

Effect of Ni₃Al Inclusion on Pore Structure in the Porous Anode for Molten Carbonate Fuel Cell

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(Received 27 September 1999 • accepted 25 July 2000)

Abstract—Microstructural changes in pure Ni, Ni/(4-10 wt%)Ni₃Al and Ni/5 wt%Ni₃Al/5 wt%Cr anodes for molten carbonate fuel cell were investigated by sintering experiment. Submicron-sized Ni₃Al intermetallic particles were dispersed in nickel powders to improve mechanical strength by dispersion strengthening and to control both densification and pore structure of these anodes during sintering. The mechanical strengths of Ni/7 wt%Ni₃Al and Ni/5 wt%Ni₃Al/5 wt%Cr anodes were considerably higher than that of the pure Ni anode by strong bonding between small nickel grains. Pore volume in the anodes which included Ni₃Al was considerably high by impeding nickel grain growth, because the retarding force exerted by the Ni₃Al inclusion obstructed the nickel grain boundary movement. Pore structure in the anodes was maintained in a relatively stable open network in contrast with that in the pure Ni anode.

Key words: Pore, Dispersion Strengthening, Ni₃Al, Anode, MCFC

INTRODUCTION

The Molten Carbonate Fuel Cell (MCFC) is a highly efficient and environmentally clean source of power generation that converts chemical energy into electrical energy. Nickel has been generally used as the porous anode material and shown to have good electrochemical activity with reasonably small polarization loss [Yuh et al., 1995]. But creep deformation of the anode occurs by the change in pore structure due to nickel grain growth at high temperature, and the creep results in an increase in internal resistance and decreases anode surface area [Watanabe, 1997].

To increase the creep resistance, nickel-based anodes sintered from Ni-Cr and Ni-Al alloy powders have been developed [Lim et al., 1999; Yuh et al., 1995]. Although these anodes have improved the creep problem to a certain degree, it is necessary to control the densification process and to obtain higher mechanical strength of the alternative porous MCFC anodes by dispersion of very fine-sized second phase particles which are more stable at elevated temperature. If not, densification and subsequent nickel grain growth result in collapse of the open pore network in the porous anodes.

In our previous works, we have manufactured submicron-sized Ni₃Al intermetallics by chemical synthesis in eutectic molten salt baths [Kim, 1997; Kim et al., 1999a], and studied the effect of Ni₃Al intermetallics on nickel grain growth inhibition for MCFC anodes [Kim et al., 1999b, c; Kim and Chun, 2000].

In this work, we investigate the microstructural changes of pure Ni, Ni/(4-10 wt%)Ni₃Al and Ni/5 wt%Ni₃Al/5 wt%Cr anodes, and suggest a suitable method for increasing the mechanical strength of the porous MCFC anode.

EXPERIMENTAL

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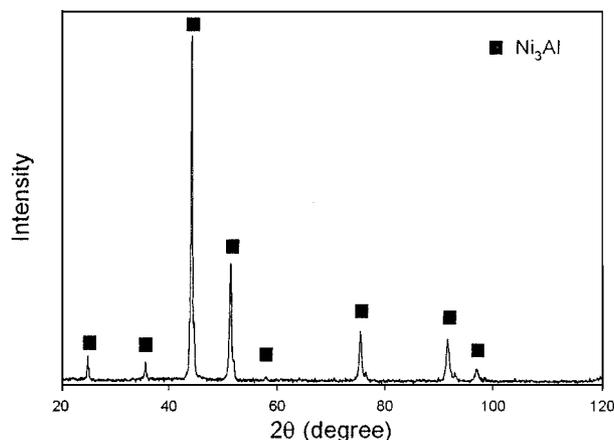


Fig. 1. XRD patterns of the Ni₃Al intermetallics produced in the eutectic molten salt bath of AlCl₃+NaCl (63 : 37 mol%) at 500 °C.

