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Abstract

Nickel-yttria stabilized zirconia (Ni-YSZ) cermet is widely used as an anode material for solid oxide fuel cells (SOFCs). While the nickel-to-nickel chain maintains the electrical conductivity path, the YSZ contributes to lowering the thermal expansion and inhibits nickel coarsening during high temperature (1000 °C) operation. An electroless technique is employed to prepare a uniform nickel coating on the YSZ powder. The process parameters for this technique are optimized. Notably, the cermet thus prepared shows percolation at a much lower nickel content (10–20 vol.%) compared with those reported in the literature.

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Short communication

Preparation of nickel coated YSZ powder for application as an anode for solid oxide fuel cells

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Abstract

Nickel-yttria stabilized zirconia (Ni-YSZ) cermet is widely used as an anode material for solid oxide fuel cells (SOFCs). While the nickel-to-nickel chain maintains the electrical conductivity path, the YSZ contributes to lowering the thermal expansion and inhibits nickel coarsening during high temperature (1000 °C) operation. An electroless technique is employed to prepare a uniform nickel coating on the YSZ powder. The process parameters for this technique are optimized. Notably, the cermet thus prepared shows percolation at a much lower nickel content (10–20 vol.%) compared with those reported in the literature.

Keywords: Electroless coating; Ni/YSZ cermet; Solid oxide fuel cell; Nickel coating

1. Introduction

The state-of-the-art anode material for solid oxide fuel cells (SOFCs) is nickel-yttria stabilized zirconia (Ni-YSZ) cermet [1–3]. The main function of the anode is to provide reaction sites for the electrochemical oxidation of the fuel during operation at 1000 °C. Hence, the anode material must be stable in a reducing environment, have sufficient electronic conductivity, have high catalytic activity, and should be chemically and thermally compatible with other cell components. It should also have sufficient porosity to allow the fuel to transport to the reaction sites. The purpose of YSZ addition in Ni-YSZ cermet is to reduce the thermal expansion of nickel (and thereby make it thermally compatible with the YSZ electrolyte) and inhibit coarsening of nickel during prolonged operation at high temperature [4–9]. As the thermal expansion co-efficient of nickel ($16.9 \times 10^{-6} \text{ K}^{-1}$) is much more than that of YSZ ($11.0 \times 10^{-6} \text{ K}^{-1}$), lowering the amount of nickel will give rise to a cermet with lower thermal expansion and thus it will be more compatible with the YSZ electrolyte. On the other hand, the conductivity cannot be compromised as this determines the current-carrying capacity of the anode material. Hence, an optimum nickel concentration has to be selected. It has been well established [3,4] that conductivity percolation within this cermet system

is attained at around 20–30 vol.% nickel via the formation of a continuous nickel-nickel chain, as determined by the preparation technique. The Ni-YSZ cermet is prepared by various techniques, e.g., mixed oxide route [4], co-precipitation route [10], slurry coating route [11], liquid dispersion route [12,13], and heat decomposable aqueous salt solution route [14]. Each technique has its own merits and demerits.

In this investigation, an attempt has been made to prepare a Ni-YSZ cermet with a lower nickel content (and hence lower thermal expansion) than conventional types without lowering the conductivity. This has been made possible by uniformly coating the surface of YSZ particles with metallic nickel via an electroless technique. It appears that the only reported work of electroless plating to prepare nickel coating on to YSZ has been that of Wen et al. [15], wherein particular emphasis was given to examining the coating morphology as a function of electroless coating bath temperature. It was found that the coating morphology could be tailored by altering the bath temperature. In the present investigation, a much simpler patented [16] electroless bath is employed. In addition, the coated particles have been sintered and their electrical conductivity has been studied to establish percolation at a relatively low Ni concentration.

2. Experimental

YSZ powder (8 mol%) (TZ-8Y, Tosoh Corporation, Japan) was sensitized and catalyzed with a Pd-Sn catalyst.

