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Short communication

Nickel-Zirconia cermet processing by mechanical alloying for solid oxide fuel cell anodes

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ABSTRACT

This paper describes the development of a process based on high energy milling (or mechanical alloying—MA) of metallic Ni and YSZ at 40 vol% Ni composition for the preparation of solid oxide fuel cell anode material. The cermet powder is consolidated using the surface activated sintering (SAS) method. The cermet pellets possess microstructural characteristics that can potentially lead to higher electrocatalytic activity and fuel reforming capability. In addition to the development of a new processing method for this purpose, a further differential of this work is the addition of Cu in partial substitution of Ni as a means to prevent the formation of carbon on its surface and, hence, the anode's degradation during service. The prepared powder samples are well dispersed and structured at the nanometric level, showing thin lamellar constituents. Suitable sintered pellets can be obtained from the powders with the required porosity and microstructure. The higher the energy delivered by MA the lower the initial sintering temperature. Activation energies are determined by stepwise isothermal dilatometry (SID) for Ni-YSZ and Ni/Cu-YSZ pellets, involving a 2-step sintering process. The Cu additive promotes sintering and leads to a refined microstructure.

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1. Introduction

The solid oxide fuel cell anodes developed to date have shown some limitations with regard to the use of different fuels and commercial applications. It is a well known fact that, besides the high activity for H_2-bearing fuel oxidation, the major challenge is to design fuel types derived from organic sources such as hydrocarbons and alcohols. In view of Brazil's energy matrix, there is much interest in ethanol and biogas fuels. However, these fuels reportedly cause anode catalyst poisoning by surface carbon deposition. Notwithstanding these technical questions, this paper reports on the development of a method to obtain cermet anode materials for SOFC based on mechanical alloying (MA) of metallic Ni and YSZ powders. A suitable cermet processing method is one of the most relevant factors to overcome the cost and lifetime-related limitations of SOFC cells.

The co-milling MA process of the constituent powders can produce the following effects [1]: (i) refinement of the material's structure, thereby increasing the 3-phase boundary site number, and (ii) increase of the powder's sinterability through the exposure of active surfaces during MA and sintering heat cycle. The surface activated sintering (SAS) method, which derives from the latter effect, is used to consolidate the material. The resulting cermets are expected to display microstructural characteristics that improve the electrocatalytic activity and the fuel reforming capability. The addition of Cu by partial replacement of Ni is also investigated as a means to mitigate carbon deposition on the Ni catalyst.

2. Materials and methods

The 40 vol% Ni(Cu)-YSZ cermet was prepared from 8 mol% yttria stabilized zirconia (8YSZ Tosoh Co., BET 13.2 $m^2\,g^{-1}$) and metallic Ni (99.6 mass% purity) with an average grain size of 29.3 μm. The purity of the Cu powder exceeded 99.9 mass% and it had an average particle size of 3 μm. The main samples were prepared by high energy milling in a shaker mill (SPEX 8000) at a rotation speed of 10 and 19 Hz for 1–16-h periods. Ultra-high molecular weight (UHMW) polyethylene and PTFE vials were used in a milling medium of 5 mm diameter tetragonal zirconia YTZ spheres. The powder-to-sphere mass ratio was 1:10. For purposes of comparison, two samples – 40 vol% Ni-YSZ and 55 vol% NiO-YSZ – were prepared by mixing and homogenizing the raw powders in alcohol slurries, and the former is referred to as homogenized cermet. The resulting powders were characterized by physical and chemical methods, and then subjected to uniaxial pressing at 100 MPa to produce pellets. Sintering was performed in a tubular furnace and a vertical TMA/dilatometer (Setaram Labsys TMA), applying

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a heating rate of 10 °C min^{-1} up to 1250–1300 °C and a 1-h dwell time, under air, argon and hydrogen atmospheres. The sintering kinetics was evaluated by stepwise isothermal dilatometry (SID) in the dilatometer under argon, with several 15-min isotherms programmed at 50 °C intervals during heating. The data was treated with the normalized volumetric shrinkage equations [2–4]:

$$\frac{dY}{dt} = nK(T)Y(1-Y)\left[\frac{(1-Y)}{Y}\right]^{1/n} \quad (1)$$

where: $Y = (L_0^3 - L_t^3)/(L_0^3 - L_f^3)$, L_i is the sample length (0, t, and f refer to initial, at time t and final times), K is a temperature function and n is a constant.

3. Results and discussion

The X-ray powder diffraction patterns of the 40 vol% Ni-YSZ samples after milling displayed broadening of the peaks, which increased with longer MA times and energy increases (Fig. 1(a)). Peak broadening is expected to reflect the high defect density caused by MA allied with particle and crystallite refinement, tending to an amorphous state. Due to the high impact the powder underwent during the process, it may have become contaminated. Milling in UHMW vials produced carbon pickup of 1.5 and 2.5 mass% after 2 and 8 h of MA processing at 19 Hz, respectively. The PTFE vials reduced this contamination to 0.7 mass% of carbon. Even so, an evaluation of the diffractograms in Fig. 1 reveals a shift in the Ni peaks, since C can become dissolved in the Ni lattice even at a low concentration. A previous study reported that Ni_3C compound can be formed after 8 h of MA at 19 Hz [1]. Fig. 1(a) compares diffractograms of Ni and YSZ raw materials and the sample compositions 40 vol% Ni-YSZ and 40%(Cu-Ni)-YSZ, in which half the volume of Ni was replaced by Cu. The addition of Cu caused a further shift of the Ni peaks. Because Cu peaks are located at slightly different 2θ degrees than Ni peaks, they can overlap at a broadened peak, thereby forming an alloy. Moreover, there was more carbon available for dissolution in Ni, since Ni was partially replaced by Cu, which repels carbon.

