Ni-YSZ SOFC Anode Processing by Mechanical Alloying and Sintering by Activated Surface

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Solid oxide fuel cell is an attractive technology for clean energy generation specially if biofuel feeding can be admitted. The actual challenge is to avoid catalyst poisoning by developing carbon tolerant anode materials. The work investigates copper alloyed Ni-YSZ to meet such requirements, processed by a new route - mechanical alloying MA - which allows the completely mixing and refining of the primary constituent powders. Once the material is obtained, the consolidation is carried out through the sintering by activated surface (SAS) method.

Introduction

Solid oxide fuel cell (SOFC) is an attractive technology for energy generation at high efficiency where biofuels are available owing to its flexibility. The anode, normally nickel-8mols%yttria-stabilized zirconia cermet (Ni-YSZ), is the key material in these devices once direct feed fuel can be achieved. Nevertheless carbon poisoned anode problem has to be overcome. The anode is most part prepared by mixing NiO and YSZ powders following by sintering under air where a second reduction step is needed to obtain metallic Ni (1-3). The present study employs new processing routes to obtain the cermet directly from YSZ and metallic Ni, allied to partially replacing Ni by Cu additive in order to improve the anode tolerance to biofuels. High energy milling (mechanical alloying – MA) is investigated as a method for cermet powder preparation while sintering by activated surface (SAS) is used for consolidation purpose. MA is expected to yield a projected microstructure consisting on intimate mixed components down to nanometric sizes, where the metallic constituents coat the ceramic thin particles. The aim is to increase 3-phase boundary site number, improving electrocatalytic activity and percolation paths. This technique also leads to powder surface activation before and during sintering heating cycle, therefore lowering sintering onset temperatures.

Experimental

Samples were prepared with composition of 40vol%Ni-YSZ using YSZ (8mols%Y_2O_3-ZrO_2, Tosoh Corp.), metallic Ni (CIRQ Cromato, 400 mesh, 99.6wt% purity) and 99.9+wt% Cu starting powders. In Cu-bearing cermets, Ni was replaced by 50%vol. MA was carried out at 2 vibratory mills of 19 and 10 Hz rotation speed during 1-16 hours into polytetrafluoroethylene (PTFE) and ultra high molecular weight polyethylene (UHMW PE) vials, using tetragonal 3mols%yttria-zirconia (YTZ) milling media 5mm diameter. The balls to powder mass ratio was 10:1. Alcoholic homogenized 55vol%NiO-YSZ and 40vol%Ni-YSZ samples were prepared for comparison purpose. The obtained powders were pressed uniaxially into pellets at 100MPa and sintered in tubular oven and at a vertical dilatometer/TMA (Setaram Labsys TMA) at 1300°C for 1

h. Air, hydrogen and argon atmospheres were used in this study. Powders and sintered pellets were analyzed by scanning electron microscope (SEM), transmission electron microscope (TEM) and X-ray diffraction (XRD). Sintering kinetics was investigated by the quasi-isothermal method SID (stepwise isothermal dilatometry) (4-6) at the dilatometer under argon, where several 15 min isotherms were imposed at every 50^{o}C. The data treatment employed the normalized volumetric shrinkage equation:

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

where: $Y = (L_o^3-L_t^3)/(L_o^3-L_f^3)$, L_i is the length, K is a function of temperature and n a constant. Thermal conductivity up to 800°C was measured by flash method at a diffusivimeter apparatus (7) using a 5000 joules visible light pulse and HgCdTe infrared sensor. Thermal quadrupole analytical method (8) was used to determine thermal diffusivity while the conductivity was derived by the product of diffusivity, density and heat capacity. The last values were withdrawn from literature (9,10).

Results and Discussion

Microstructure analyses of mechanical alloying (MA) processed powders have shown a typical lamellar structure when milled up to 4 hours, whereas the lamellae have been refined and a rather homogenized powder is obtained for longer milling times (Figure1). TEM analysis has shown the ultimate particle size is nanometric (Figure2). Measurements of d-spacing show Ni and YSZ domains that are intimated mixed in small areas, where high defect concentration is present.