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The Pd-Sn hydrosol was formed by the reaction of solution of high purity stannous chloride (Qualigens, India,) and palladium chloride (E-mark, India) in a single-step process [17] as opposed to double-step sensitization and catalysation [15]. The single-step sensitization and catalysation process involved surface treatment of YSZ powder with a mixed solution (acidified with HCl) of $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$ and PdCl_2 , followed by ultrasonication for 2–5 min, and finally washing. Metallic nickel was then coated on the treated YSZ powder by the above-mentioned patented electroless process. Throughout the coating process, the YSZ powders were kept suspended within the plating bath by magnetic stirring. The amount of nickel deposited was estimated by a gravimetric method. Nickel concentration in the prepared cermet was varied in the range 5–60 vol.%. The phases present in the samples were characterized by X-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation (Phillips-PW 1730). Rectangular, bar-shaped samples of dimension 15 mm \times 3 mm \times 2 mm were prepared by uniaxial pressing of the powders under 225 MPa followed by sintering in the temperature range 1200–1350 °C for 2–4 h. The conductivities of pressed pellets (at room temperature) and the sintered pellets (at 1000 °C under $\text{H}_2 + \text{Ar}$ atmosphere) were measured by a four-probe dc technique using a 7.5-digit multi-meter (HP 3458A).

3. Results and discussion

In order to initiate electroless plating on insulating powder (YSZ, in our case) surfaces, it is necessary to activate the surface. In general, palladium metal is employed as a catalyst and the following two methods have primarily been used to deposit palladium particles on the insulator surface [17]: (i) the insulating surface is consecutively treated with acidified SnCl_2 and PdCl_2 solutions (known as two-step process); (ii) the treatment of insulating surface with a mixed acidic solution of SnCl_2 and PdCl_2 (known as single step process) in the form of a hydrosol. The original Pd-Sn hydrosol formulation consisted of 1 g PdCl_2 , 22 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 60 ml HCl to make 1 l of the solution [17]. The following sections discuss the effects of different processing parameters, such as palladium chloride concentration in the sensitization bath, YSZ particle concentration of the sensitization, as well as that in the electroless bath, and the time of deposition, on the deposition kinetics.

3.1. Effect of PdCl_2 concentration in sensitization bath

In order to study the effect of concentration of palladium chloride solution in the sensitization bath on Ni deposition, a fixed amount of YSZ powder (80 g l^{-1}) was treated in an aqueous sensitizing bath that consisted of stannous chloride (22 g l^{-1}) HCl (60 ml) with a varying concentration of palladium chloride (0.01–0.06 wt.%). The activated powder was then washed followed by electroless coating with nickel. The

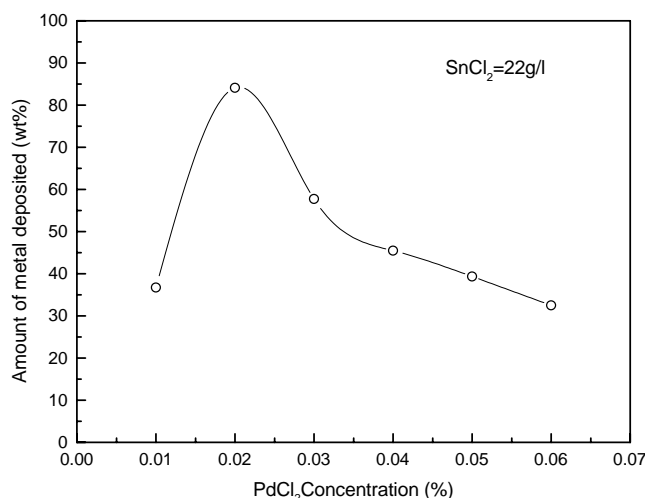
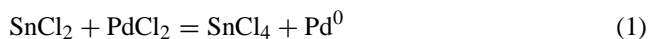


Fig. 1. Effect of PdCl_2 concentration on percentage nickel deposition during electroless coating. PdCl_2 concentration in sensitization bath is 22 g l^{-1} . YSZ concentration in sensitization bath and electroless bath is 80 and 8 g l^{-1} , respectively.

activated YSZ powder concentration in the electroless bath was maintained at 8 g l^{-1} . The deposition was carried out at 80 °C. The commencement of the reaction was indicated by the appearance of frothing in the bath from gas released during reduction of Ni^{2+} to Ni^0 . After 30 min of deposition, the nickel-coated powder was filtered, washed and dried at 80 °C for 24 h in an oven. The amount of nickel deposited in each case was calculated from the weight gain of the powder upon oxidation in air at 1000 °C for 1 h. The variation of wt.% of metal deposited as a function of PdCl_2 concentration in the sensitization bath is shown in Fig. 1. It is seen that the amount of metal deposited after 30 min of deposition is maximum at a PdCl_2 concentration of 0.02 wt.%. In the sensitization bath, SnCl_2 and PdCl_2 react with each other in an acidic medium and metallic Pd is formed [18,19] by the following reaction:



The metallic Pd is in colloidal form and is adsorbed on the YSZ surface. The adsorbed colloidal Pd particles act as catalyst for nickel deposition during subsequent electroless coating. The catalytic activity of the adsorbed Pd layer is strongly dependent on the relative sizes of the colloidal Pd particles and the core (YSZ) particles [17]. It is most likely that the particle size of the colloidal Pd increases with increasing concentration of PdCl_2 solution in the sensitization bath. The observed peak at 0.02 wt.% PdCl_2 may be due to the formation of colloidal Pd particles of optimum size that gives maximum adsorption on the YSZ particle surface.

