Creep Mechanism of the Porous Ni/Ni_3Al Anodes for Molten Carbonate Fuel Cell

용융탄산염 연료전지용 다공성 Ni/Ni_3Al Anode의 크립기구

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1. Introduction

Molten Carbonate Fuel Cell (MCFC) is a highly efficient and environmentally clean source of power generation. Anode, one of the most important constituent elements of MCFC, still needs substantially improvement before commercialization. One of the important problems to be solved is to maintain structural stability in the porous anode under pressurized condition at elevated temperature[1-2]. Nickel has been shown to have good electrochemical activity with low polarization loss, which has been used widely as the anode material for the past two decades. Without strengthening, the porous nickel anode would creep significantly due to change of pore structure by compressive stress during operation. And the creep deformation gives rise to collapse stable pore structure, which results in the decrease in surface area and electrochemical performance of the MCFC[3-4].

Therefore, prior major research effort has been to strengthen the nickel anode. Partially sintered Ni anodes dispersed Al_2O_3, Cr or Al particles have shown acceptable strength thanks to dispersion strengthening[5]. Although the creep resistance in these anodes has been improved, mechanical strength in the anodes has been slightly increased due to the dispersed particles.

In our previous study, we had investigated the sinterability of the porous anode strengthened by Ni-Al intermetallics, especially Ni_3Al, produced by chemical synthesis in acidic eutectic melt[2]. It was investigated that nickel grain growth in the porous anode strengthened by the second-phase particle inclusion had been retarded during sintering, and stable open pore network could be maintained by controlling inclusion amount of the Ni3Al inter-metallics[4].

In this study, we have investigated creep behaviors of the porous

Ni/(4-7wt%)Ni_3Al anodes and Ni/5wt%Ni_3Al/5wt%Cr anode prepared for obtaining synergistic effect by dispersion strengthening and solid solution strengthening. And we have suggested a creep equation for the porous anodes different from the equation applicable to high-density polycrystalline materials.

2. Experimental

Creep experiment was performed on samples (1×1cm) fabricated from pure Ni, Ni/(4-7wt%)Ni_3Al, Ni/5wt%Ni_3Al/5wt%Cr and Ni/10wt%Cr anodes sintered to maintain porosity of 62%.

The samples were first placed in position in the creep test apparatus, as shown in Fig. 1. And the furnace was heated at heating rate of 100℃/hr, and temperature was maintained ranging from 450 to 650℃ to estimate creep activation energy in these anodes. 70%H_2/CO_2 mixed gas was flowing in the apparatus at a rate of 100mℓ/min. The external load was transmitted to the samples by a pressing rod driven by an air cylinder, and the load ranging from 50 to 200psi was applied to the sample for calculating the creep exponent related to the nature of the creep mechanism. In a separate set of experiments, the test was terminated after times between 0 and 100hrs.

The mass and dimensions of these samples were measured with a micrometer before and after they were tested and the density, when closed porosity had been reached, was determined by Archimedes principle. And their pore size distributions of the samples were obtained by mercury porosimetry (Micrometrics Autopore II 9215).

The fracture surfaces and surfaces of the samples before and after the tests were examined using scanning electron microscopy (Jeol JSM-5200). Microstructure of the anodes is analyzed by SEM-EDS (Jeol JSM-5310LV, Rontec EDWIN M1) and EPMA (Jeol JXA-8600, Shimadzu EPMA-1600). To obtain mechanical strength in these porous anodes, tensile strengths of the anodes were measured by universal test machine (Instron UTM 4467).

3. Results and Discussion

Fig. 1 shows the effect of the compressive load and temperature of the anodes on the creep strain. Thickness strain for the anodes with Ni_3Al inclusion or Ni_3Al & Cr inclusion exerted by the applied load of 100 psi at room temperature after 100 hrs is considerably lower than that obtained in incompressive creep experiment at 650℃ except for the pure and Ni/10wt%Cr anodes. Because creep deformation of the porous anodes is generally influenced by the sintering shrinkage rather than the applied load, the Ni_3Al inclusion increases the sintering resistance due to nickel grain growth inhibition [3,4]. Therefore, it is thought from these experiments that sintering resistance is one of the most important factors to increase creep resistance of the porous anode. Especially Ni/5wt%Ni_3Al/5wt%Cr anode has higher creep resistance than any other anodes after creep test. It is investigated that the creep resistance of the porous anode with the Ni_3Al can be increase by the synergistic effect of dispersion strengthening and solid solution strengthening.