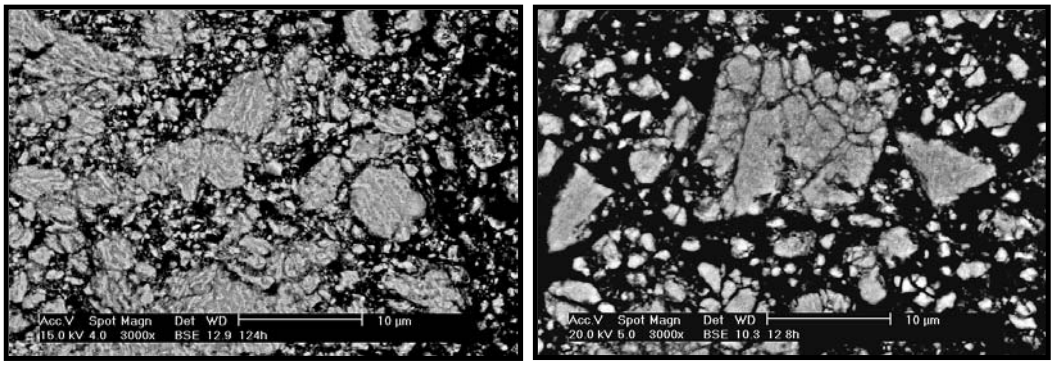


Figure 1. 40vol%Ni-YSZ high energy milled powders for 4 (left) and 8 hours (right) SEM - BSE.

Figure 3(a) shows the X-ray powder diffraction patterns for MA 40vol%Ni(Cu)-YSZ samples along with the constituent original profiles. The peaks broadening reflects the particle and crystallite refining as well as high defect density caused by MA. Due to high impact energy and wearing during the process, the powder can be contaminated with carbon up to 2.5 mass% when UHMW vial is used, however being reduced to 0.9 mass% for PTFE vial. Nevertheless, by evaluating the diffractograms at Figure 3, one can verify Ni peaks are shifted once C can be solved in Ni lattice, even at low concentration. Cu

addition has been found to further increase Ni peaks shifting. Since Cu peaks are absent after high energy co-milling of powders, the result indicates that a Ni-Cu alloy can be formed. Figure 3(b) demonstrates the peak shifting is higher when the MA processing time and energy increase.

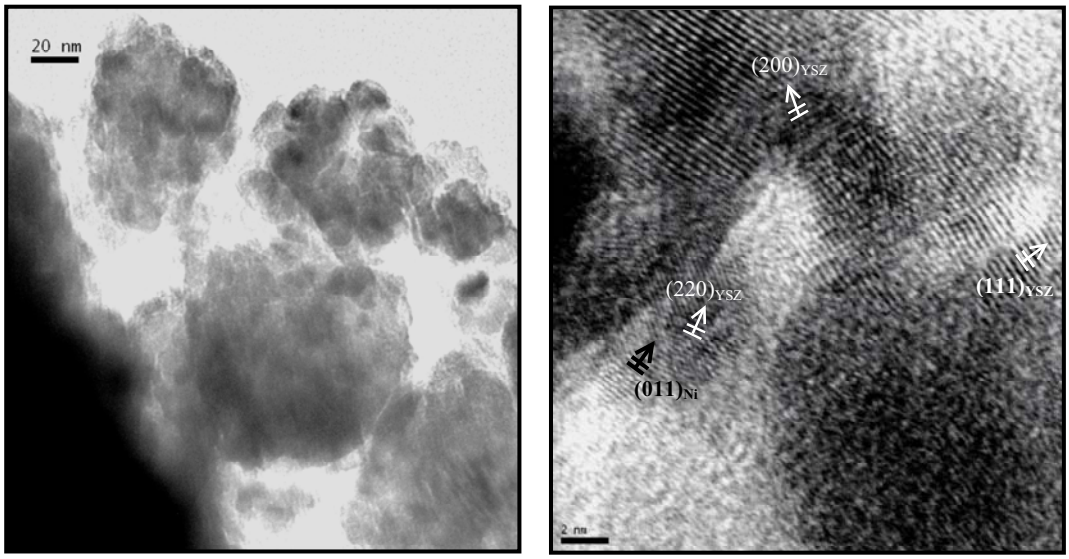
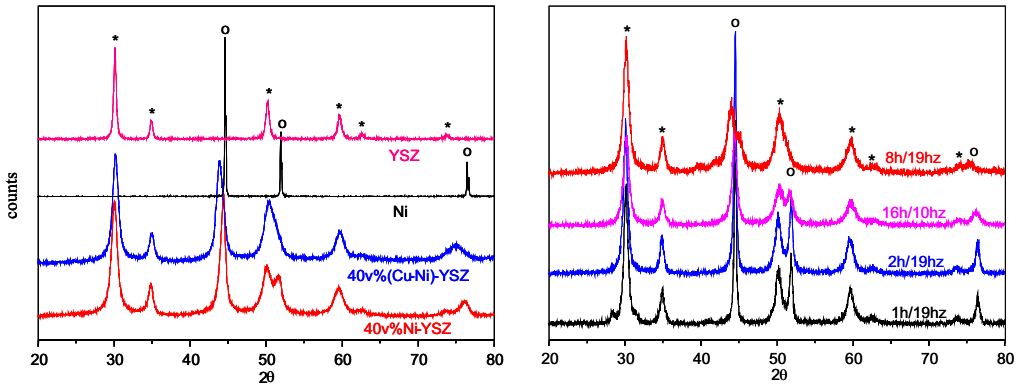


