Sintering characteristics of a porous Ni/Ni_3Al anode for molten carbonate fuel cells

Yun-Sung Kim, Hai-Soo Chun [*]

Department of Chemical Engineering, Korea University, Seoul 136-701, South Korea

Abstract

Studies of sintering behaviour and microstructural pore evolution during sintering of pure Ni particle — and $Ni/(4–10\ wt.\%)Ni_3Al$ intermetallics — green sheets for the molten carbonate fuel cell (MCFC) anode are conducted. The pore structure in the Ni/Ni_3Al anode can be maintained as an open pore network by restraining the initial stage of sintering. Ni_3Al intermetallics inserted on nickel grain boundaries act as a barrier, which inhibits nickel grain boundary diffusion and controls both densification and nickel grain growth. Pores in the pure nickel anode become smaller than those in the Ni/Ni_3Al anode by an intermediate stage of sintering which results in densification and nickel grain growth. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: MCFC; Anode; Ni_3Al intermetallics; Sintering; Grain boundary

1. Introduction

The molten carbonate fuel cell (MCFC) is a most promising energy conversion device that converts chemical energy into electrical energy. It is a highly efficient and environmentally clean source of power generation.

Porous anode materials, important basic elements used in MCFCs, must have good electrical conductivity, good catalytic activity, and adequate creep resistance and sintering resistance in molten carbonate electrolyte at elevated temperature [1]. Porous nickel is the most widely used and has relatively acceptable physical properties, but suffers from high creep deformation due to the change of pore structure in the anode by nickel grain growth and sintering during MCFC operation.

To increase creep resistance and then to maintain a pertinent pore structure in the anode, many researchers have developed new materials. To date, Ni–Cr, Ni–Cu, Ni–Cu–Al and Ni–Al alloys, which include Ni–MgO, Ni–Al solid solution, or Ni–Al intermetallics, have been considered as possible alternative anodes [1,2]. Although

these have improved the creep resistance to a certain degree, the pore structure in the anodes is changed by densification and subsequent nickel grain growth during long-term operation. One of the most important factors to be considered in the development of an alternative anode is the cost reduction that can be achieved by using low-cost materials, reducing the quantity of materials used, and improving manufacturing methods [1]. From this point of view, it is thought that the most reliable way to increase both creep resistance and sintering resistance is to include fine Ni–Al intermetallics as second-phase particles in the porous nickel anode. This is because the mechanical strength of the sintered anode must be inevitably influenced by nickel grain size, which can be controlled by the intermetallics inserted between the nickel particles [3].

In our previous work, we have manufactured sub-micron grade Ni–Al intermetallics by chemical synthesis in eutectic salts [4] or by the pack aluminization method [5], and have investigated their applicability in a porous Ni anode mixed with Ni_3Al. This anode has relatively higher structural stability and strength compared with other crystallographic Ni–Al intermetallics [6,7].

In this study, an analysis is made of the sintering behaviour and changes in the pore microstructure in a Ni/Ni_3Al and a pure nickel anode during sintering. It is shown that the densification and the nickel grain size of

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[*] Corresponding author. Tel.: +82-02-3290-3292; fax: +82-02-926-6102; E-mail: hschun@kuccnx.korea.ac.kr

the anodes are affected by the inclusion of the Ni_3Al intermetallics.

2. Experimental

Sub-micron grade Ni_3Al intermetallics were manufactured by chemical synthesis of anhydrous $NiCl_2$ (Wako) and Al powder (High Purity Chemical) in $(K + Na)Cl$ eutectic salts at 700°C [4]. The green sheets for MCFC anodes, which were mixed filamentary nickel (Inco #225) with 4 to 10 wt.% Ni_3Al intermetallics or with no intermetallics, were prepared by the tape-casting method. The slurry fed to the tape casting machine consists of solid (55–70 wt.%), dispersant, binders and plasticizer.