Fig. 2 shows tensile strength and Youngs modulus measured by universal test machine (UTM). Mechanical property of the Ni/5wt%Ni_3Al/5wt%Cr anode is considerably higher than that of the pure anode by synergistic effect of dispersion strengthening and solid solution strengthening. It is found from the strength test that the higher tensile strength of the porous anode results in higher creep resistance.

Considering relative density of a porous anode for MCFC, its creep rate equation can be suggested as following equation (1):

$$\dot{\varepsilon} = A\sigma^{n}\exp[-\frac{Q}{RT}]\exp[-B\rho] \quad (1)$$

where A is a fitting parameter and B is a resistance coefficient which represents resistance against creep deformation. In this equation, term dependent on powder geometry of the anode is expressed simply by the relative density which represents ratio of actual sintered density to theoretical sintered density, when porosity of the anode is considerably high.

The average creep exponents of these anodes measured during creep test after 8 hrs and the creep activation energy are shown in Table 1. The creep exponent of the pure Ni anode is similar to that of Nabarro-Herring or Coble creep, for which n=1.0 is obtained from the creep test

In the case of the Ni/7wt%Ni_3Al and Ni/5wt%Ni_3Al/5wt%Cr anodes, the creep exponents are less than 1.0. Creep activation energies for the anodes obtained from creep test were relatively lower than those of high-density materials.

Relationships between creep rate estimated from model equation (1) and the creep rate measured after creep test for 100 hrs are shown in Fig. 3 by plotting logarithmically creep rate against relative density. The experimental results are consistent with the model equation used to explain the creep behaviors of the porous anodes. The A and B values estimated by the equation (1) are shown in Table 1.

4. Conclusions

Creep behavior of porous anodes for MCFC, such as pure Ni, Ni/(4-7)wt%Ni_3Al, Ni/5wt%Ni_3Al/5wt%Cr and Ni/10wt%Cr anodes, was classified into two stages under applied uniaxial load, which was different from three stages of high-density polycrystalline materials. The first stage was related to particle rearrangement which results from destruction of large pores by the applied load, and small pores was collapsed by subsequent sintering process under the load in the second stage. The creep rate of the Ni/Ni_3Al anodes was considerably decreased rather than that of the pure Ni anode, and tensile strength of the Ni/5wt%Ni_3Al/5wt%Cr anode was increased especially by the synergistic effect of dispersion strengthening and solid solution strengthening. The creep rate estimated by a model creep rate equation proposed for the Ni/7wt%Ni_3Al and Ni/5wt%Ni_3Al/5wt%Cr anodes was well consistent with that measured during creep test. Creep mechanism for the anodes which were sintered in the initial stage of sintering was affected by actual microstructure of the porous anodes. The microstructural dependency of the creep deformation was non-linear, obeying a power law with a creep exponent $n < 1$, in contrast with that of high-density material which exhibit linear Nabarro-Herring or Coble creep under the applied load.