Figure 2. Powder TEM image; 2 hrs 19hz milled; ultimate particle size (left); phase domains (right).

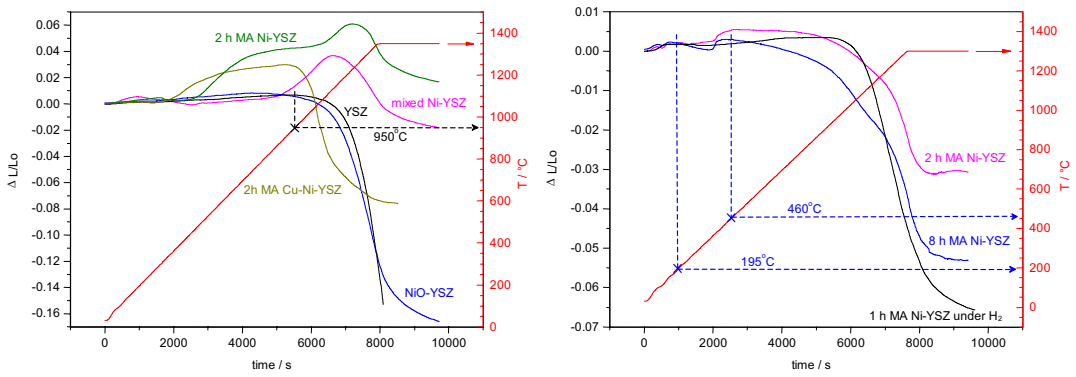


(a) (b)

Figure 3. X-ray diffractograms: (a) MA 40vol% Ni-YSZ e 40vol%(Cu-Ni)-YSZ; (b) MA 40vol%Ni-YSZ different times processed powders; *(YSZ), °(Ni).

Sintering experiments by dilatometry show smaller initial sintering temperature as the energy delivered to a powder increases through longer MA processing periods. In spite of the expansion caused by oxidation during sintering under air, the behavior is the same under all atmospheres studied. MA processed powder for 8 hours starts to sinter slowly

earlier at 195°C, followed by an expansion and resuming sintering at 460°C. Comparing to pure YSZ retraction onset temperature (950°C) and similar behavior for mixed (not milled) Ni-YSZ and NiO-YSZ, MA powders are much more active regarding the sintering process. Moreover, total densification is smaller for MA powders due to thin ceramic particles effect on inhibiting Ni sintering (11). Actually the sintering behavior is established by the balance among this effect and the activation of surfaces and defect structures of very thin and deformed Ni particles produced at milling, which tends to sinter at low temperatures (12,13).