All the green sheets were pressureless-sintered in a 20% H_2/N_2 mixed gas atmosphere in a tube-type furnace with a programmable controller. The green sheets were sintered at 600°C to 1000°C for 1 to 10 h for reliable grain growth.

The sintered densities of the porous MCFC anodes were determined by the Archimedes' principle and their pore-size distributions were obtained by mercury porosimetry (Micrometrics Autopore II 9215). The fracture surfaces of these anodes were examined by means of scanning electron microscopy (Hitachi S-2700). The average grain size in the anodes was determined by the intercept method from the measured lengths of random straight lines drawn directly on the electron micrographs.

3. Results and discussion

The relative sintered density of porous MCFC anodes with varying solid contents in slurry at various sintering temperatures is shown in Fig. 1. The relative sintered densities of pure-nickel anodes tend to increase rapidly as solid contents in slurry fed to the tape-casting machine are increased, but the slopes of the relative density of Ni/7 wt.% Ni_3Al anodes are considerably lower than that of the pure material. When the solid contents in the slurry are increased, the porosity of the green sheet is decreased and, generally, a dense green sheet is obtained by the increasing particle compactness. With increase in the sintering temperature, many grain boundaries form between the contacting nickel particles in the pure-nickel anode, and then the grain boundaries grow by vigorous mass transport paths. Thus, the pore structure in the pure anode is abruptly changed by densification due to grain boundary diffusion and by nickel grain growth through grain boundary movement during sintering [6]. On the other hand, the relative sintered density of the Ni/Ni_3Al anode is lower than that of the pure anode regardless of increasing solid content. In our previous studies [6,8], we have obtained a grain-growth
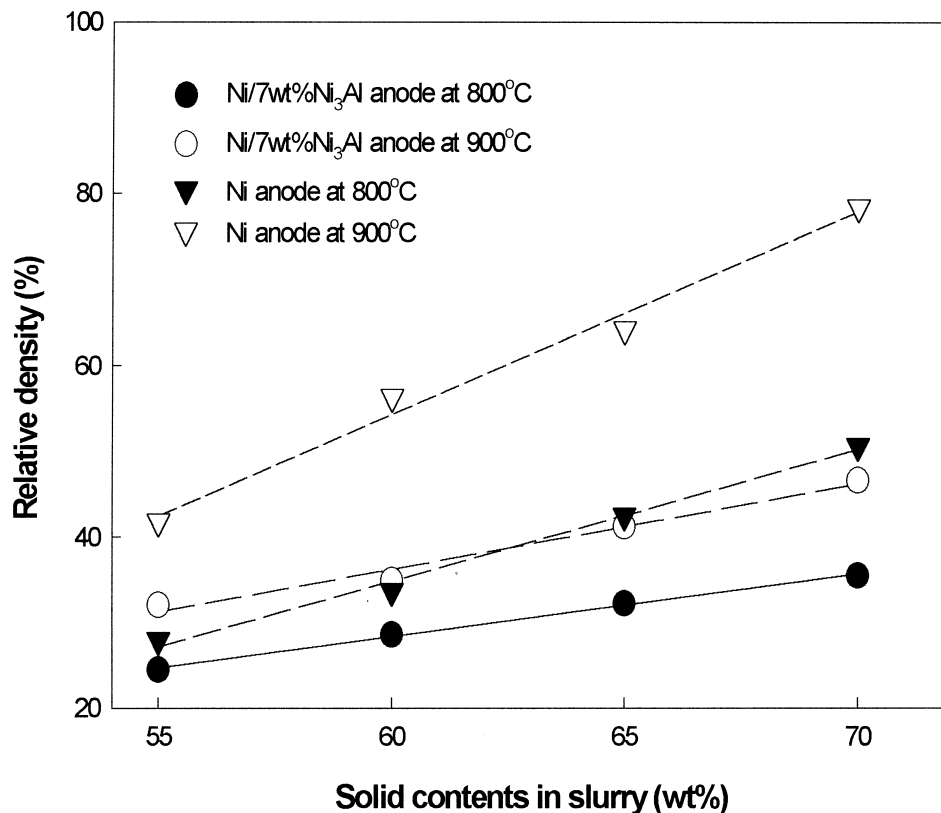