3.2. Effect of YSZ concentration in sensitization bath on initialization time of reaction

Initialization time for deposition is defined as the time taken to start the reaction for metal deposition in the elec-

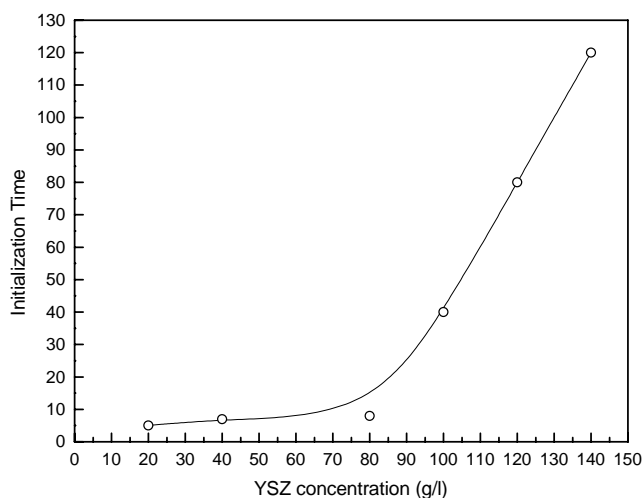


Fig. 2. Effect of YSZ concentration in sensitization bath on initialization time. Sensitization bath consists of PdCl_2 solution (0.02 wt.%) and SnCl_2 (22 g l^{-1}) YSZ concentration in electroless bath (8 g l^{-1}).

troless plating bath (indicated by froth formation and blackening of YSZ particles). The effect of YSZ power concentration in the sensitization bath on initialization time was studied in an optimized sensitization bath which contained 0.02 wt.% PdDl_2 . The YSZ particle concentration in the sensitization bath was varied in the range from 20 to 140 g l^{-1} . The activated YSZ particle concentration in the electroless bath was however, kept fixed at 8 g l^{-1} for each of the batches. The deposition was carried out at 80°C . The variation of initialization time with YSZ particle concentration in the sensitization bath is given in Fig. 2. The initialization time remains of the order of a few minutes with low YSZ concentration in the sensitization bath (up to 80 g l^{-1} in this case) but then increases sharply with further increase in YSZ concentration. The latter behavior may be due to an insufficient surface coverage by the colloidal Pd particles formed during sensitization.

3.3. Deposition behavior with time of deposition

In order to investigate the deposition behavior with respect to time, two series of batches with different YSZ loading in the electroless bath were prepared. The YSZ powders for each batch were treated in the sensitization bath under optimum conditions, as discussed in the previous sections. The amount of metallic nickel deposited as a function of time is shown in Fig. 3. The time reported in this plot refers to the time after initialization of reaction. It is clear that about 80% metal deposition takes place within the first 30 min for a YSZ concentration 16 g l^{-1} in the electroless bath; whereas the deposition is only 45% when the corresponding concentration is kept at 2 g l^{-1} .

Although, the deposition behavior is similar for different YSZ concentration in the electroless bath, the rate of deposition is found to be faster for higher YSZ concentration.

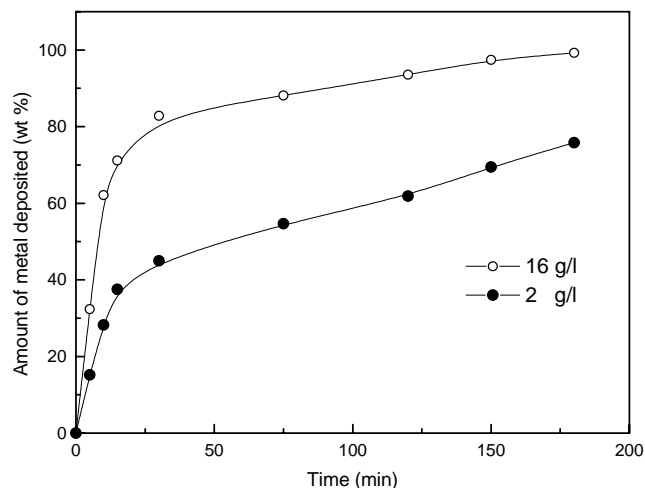


Fig. 3. Deposition behavior of electroless nickel as a function of time. Sensitized under conditions as mentioned in Fig. 2.