1. Preparation of Green Sheets

Fig. 1 shows the XRD patterns of the submicron-sized Ni₃Al intermetallics produced by reaction of anhydrous NiCl₂ and high purity Al powders in an eutectic molten salt bath of AlCl₃+NaCl (63 : 37 mol%) at 500 °C [Kim, 1997; Kim et al., 1999a].

Green sheets for MCFC anode were prepared by tape casting method using 55 to 70 wt% slurry which consisted of filamentary nickel powders (Inco #255) and the Ni₃Al intermetallics ranged from 4 to 10 wt%. Dispersant, binders and plasticizer were also added to the slurries to maintain adequate strength of the green sheets. The green sheets for pure Ni and Ni/5 wt%Ni₃Al/5 wt%Cr anode were also prepared by the same procedure.

2. Sintering

Sintering of all the green sheets was carried out in 20%H₂/N₂ mixed gas atmosphere in a tube type furnace at 800 °C to 1,000 °C for 1 to 10 hrs. The given sintering temperature was kept by a pro-

grammable controller. Average heating rates from 100 to 200 °C/hr were used to the desired sintering temperature for reliable grain growth.

3. Microstructural Measurements

The densities and porosities of these anodes after sintering were determined by Archimedes' principle, and their pore size distributions and differential pore volumes were investigated by mercury porosimetry (AutoporeII9215, Micrometrics). Axial shrinkage data were obtained from measurements by a caliper before and after sintering. Relative densities were defined by the ratio of actual sintered densities to theoretical ones. The fracture surfaces of the anodes were examined with a Scanning Electron Microscope (S-2700, Hitachi).

To obtain the mechanical strength of the anodes, tensile strengths of the MCFC anodes were measured by universal test machine (Instron UTM 4467). And electrochemical performances of the anodes were measured during unit cell (1×1 cm) test for 100 hrs.

RESULTS AND DISCUSSION

1. Densification

Fig. 2 shows the relative sintered density of various green sheets with respect to solid contents in slurry after sintering. Because contact area between nickel powders in green sheet is increased with increasing solid contents, the relative density of pure Ni anode is considerably increased compared with that of Ni/Ni₃Al anodes. The Ni/Ni₃Al anodes are sintered more slowly than pure Ni anode, while the pure Ni one is densified by vigorous mass transport between contacting nickel particles as sintering temperature is increased. It is thought that Ni₃Al intermetallics dispersed between nickel grains retard the nickel grain boundary movement and then subsequently obstruct densification [Kim et al., 1999b, c; German, 1994, 1996]. Hereafter the sintering experiments are carried out using green sheets which are fixed solid contents of the slurry to 65 wt% for reliable grain growth.

Axial shrinkage curves for the various MCFC anodes are shown in Fig. 3. These data are obtained from measuring the anode thickness before and after sintering. As amounts of Ni₃Al intermetallics

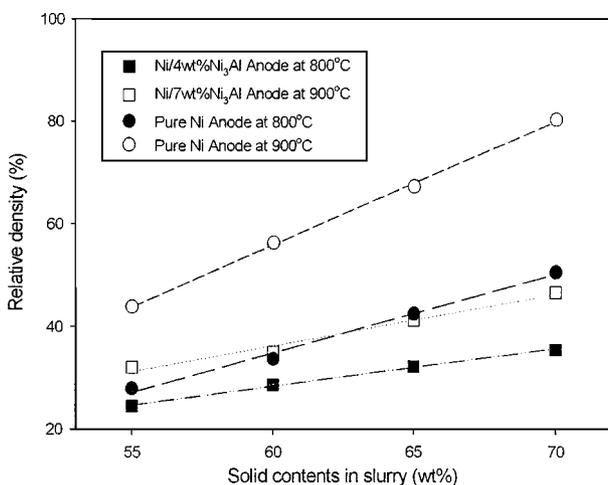


Fig. 2. The relative sintered density of porous MCFC anodes with varying solid contents in slurry.