Fig. 1. The relative sintered density of porous MCFC anodes with varying solid contents in slurry.

exponent of 4.0 in the equation for grain-growth kinetics [6,8], and it is consistent with dominant mass transport by surface diffusion [8–10]. It is obvious that Ni_3Al intermetallics obstruct grain boundary diffusion, and surface diffusion acting on surfaces of contacting particles is the dominant diffusion process. It is predicted that Ni/Ni_3Al anodes maintain a considerably stable open pore network compared with the pure anode which is shrunk by densification during sintering.

The effect of Ni_3Al intermetallics on the porosity of sintered MCFC anodes is shown in Fig. 2. As the Ni_3Al content is increased, the porosity of the anodes appears to increase. It is known that the porosity is maintained over 50% in the case of Ni_3Al dispersion. In general, the required porosity for a MCFC anode is between 50% and 70% [11].

Increasing sintering temperature leads to fast densification through various mass transport paths during sintering (see Fig. 3).

From a thermodynamic point of view, sintering of green sheet for a MCFC anode is a thermally activated process during which the total interfacial free energy of the nickel particles in the equilibrium chemical composition of the anode decreases. In the anode, the total decrease in the solid–vapour interfacial energy is larger than the total increase in the solid–solid interfacial energy. These energy changes occur via various mass transport mechanisms. Therefore, the driving force for the sintering process is the reduction in the total interfacial energy of the system [9,10].

The nickel grain boundary area in the pure nickel anode increases by grain boundary diffusion which is the controlling step of densification during sintering. Then, the grains must grow to decrease the grain boundary area which has a higher energy than atoms in the nickel particle. Consequently, porosity of the anode is rapidly decreased and the pores become smaller.

In the case of Ni/Ni_3Al anodes, it is thought that grain boundary diffusion is obstructed by a pinning effect which is due to a retarding force acting on the moving nickel grain boundary, as proposed by Zener and Smith [12–14], and porosity of the anodes can be maintained at a higher value regardless of increasing temperature.

The pore-size distribution of porous Ni/Ni_3Al anodes sintered at 900°C is shown in Fig. 4. The greater the Ni_3Al inclusion at the nickel grain boundary, the higher the cumulative pore volume in the sintered anode. It is suggested that the pore-size distribution in the Ni/Ni_3Al anodes is adequately maintained in the range 3 to 6 μm which is suitable for the electrochemical reaction in MCFC operation.

The pore-size distribution of various green sheets and sintered anodes is shown in Fig. 5. In the case of the pure-nickel anode, the increasing sintering temperature causes the pore volume to decrease during sintering. But the difference in the pore size of Ni/7 wt.% Ni_3Al green