Thus, nearly 100% deposition is found to take place within about 3 h of deposition for a YSZ concentration of 16 g l^{-1} in the bath. During the same period of deposition, however, only 75% of the Ni is deposited when the YSZ concentration is 2 g l^{-1} in the electroless bath. It is also interesting to note from Fig. 3 that there is a slope change in the deposition curve for both cases. During the initial period of time (up to about 30 min), the deposition rate is quite high and beyond 30 min the deposition rate slows down for both the cases. Also, the rate of deposition during the initial period is higher with higher YSZ concentration in the bath. It can therefore be inferred that the deposition of metallic Ni on pre-treated YSZ powder is catalytic in nature. This is because, with increasing YSZ concentration in the electroless bath, more and more catalytically active sites (i.e., colloidal Pd deposited on YSZ during sensitization) are available for Ni deposition. This is indicative of a surface-controlled reaction arising from the catalytic nature of the sensitized YSZ powder. The change in slope after this time period indicates diffusion-controlled deposition behavior from the bulk of the solution.

3.4. Characteristics of Ni-coated YSZ powder

The XRD patterns of the YSZ powder before and after coating are presented in Fig. 4. These indicate that the coated powder contains a metallic nickel phase along with YSZ. No other traceable impurity phases are present. Electroless coating techniques [17–20] indicate that the nickel deposition is often associated with phosphorous, which causes formation of low-melting nickel phosphates during sintering. Phosphorous-free electroless nickel deposition has also been reported [21], but a boron-containing reducing agent introduces boron into the system. Due to the very nature of the electroless-plating bath used here, other impurity phases associated with conventional electroless nickel deposition can be eliminated.

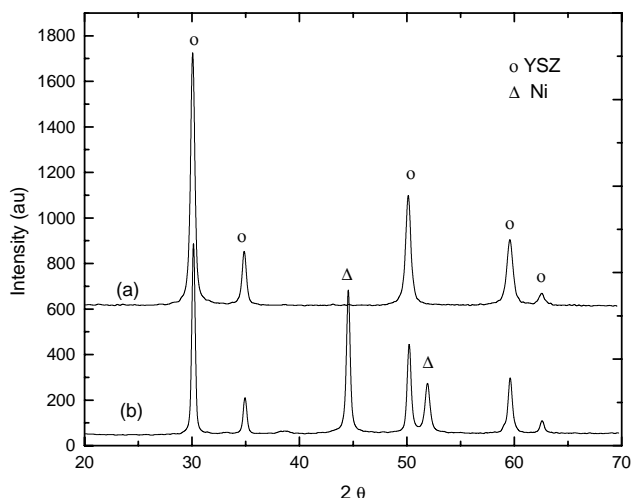


Fig. 4. XRD pattern of YSZ (top) and Ni-coated YSZ powder (bottom).

It is quite interesting to note that even the ‘as-pressed’ samples are electrically conducting. The electrical conductivity of the ‘as-pressed’ pellets at room temperature and the electrical conductivity of sintered samples measured at 1000 °C as a function of nickel concentration are shown in Fig. 5. A typical ‘S-shaped’ curve is obtained, as predicted by the percolation theory proposed for other composite materials [22]. It is very encouraging to note that the conductivity percolation threshold lies at a much lower nickel concentration (as low as 20 vol.%) compared with that (30–35 vol.%) reported by other investigators [4,23–25]. In the present study, however, the absolute conductivity value of the as-pressed samples measured at room temperature is lower than that of sintered samples measured at 1000 °C. This is because of the fact that these sample are very porous (>55% porosity), and the conductivity value decreases markedly, with porosity. The conductivity of sintered samples bearing a constant matrix porosity of around

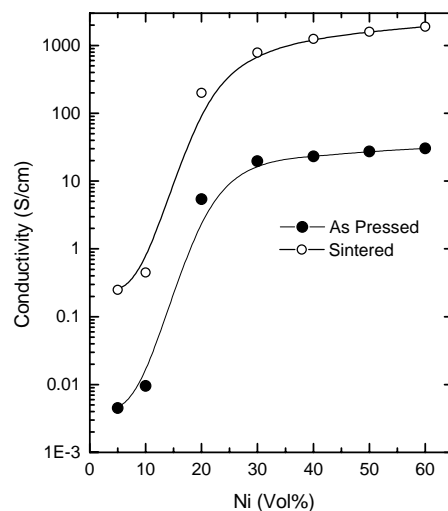


Fig. 5. Conductivity of Ni/YSZ Cermet at room temperature as function of nickel content.