(a) (b)

Figure 3. Sintering dilatometric curves under (a) air and (b) argon atmospheres (sample 1hr milled was sintered in pure H_2 up to 1350°C)

Copper addition increases the densification of MA powders, as can be also noted in sintering kinetics study. Figure 4 shows the treated data accordingly equation (1). From the Ahrrenius plots (Figure 5) the corresponding activation energy for sintering is derived by SID method. The Cu-bearing powder has significant smaller activation energy, indicating the additive promotes sintering. The lower melting point of Cu and the probable occurrence of liquid phase sintering process can explain the promotion effect. Based on the activation energy slopes the sintering mechanisms can be divided in 2 steps: metallic sintering at low temperature followed by YSZ sintering when the activation energy trend shows an increase. The slope changing point is evaluated at 750°C, meaning the ceramic densification is anticipated compared to pure YSZ or NiO-YSZ.

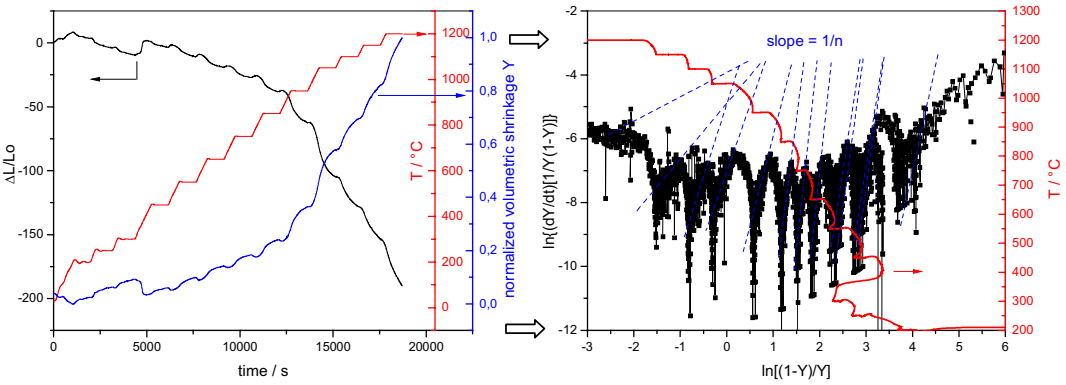


Figure 4. dilatometric data treatment accordingly SID kinetic method.

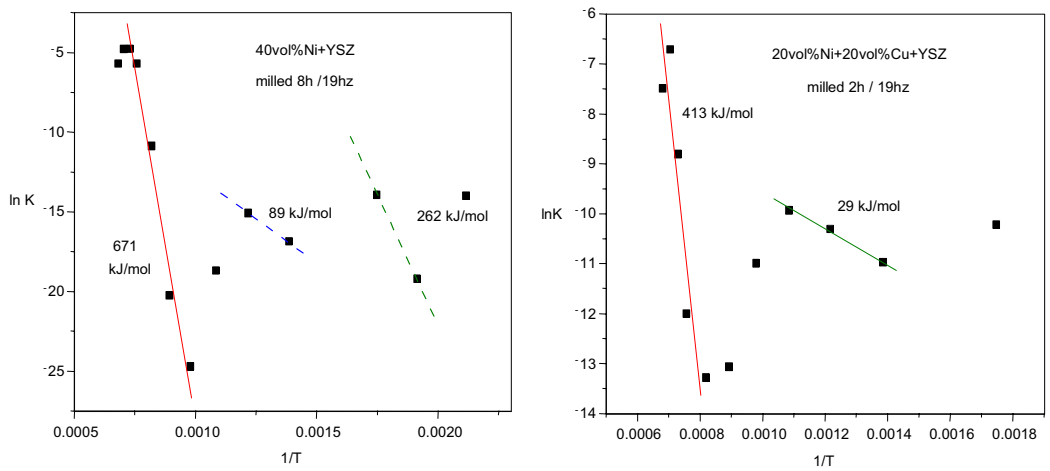


Figure 5. Arrhenius plots obtained by SID sintering kinetics method.