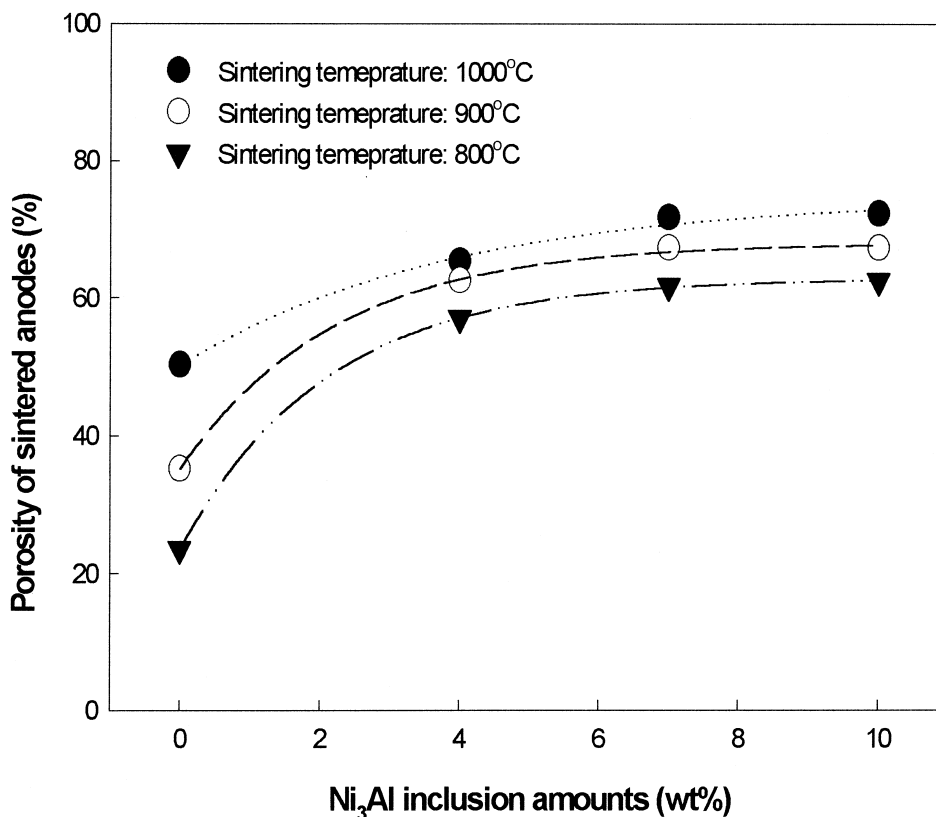

Fig. 2. Effect of Ni_3Al on the porosity of porous MCFC anodes (sintering rate: 100°C/h, sintering time: 1 h).
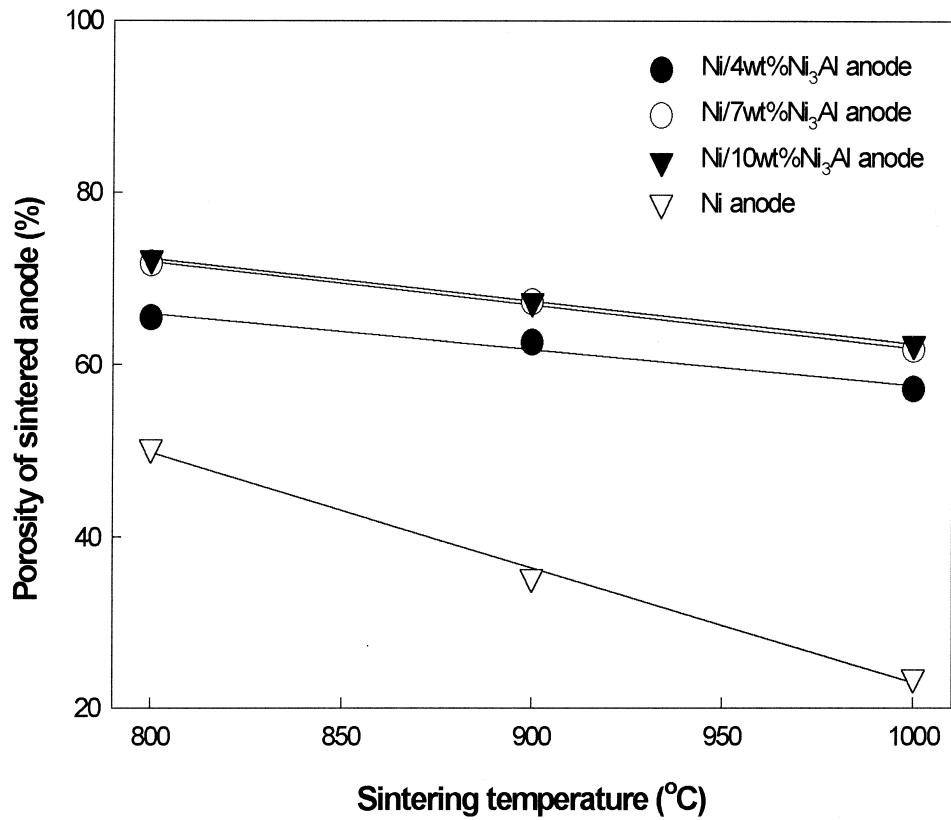