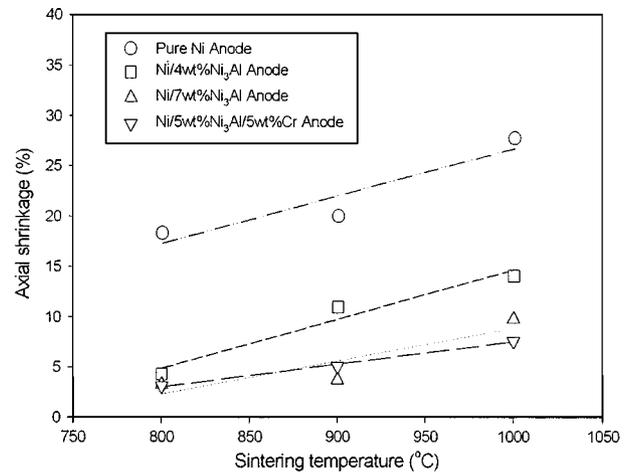


Fig. 3. Axial shrinkage curves for the sintered MCFC anodes (heating rate=100 °C/hr, sintering time=1 hr).

dispersed increase, the shrinkage decreases due to the pinning effect resulting from retarding force exerted by inclusion of second phase particle on the nickel grain boundary [Kim and Chun, 2000].

It is also shown that the shrinkage of Ni/5 wt%Ni₃Al/5 wt%Cr anode is similar to that of Ni/7 wt%Ni₃Al anode. This trend is probably caused not only by dispersion strengthening but also solid solution strengthening, and it is possible to analyze quantitatively by measuring mechanical properties, such as tensile strength.

Fig. 4 illustrates tensile strength and Young's modulus of the porous MCFC anodes measured by universal test machine (UTM). Mechanical strength of the Ni/Ni₃Al/5 wt%Ni₃Al/5 wt%Cr anode is considerably higher than that of the pure anodes by synergistic effect of dispersion strengthening and solid solution strengthening. To keep up their porosities to about 65%, sintering of these anodes is controlled within a temperature range from 600 °C to 900 °C by different mass transport mechanisms between nickel particles. The mechanical strength of Ni anode strengthened by Ni₃Al or Ni₃Al and Cr during tensile stress can be considerably increased due to

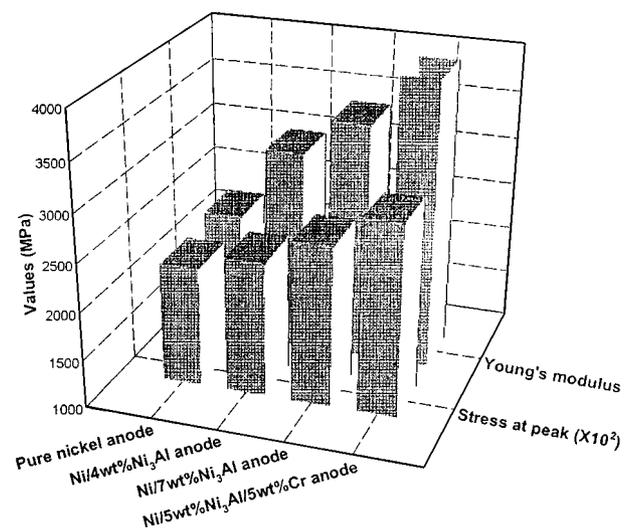


Fig. 4. Mechanical properties of the porous MCFC anodes measured by UTM.

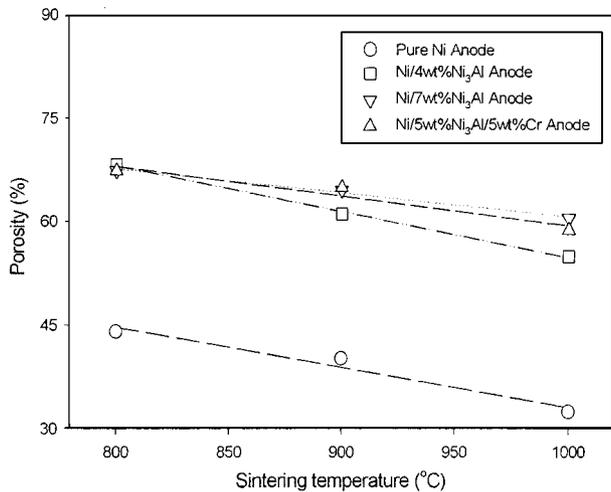


Fig. 5. Effect of sintering temperature on porosity of the sintered MCFC anodes (heating rate=100 °C/hr, sintering time=1 hr).