Sintered microstructures at 1300°C shown in Figure 6 demonstrate the MA processing effect on refining and dispersing the constituents. The higher density of Cu-Ni-YSZ material is clearly seen, in agreement with kinetics analysis. The Cu-bearing powder can therefore be sintered at lower temperatures or be tuned to the desired density. The addition of Cu to the cermet also leads to more refined microstructure, where the percolation paths can be recognized by the backscattered electron (BSE) image contrast. Thermal conductivity results measured by flash method are shown in Figure 7. The temperature dependence of this property is different with Cu additive. Both values approach to 3.5 W/mK at 800°C in accordance with some accepted ones (14,15).

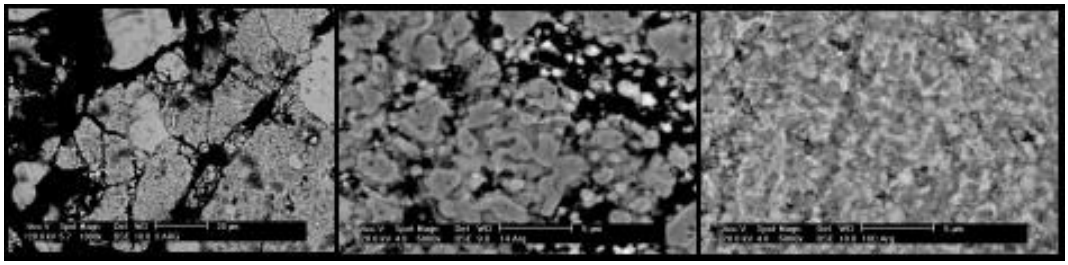


Figure 6. SEM BSE sintered microstructures: as mixed, Ni-YSZ and Cu-Ni-YSZ; white field is YSZ.

The novel MA-SAS combined method, presently investigated at a laboratory scale, can represent an alternative process for preparation of cermet anodes. The main advantages lie on the material homogeneity and refining, on the capability of microstructure and pore volume tuning, as well as on reducing the unit process steps by direct preparation of the cermet. These advances are expected to compensate the implementation of MA process, where better performance materials can be obtained.

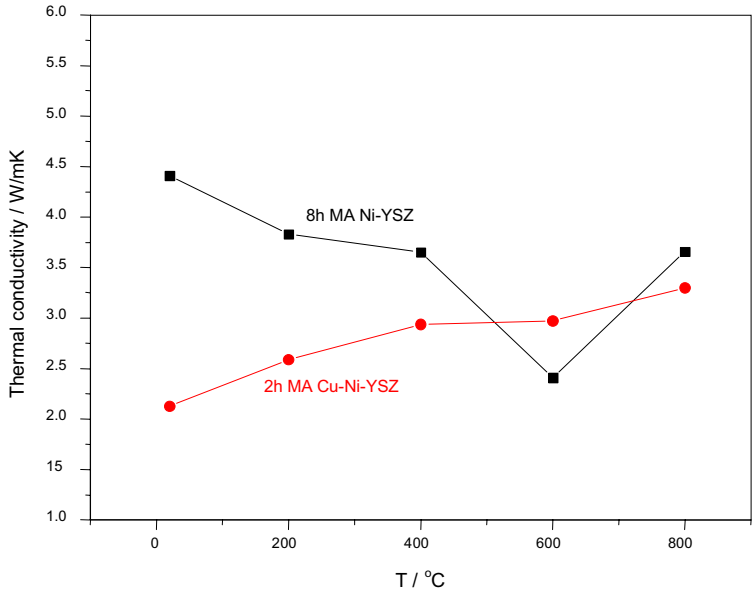


Figure 7. Thermal conductivity measured by flash method with thermal quadrupole approach.

Conclusions

Mechanical alloying process allied to SAS consolidation method is a promising route for SOFC anode preparation, leading to good dispersion and porosity distribution, where percolation paths are obtained. The addition of Cu promotes sintering and leads to the refining of the microstructure. The results are confirmed by conventional dilatometry and sintering kinetics evaluation.

Acknowledgments

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