Fig. 3. Effect of sintering temperature on the porosity of various anodes (sintering rate: 100°C/h, sintering time: 1 h).
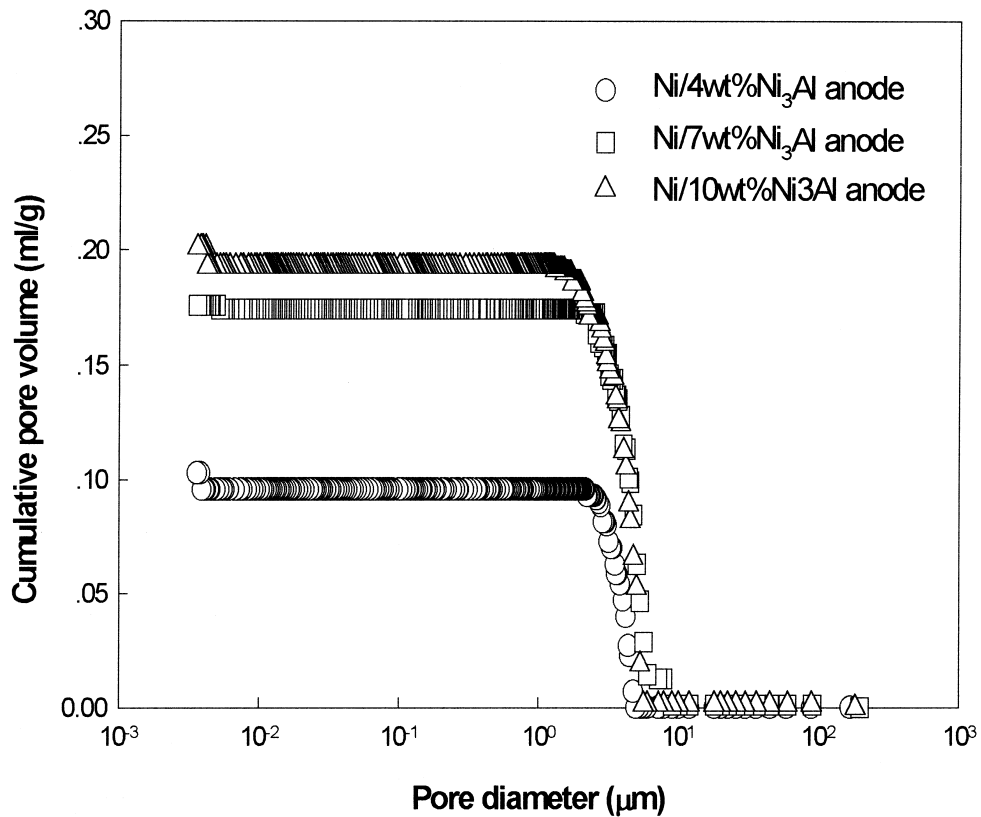

