasing feed rate of raw powder decreases the specific surface area of powders and increases the amount of coarse particles. Dependence of the specific surface area of powder and of the amount of coarse particles on the feed rate of raw materials and on the cooling rate can be explained by incomplete evaporation of the raw particles, as well by coalescence of liquid droplets at a high concentration of particles

Table 1. Characteristics of some as-prepared powders

Sample no.	*Composition*	*Specific surface area (m^2 g^{-1})*	*Average particle size (nm)*	*ZrO_2 (mol%)*	*Y_2O_3 (mol%)*	*NiO (mol%)*	*Phase composition*
1	NiO	15·4	52	—	—	99·9	NiO
2	ZrO_2	28·2	37	99·9	—	—	t-, m-ZrO_2 (15%)
3	NiO/ZrO_2	29·1	35	79·9	—	20	t-, m-ZrO_2 (9·6%), NiO
4	NiO/ZrO_2	25·2	34	39·8	—	60·1	t-ZrO_2, NiO
5	1·6YSZ	29·3	35	98·3	1·6	—	t-, m-ZrO_2 (6%)
6	5·5YSZ	28·7	36	94·4	5·5	—	t-, c-ZrO_2
7	NiO/1·6YSZ	24·1	37	39·3	0·64	60	t-, c-ZrO_2, NiO
8	NiO/5·5YSZ	23·6	37	37·7	2·2	60	c-ZrO_2, NiO

Feed rate of raw powder 0·6 kg h^{-1}, flow rate of cooling gas 6·0 m^3 h^{-1}.

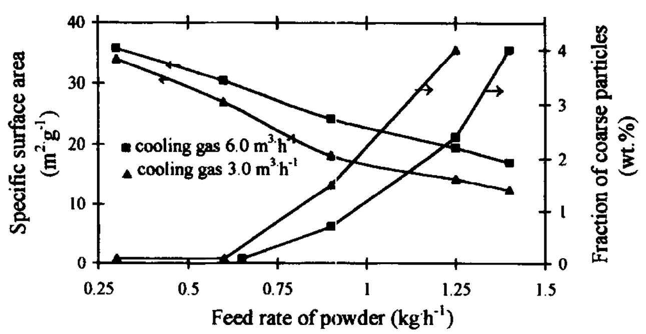

Fig. 2. Specific surface area and amount of coarse particles of NiO (60 mol%)/YSZ (8 mol%) powder as function of the feed rate of raw materials at rates of cooling gas of 3·0 and 6·0 m^3 h^{-1}.

in the gas flow. Besides this the specific surface area and average particle size of produced NiO/YSZ powder depend on the NiO content (Fig. 3). The decreasing particle size of NiO/YSZ powder at low content of NiO can be explained by blocking the surface of growing YSZ particles by NiO molecules. At high content of NiO the average particle size is determined mainly by NiO particles formed, whose growth time in the plasma flame is higher than for zirconia because the lower condensation and melting temperatures of NiO. The calculated average particle size is consistent with results of TEM studies. The singly prepared NiO particles have a cubic shape and size from 20 to 80 nm (Fig. 4). It means that nanosize NiO particles tend to reveal the morphology characteristic of its crystal structure. The similar shape of NiO particles has been established for powder prepared by spray-ICP technique of an aqueous solution of nickel nitrate.[5] At the same time the particles of NiO/ZrO$_2$ and NiO/YSZ composite powders have characteristic ZrO$_2$ spherical form particles (Fig. 5). It is possible that NiO condenses on the surface of the spherical YSZ particles formed before at the higher temperature. Formation of such coated particles is characteristic for many other plasma-chemical processes of manufacture for composite powders if the formation or boiling temperatures of components differ.[4] Therefore plasma synthesis allows to produce spherical nanosize NiO/YSZ powders with various average particle sizes and ratio of components.

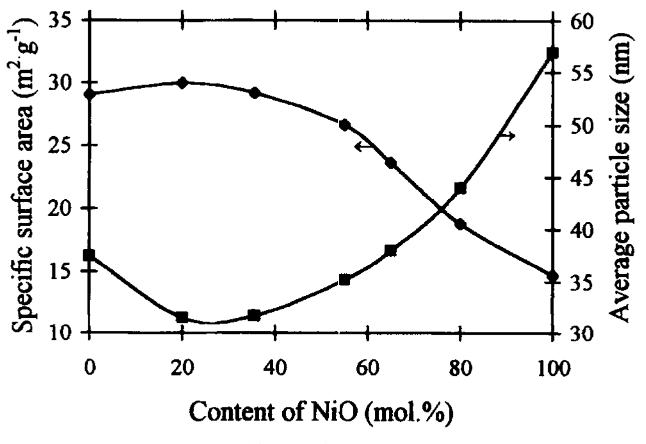

Fig. 3. Change of specific surface area and average particle size of NiO/YSZ (8 mol%) powder with NiO content.