참고문헌

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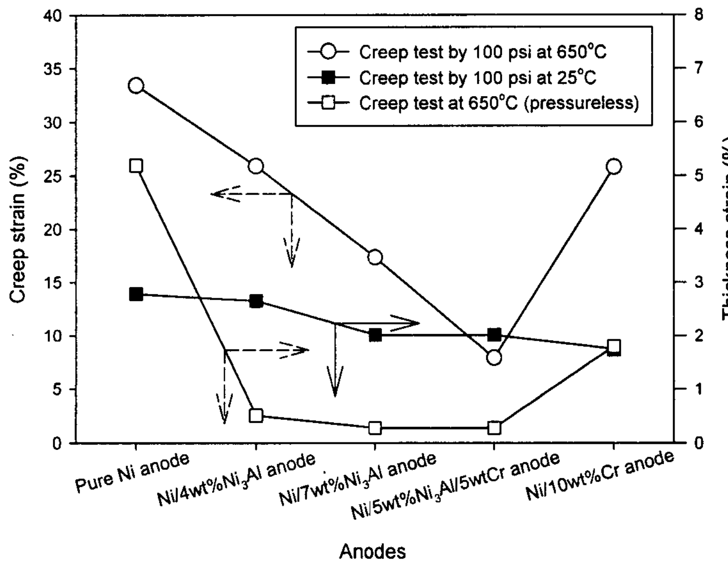

Fig.1. Creep and thickness strain for the anodes under different test conditions.

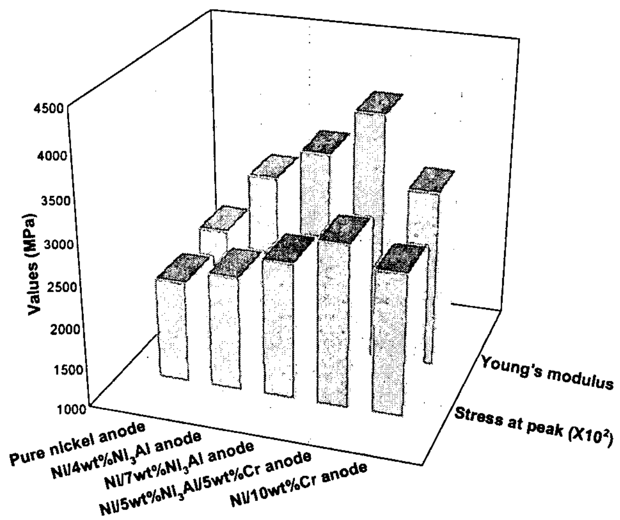

Fig.2. Mechanical properties of the anodes measured by UTM.

Table 1. Parameters of the creep rate equation obtained from the creep test.

Anodes	n [-]	Q [kJmol^{-1}]	A [MPa^{-n}]	B [-]
Pure Ni	1.3	24.18	2.64×10^{2}	21
Ni/7wt%Ni3Al	0.5	41.15	9.63×10^{17}	98
Ni/5wt%Ni_3Al/5wt%Cr	0.9	38.06	4.85×10^{14}	85

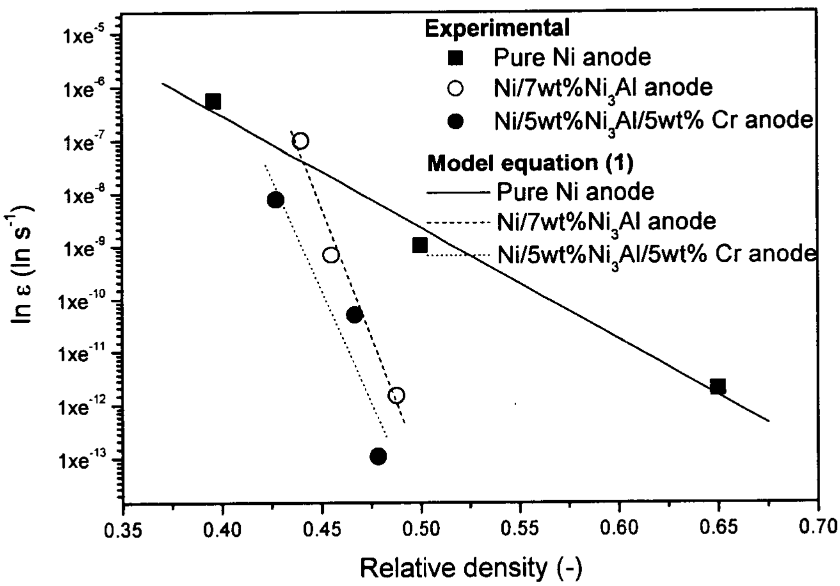

Fig.3. Effect of relative density on the creep rate during creep test.