Fig. 4. Pore size distribution of various porous Ni/Ni$_3$Al anodes (sintering temperature: 900°C, sintering rate: 150°C/h, sintering time: 1 h).
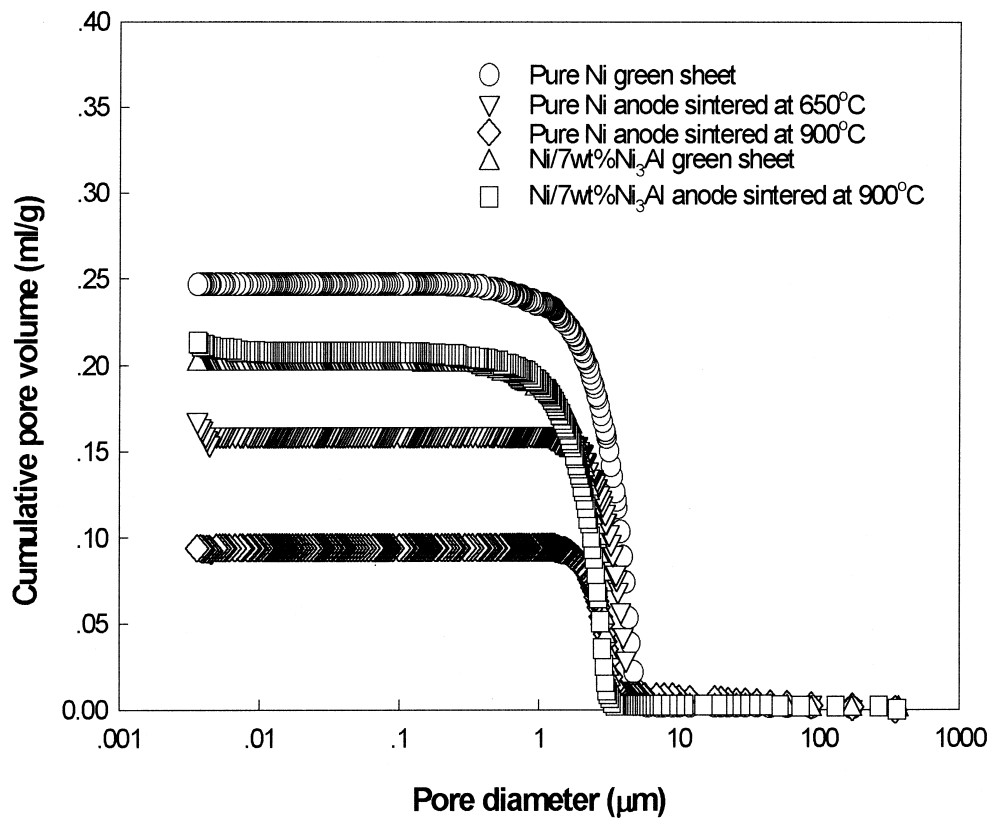
Fig. 5. Pore size distribution of various green sheets and their sintered anodes (sintering rate: 100°C/h, sintering time: 1 h).
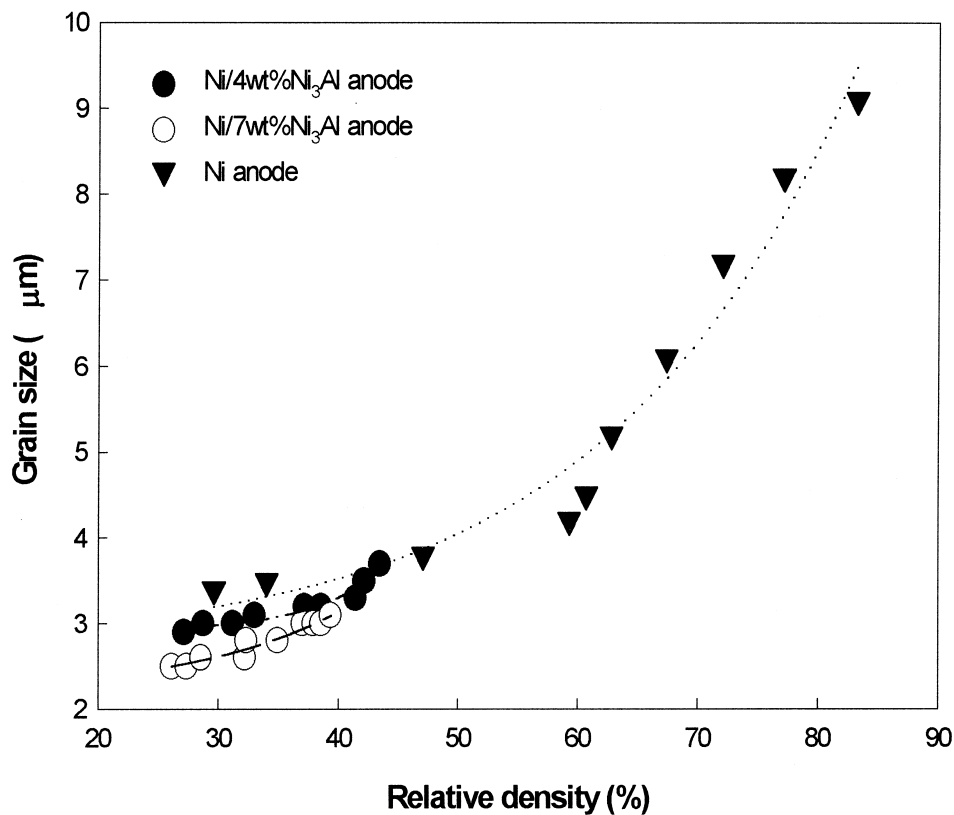