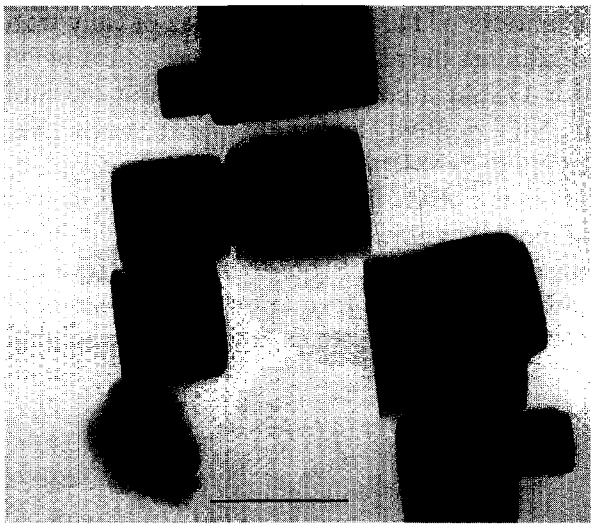

Fig. 4. Transmission electron micrograph of NiO powder (bar = 100 nm).

3.2 Phase composition of powders

The phase composition of the nanosized powders produced depends on the content of yttria and NiO (Figs 6 and 7). In the NiO/ZrO$_2$ system as well as in the NiO/YSZ the amount of the monoclinic phase decreases with increasing content of NiO (Fig. 8). The XRD pattern of NiO/ZrO$_2$ powder containing 65·5 mol% NiO shows only insignificant traces of monoclinic phase while singly prepared ZrO$_2$ contains 15% of the monoclinic phase. Similarly the NiO/YSZ powders contain smaller amount of the monoclinic phase than that of single YSZ and this amount decreases with concentration of NiO. As-prepared nanosize NiO/YSZ powders containing yttria above 2·4 mol% and NiO above 20 mol% are fully stabilized.

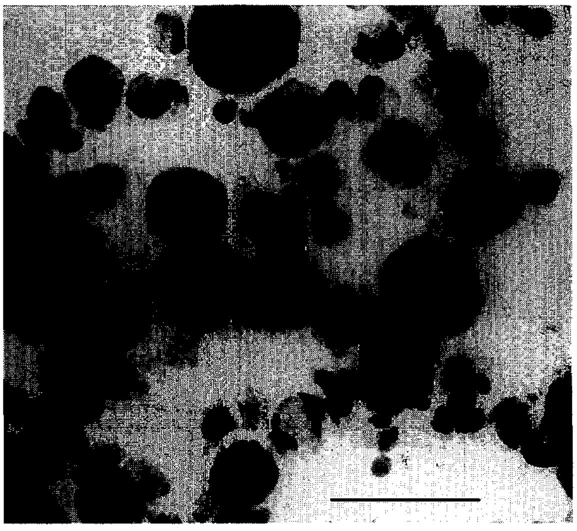

Fig. 5. Transmission electron micrograph of NiO/YSZ powder (bar = 100 nm).

The amount of the tetragonal phase of fully stabilized zirconia decreases with concentration of NiO and Y_2O_3. At a content of yttria about 5·5 mol% and NiO content higher than 10 mol% XRD patterns of powders show that the major phase of zirconia is c-ZrO_2. In the singly prepared nanosize YSZ powder cubic phase dominates at yttria contents about 6 mol%. From these results it appears that NiO promotes formation of stabilized ZrO_2 phases in the both systems, although the solubility of the NiO is remarkable only in Y_2O_3-stabilized ZrO_2.[7]

Calcination of NiO/ZrO_2 powder at high temperature, followed by furnace cooling causes t → m phase transformation (Fig. 9). For all samples of NiO/ZrO_2 heated to 1300°C the major phase is the monoclinic phase of ZrO_2. Increasing the amount of NiO increases the temperature of the phase transformation and decreases the degree of phase transformation at low temperatures. For NiO/ZrO_2 samples with high content of NiO significant t → m phase transformation occurs at temperatures of 900–1200°C. Therefore the presence of NiO in the nanosize NiO/ZrO_2 powder hinders but does not prevent t → m phase transformation of ZrO_2.