strong bonding between small nickel grains, while sintering makes progress at relatively lower sintering temperature by retarding rapid densification between the nickel particles in the case of the pure Ni anode [Kim et al., 1999b; McHugh et al., 1966]. It is thought that the higher mechanical strength of the porous anode results in higher creep resistance.

2. Microstructure of Porous MCFC Anodes

Fig. 5 shows the effect of sintering temperature on porosity of various sintered anodes. In contrast with the pure Ni anode which results in rapid change in the pore structure by reduction of surface area during sintering, porosities of the Ni/7 wt%Ni₃Al and Ni/5 wt%Ni₃Al/5 wt%Cr anodes obtained considerably higher values by the pinning effect on moving nickel grain boundary within sintering temperature ranges of this experiment. It is found that pores of these anodes can be maintained in a relatively stable open network structure regardless of increasing sintering temperature [Kim et al., 2000].

Figs. 6, 7 and 8 show the pore size distributions and differential

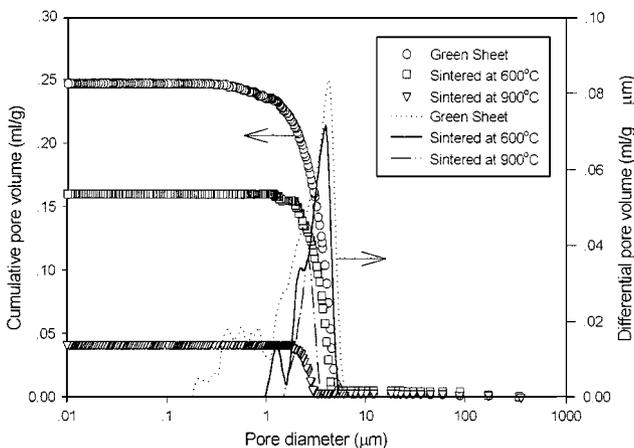


Fig. 6. Pore size distribution and differential pore volume for the pure Ni anode sintered at various temperatures (heating rate=100 °C/hr, sintering time=1 hr).

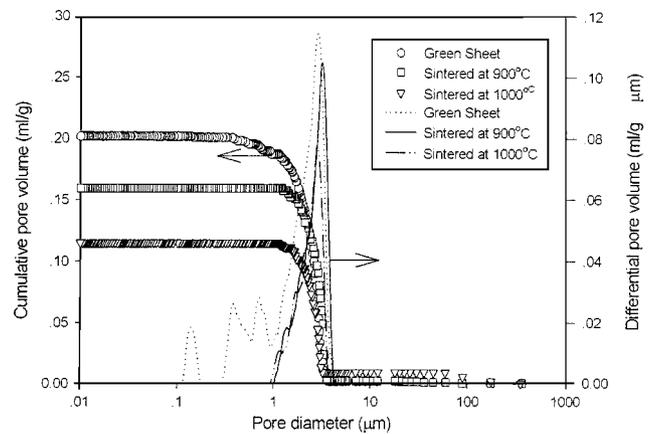


Fig. 7. Pore size distribution and differential pore volume for the Ni/7 wt%Ni₃Al anode sintered at various temperatures (heating rate=100 °C/hr, sintering time=1 hr).