Fig. 6. Relation of the nickel grain size and relative density of various sintered anodes.

sheet and its anode sintered at 900°C is negligible due to nickel grain growth being retarded by Ni_3Al dispersed on the nickel grain boundary.

Although the pure-nickel green sheet has a higher pore volume compared with that of the Ni/7 wt.% Ni_3Al counterpart, it is found that the pore volume in the latter anode is higher and more stable after sintering.

To increase the mechanical strength of the porous MCFC anode, which is important for enhancing both creep and sintering resistance, it is necessary to obstruct rapid densification and grain growth during sintering and to maintain an open pore network in the anode. While it is possible to control densification by decreasing the sintering temperature, the mechanical strength of the anode is weakened considerably and the pore-size distribution may broaden and develop macropores. Such a development is illustrated by unstable neck growth due to poor mass transport in the vicinity of the necks formed between contacting nickel particles. Unfortunately, abnormal nickel grain growth may also occur via rapid mass transport if the sintering temperature is increased to enhance the mechanical strength. Then, the pore network in the anode is closed between the growing nickel grains, the pores disappear and the theoretical density is reached.

In summary, one of the most promising methods to maintain the mechanical strength of the porous anode is to control nickel grain size and its neck growth by Ni_3Al inclusion with intermetallics which have relatively high structural stability at elevated temperature.

According to solid-state sintering theory [8–10], the initial and the intermediate stages of sintering are characterized by the presence of a continuous open pore network. In the initial stage, there is no change in the pore network and no grain growth, while in the intermediate there is a decrease in pore size and grain growth. Grain growth also generally continues with heating after the density reaches the theoretical value [15].

The relation between nickel grain size and relative density is shown in Fig. 6 for anodes sintered at various temperatures, times and heating rates. Up to some critical relative density, the grain size in the pure nickel anode is relatively constant and about 3.3 μm. Densification up to this point corresponds to the initial stage of sintering. Above the critical relative density, which is approximately 40%, the grain size is rapidly increased. This is the intermediate stage of sintering. Nickel grain growth occurs at the end of the initial stage of sintering by increasing grain boundary area.

In the case of Ni/Ni_3Al anodes with 4 to 7 wt.% Ni_3Al, the mass transport of nickel is restricted to surface diffusion due to the pinning effect of Ni_3Al on the grain boundary movement. The grain sizes are essentially lower and more constant than those in the pure anode during the initial stage of sintering.