The decomposition of NiO and ZrO_2 solid solution at temperatures about 1000°C[8] can promote the phase transformation, but the small solubility of NiO in ZrO_2 and remarkable dependence of t → m phase transformation temperature on NiO content indicate that the tetragonal phase can be stabilized mainly by small particle size.[9] The remarkable dependence of particle size on their

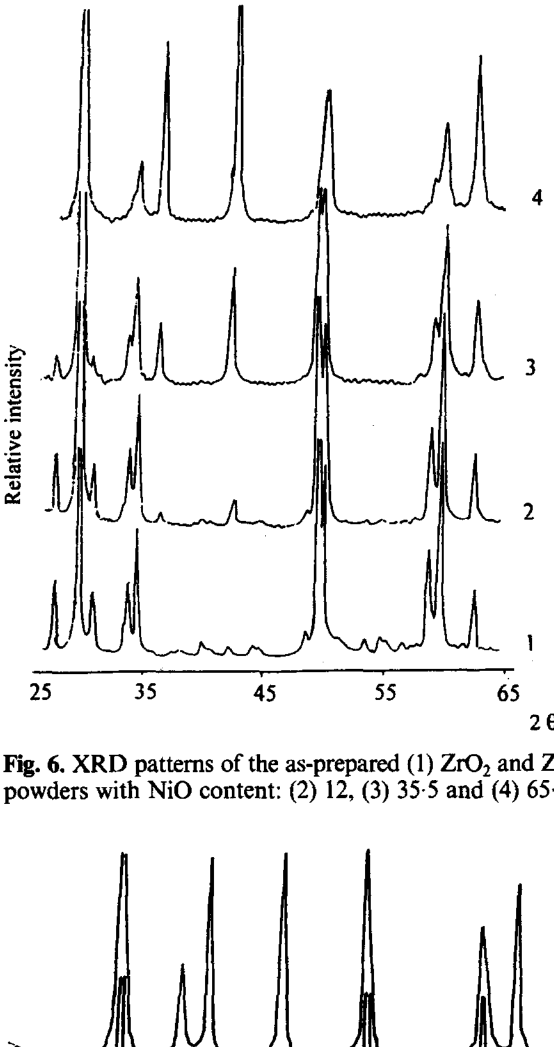

Fig. 6. XRD patterns of the as-prepared (1) ZrO_2 and ZrO_2/NiO powders with NiO content: (2) 12, (3) 35·5 and (4) 65·5 mol%.

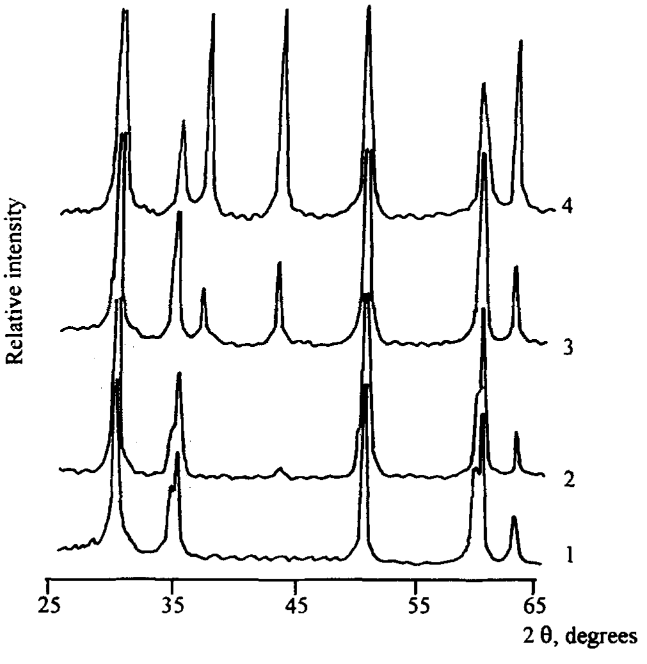

Fig. 7. XRD patterns of as-prepared (1) YSZ (2·8 mol%) and NiO/YSZ (2·8 mol%) powders with NiO content: (2) 8·2, (3) 35·5 and (4) 65·6 mol%.

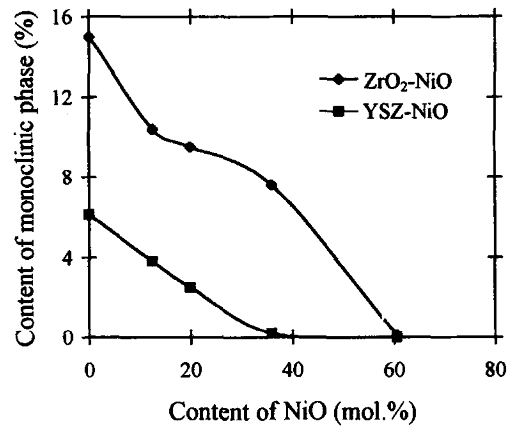

Fig. 8. Change of the fraction of monoclinic phase in NiO/ZrO_2 and NiO/YSZ (1·6 mol%) powders with NiO content.