pore volumes for the pure Ni, Ni/7 wt%Ni₃Al and Ni/5 wt%Ni₃Al/5 wt%Cr anodes, respectively. The most basic plot from a mercury intrusion analysis is pore diameter vs. the corresponding specific cumulative pore volume. Also differential pore volume represents a convenient means of reducing the cumulative pore curve to the distribution curve which gives the pore volume per unit pore diameter interval [Lowell and Shields, 1991; Webb et al., 1997]. In the pure Ni anode, the cumulative pore volume from green sheet to the anode sintered at 900 °C is rapidly reduced, and the differential pore volume becomes much more smaller when sintering temperature is increased, as shown in Fig. 6. On the other hand, the cumulative pore volumes and the differential pore volumes of Ni/7 wt%Ni₃Al and Ni/5 wt%Ni₃Al/5 wt%Cr anodes are maintained considerably higher than those of the pure Ni anode by impeding rapid densification with the Ni₃Al inclusion, as shown in Fig. 7 and Fig. 8. It is thought that pore structures in these anodes are stable open pore networks compatible with electrochemical reaction.

Fig. 9 shows the SEM photographs of the fracture surface for the pure Ni, Ni/7 wt%Ni₃Al and Ni/5 wt%Ni₃Al/5 wt%Cr anodes sintered at various temperatures with same porosity of about 65%, respectively. From the observation of the fracture surfaces, the pore

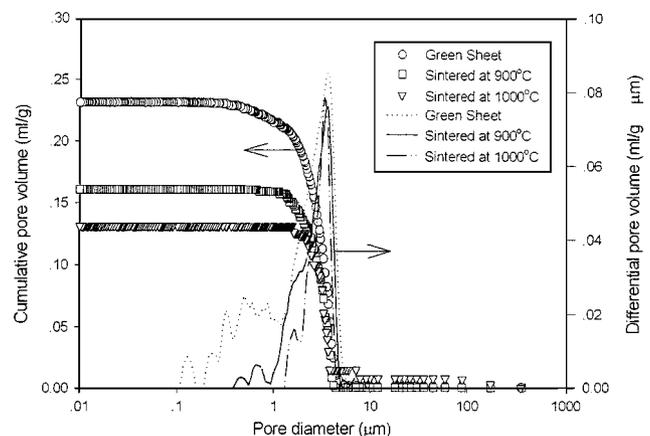


Fig. 8. Pore size distribution and differential pore volume for the Ni/5 wt%Ni₃Al/5 wt%Cr anode sintered at various temperatures (heating rate=100 °C/hr, sintering time=1 hr).