35% is higher as its matrix density increases. Moreover, the room-temperature conductivity of the sintered samples after reduction under a $H_2 + Ar$ atmosphere is more than that reported at 1000 °C. The constant matrix porosity in the cermet has been obtained through sintering in the temperature range 1200–1350 °C for a sintering time that ranged from 2 to 4 h, the data in Fig. 5 also show that the conductivity percolation occurs at a concentration as low as 10–20 vol.% and the conductivity value (at 1000 °C) of the cermet containing only 20 vol.% Ni is as high as $200 S cm^{-1}$.

Optical microphotographs of polished surfaces of sintered cermets containing 10 and 20 vol.% Ni are presented in Fig. 6. The gray particles are YSZ and the white ring around these particles represents Ni. The formation of a nickel ring around the YSZ particles indicates the effectiveness of the coating process. From Fig. 6, it is also clear that for samples containing 10 vol.% of Ni, the Ni ring around the YSZ par-

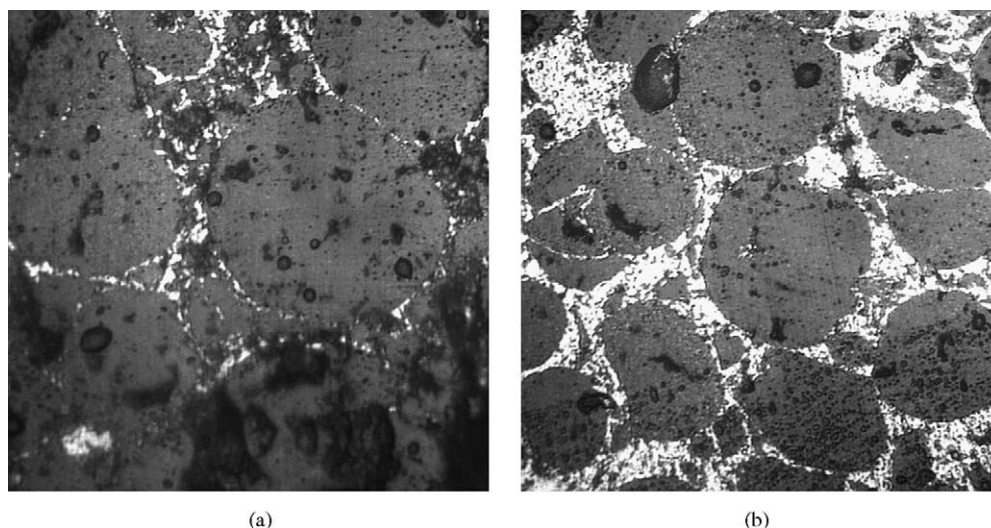


Fig. 6. Optical microphotographs of polished surfaces of 10 vol.% Ni (left) and 20 vol.% Ni (right). Magnification: 400 \times .

ticles is not in the form of a continuous network and, as a result, these cermetes have much lower conductivity (Fig. 5). On the other hand, the Ni ring around the YSZ particles becomes continuous and thicker when the Ni content increases to 20 vol.%. Therefore, samples containing 20 vol.% Ni shows metallic behavior with high conductivity.

4. Conclusion

1. Nickel coated YSZ powder can be produced by electroless technique without any impurity phase.
2. The amount of Ni deposited from a particular bath depends on several factors such as, PdCl₂ concentration in the sensitizer bath, YSZ concentration in the sensitizer as well as in the electroless bath, and time of deposition.
3. Depending on YSZ concentration (or more precisely, surface area) in the electroless bath, the kinetics of Ni deposition may be either surface reaction controlled or diffusion controlled from reactants from the bulk.
4. Even 'as-pressed' samples are electrically conducting and the conductivity percolation threshold is as low as 10–20 vol.% of Ni. This value is much lower than that (20–30 vol.% of Ni) for conventional Ni-YSZ cermetes. The conductivity value at 1000 °C of a sintered cermet containing only 20 vol.% of Ni is as high as 450 S cm⁻¹. Therefore, Ni-YSZ cermetes prepared by this technique should be better suited for SOFC anode applications than those prepared by conventional techniques.

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