Electron micrographs of typical fracture surfaces in MCFC anodes after sintering at 900°C are presented in Fig. 7. In spite of sintering at a relatively low temperature, it is found that pore network in the pure anode has mostly collapsed under the action of nickel grain growth. The pore network in the Ni/4 wt.% Ni_3Al anode is well-developed. By inserting Ni_3Al between the nickel grain boundaries, the pore network is appropriately maintained. Moreover, the grain size is small and almost uniform because Ni_3Al retards grain boundary movement during sintering. It is also thought that if the mechanical strength is enhanced by increasing the contact area between the small nickel grains, then the creep resistance can be increased by impeding particle rearrangement and plastic deformation in the anode when uniaxial loads are applied [16].

For the Ni/Ni_3Al anode, from an analysis of the relationship between grain size and microstructure, it is found that no closed pores are formed and densification can be restricted to the initial stage of sintering. Also, nickel grain growth is retarded by the pinning effect.

But in the case of the pure-nickel anode, almost all pores become smaller and nickel grain growth implies the onset of the intermediate stage of sintering. Nevertheless, continuous open pores are still present (Fig. 7).
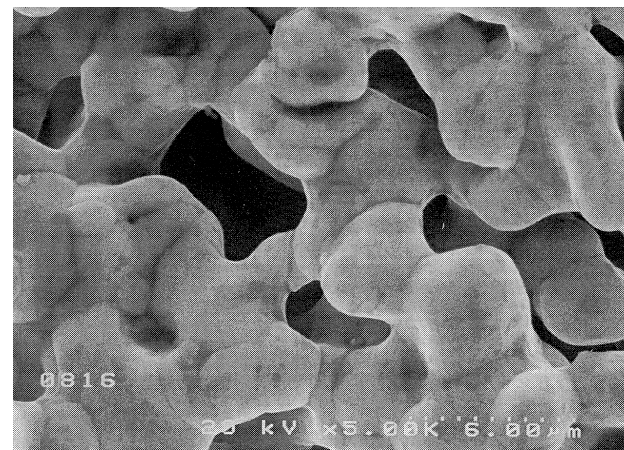
(a)
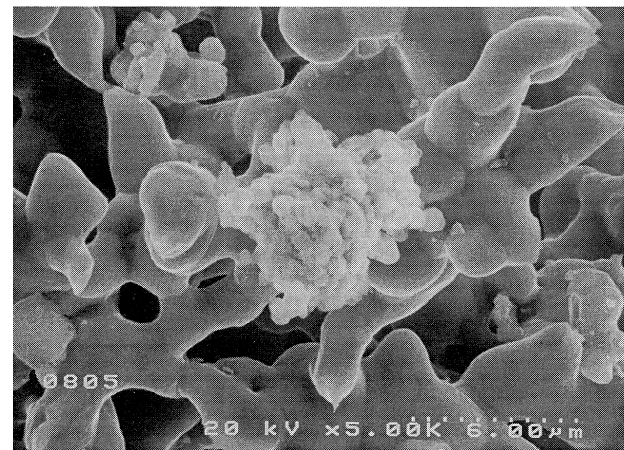
(b)

Fig. 7. SEM photographs of the fracture surface of MCFC anode sintered at 900°C. (a) Pure nickel anode, (b) Ni/4 wt.% Ni_3Al anode.

The mechanical strength of a porous Ni/Ni_3Al anode can be reinforced by maintaining small grains compared with those in a pure-nickel anode under conditions of similar porosity. This is achieved by inter-particle neck growth in the initial stage of sintering and by inhibition of grain growth by the pinning effect of Ni_3Al.

4. Conclusions

The sintering behaviour of both porous Ni/Ni_3Al and the pure nickel anodes has been investigated. The changes in the microstructure of the pores were observed by sintering experiment. Sintering of the Ni/Ni_3Al anode is controlled by the initial stage of sintering and its pore structure is maintained as an open pore network by interparticle neck growth. Pores in a pure-nickel anode became smaller during the intermediate stage of sintering and this is due to both nickel grain growth and densification. It is known that Ni_3Al inclusion at a nickel grain boundary in a porous MCFC anode is also important for enhancing mechanical strength for maintaining adequate grain-size and pore-size distribution.

Acknowledgements

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