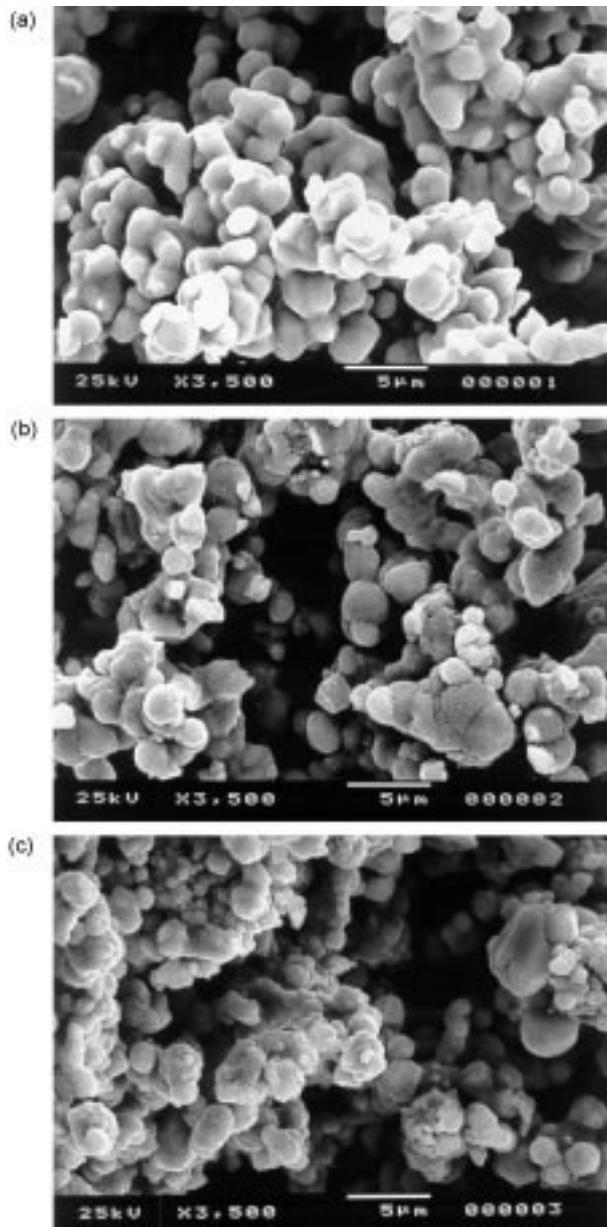


Fig. 9. SEM photographs of fracture surfaces of (a) the pure Ni anode sintered at 600 °C, (b) the Ni/7 wt%Ni₃Al anode sintered at 900 °C, and (c) the Ni/5 wt%Ni₃Al/5 wt%Cr anode sintered at 900 °C.

structures in the latter two anodes show no difference from that of the pure Ni anode poorly sintered at lower temperature. Although the porosities of these three anodes are almost the same, mass transport mechanisms between nickel particles of Ni-based anodes containing Ni₃Al are different from that of the pure Ni one, and it is possible to keep up a higher sintering temperature in the latter two cases [Kim et al., 1999a]. It is noted that the mechanical strengths of the Ni/7 wt%Ni₃Al and Ni/5 wt%Ni₃Al/5wt%Cr anodes sintered at relatively higher temperature can be improved by Ni₃Al inclusion, as shown in Fig. 4.

3. Electrochemical Performance

From microstructure analysis, the Ni/7 wt%Ni₃Al and Ni/5 wt%Ni₃Al/5 wt%Cr anodes are selected as alternative anodes for MCFC.

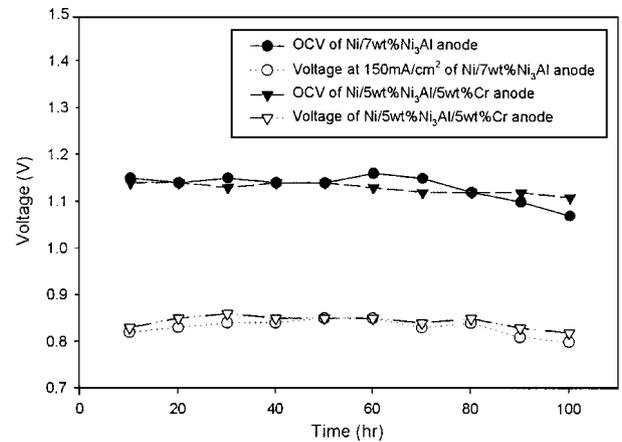


Fig. 10. The performance of unit cells of the porous MCFC anodes.

Fig. 10 shows the electrochemical performance of the anodes measured using a unit cell test for 100 hrs. High cell voltage over 0.84 V is obtained at current density of 150 mA/cm² in the case of the anodes. Considering that the electrochemical reaction actually occurs by three-phase contact area in micro-pores of the anode, it is thought that porous anode strengthened by Ni₃Al inclusion has the advantage of controlling relatively stabler and smaller pore size distributions than the pure Ni anode.

CONCLUSION

Pore structures of pure Ni, Ni/(4-10)wt%Ni₃Al and Ni/5 wt%Ni₃Al/5 wt%Cr for MCFC anodes were investigated by sintering experiment. The porous Ni-based anode strengthened by second phase particles, such as Ni₃Al intermetallics, maintained stable open pore network by controlling the nickel grain size and pore volume due to the retarding force of the Ni₃Al on nickel grain boundary movement during sintering. The mechanical strengths of these anodes were improved considerably more than that of the pure Ni by strong bonding between small nickel grains. In addition, the pore structures of Ni/7 wt%Ni₃Al and Ni/5 wt%Ni₃Al/5 wt%Cr anodes were well-developed to be suitable for electrochemical reaction.

ACKNOWLEDGEMENT

This work was supported in part by grant No. 981-1106-031-2 from the Basic Research Program of the Korea Science and Engineering Foundation.

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