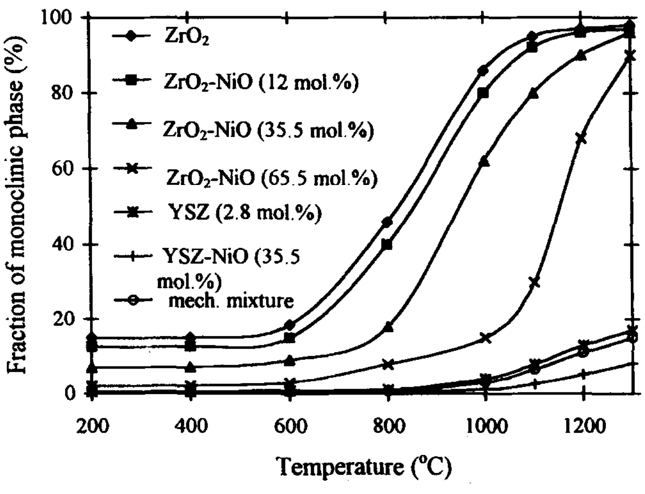

Fig. 9. Change of the fraction of monoclinic phase in ZrO_2, NiO/ZrO_2, YSZ (2·8 mol%), NiO (35·5 mol%)/YSZ (2·8 mol%) and mechanical mixture of nanosize YSZ (2·8 mol%) and NiO (35·5 mol%) with calcination temperature.

concentration in the plasma flame should reduce the size of ZrO_2 particles during synthesis of NiO/ZrO_2 composite powder at high content of NiO. According to the suggestion of 'size effect' on the tetragonal phase fraction this should increase the content of metastable tetragonal phase of ZrO_2, as has been established in plasma-prepared zirconia.[10] On the other hand it is well known that heat treatment at temperature about 550°C and recrystallization of fine ZrO_2 particles cause the transformation of metastable tetragonal phase to monoclinic.[11] However, in the NiO/ZrO_2 system nanosize particles are separated from each other by NiO particles or by a thin NiO layer on their surface, which should retard the grain growth of ZrO_2 which may contribute to the stabilization of the t-ZrO_2.

Heat treatment of NiO/YSZ samples causes t → m phase transformation at temperatures of 850–1000°C only for samples containing yttria and NiO less than 3 and 10 mol% respectively. The level of t → m phase transformation of plasma-prepared NiO/YSZ powder is lower than that for pure YSZ or a mechanical mixture of nanosize YSZ and NiO powders. This confirms that as-prepared NiO/YSZ composite powder is not a simple mechanical mixture of ZrO_2 and NiO, but there is mutual interaction between components, possibly due to deposition of NiO on the surface of ZrO_2 particles and increased solubility of NiO in YSZ. Together with Y_2O_3 the nickel oxide promotes formation of high temperature phases of ZrO_2 and suppresses the t → m transformation.

YSZ–NiO powders show characteristic high stability against stress-induced phase transformation even at low content of Y_2O_3. The fraction of monoclinic phase of ZrO_2 in pressed NiO/YSZ powders increases only if the content of yttria and NiO is less than 3 and 10 mol% respectively (Fig. 10). In all cases the fraction of monoclinic phase in pressed NiO/YSZ powders is less than that in a pressed mechanical mixture of YSZ and NiO or YSZ alone. This might imply that NiO promotes the formation of non-transformable t′-ZrO_2 at a low content of Y_2O_3.

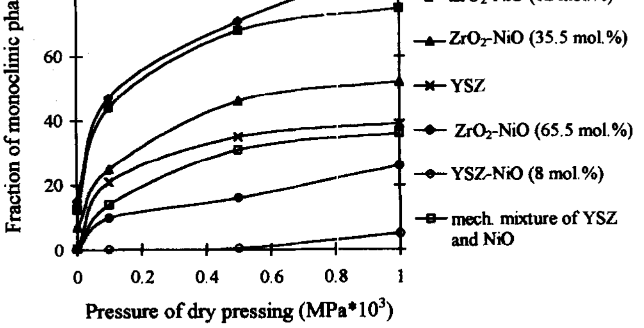

Fig. 10. Change of the fraction of monoclinic phase in ZrO_2, NiO/ZrO_2, YSZ (2·8 mol%), YSZ (2·8 mol%)/NiO and mechanical mixture of nanosize YSZ (2·8 mol%) and NiO (35·5 mol%) with pressure of dry pressing.

4 Conclusions

The thermal plasma technique could be extended successfully to producing nanosize NiO/ZrO_2 and NiO/YSZ powders with average particle size in the range of 16–55 nm and specific surface area of 15–35 $m^2\ g^{-1}$. The phase and granulometric composition of the powders produced depend on reagent concentration in the plasma flame and cooling rate, on the content of Y_2O_3 and NiO. In the NiO/ZrO_2 system, NiO increases fraction of metastable tetragonal phase of ZrO_2 but in the NiO/YSZ system promotes formation of non-transformable t′-phase and cubic ZrO_2.

Acknowledgment

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