A scanning electron microscopy (SEM) analysis of 4-h MA powder samples revealed a typical lamellar morphology composed of alternating thin white and gray lines, which tended to become refined as the MA processing time increased (Fig. 2). After 8 h of processing, the lamellar structure was hardly visible. Fig. 3 shows transmission electron microscope (TEM) images indicating that the powder's ultimate particle size was in the nanometric range. The cermet was structured primarily as an embedded aggregation of elongated YSZ and Ni particles, with some spots containing nanoparticles of less than 5 nm.

The energy transferred to the materials by MA allowed for lower initial sintering temperatures, as indicated by the dilatometric experiments, and the behavior was independent of the type of atmosphere. Fig. 4 shows sintering curves for samples processed by MA for different lengths of time under air. Pure YSZ and NiO-YSZ samples are included, showing initial sintering temperatures of around 950 °C. However, the MA cermets initially displayed expansion caused by metal oxidation. It was found that

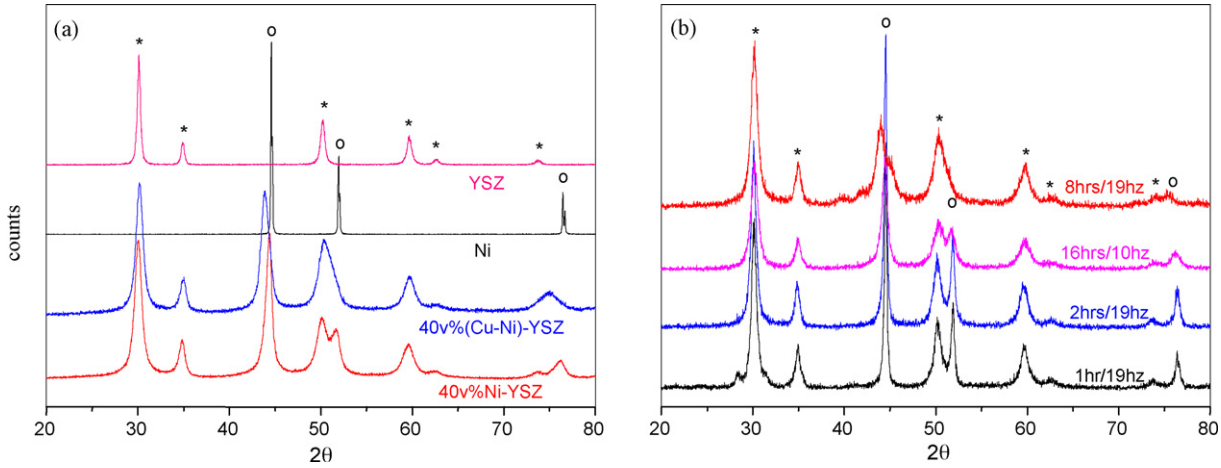

Fig. 1. X-ray diffraction profiles: (a) 40 vol% Ni-YSZ and 40 vol%(Cu-Ni)-YSZ processed by MA for 2 h; (b) 40 vol% Ni-YSZ powders processed by MA for different periods; (*) YSZ and (°) Ni.

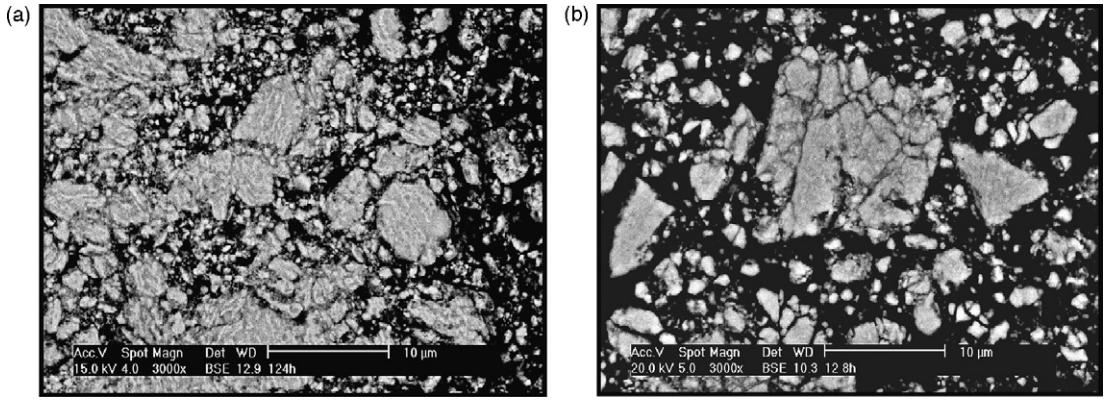

Fig. 2. SEM–BSE images of 40 vol% Ni-YSZ powders milled for 4 h (a) and 8 h (b).

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