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Effect of microstructure on oxygen permeation in $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$

K. ZHANG, Y. L. YANG, D. PONNUSAMY, A. J. JACOBSON, K. SALAMA
Materials Research Science and Engineering Center, University of Houston, Houston, TX 77204, USA

The effect of microstructure on oxygen permeation in $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ membranes was investigated using disc samples fabricated under different processing conditions of applied pressure and sintering temperature. The average grain size of the samples was found to remain unchanged as a function of applied pressure, but increased considerably when the sintering temperature was increased from 950 to 1200 °C. This change in grain size has a strong effect on the oxygen permeation flux, which increased considerably as the grain size was decreased. The density as well as the microhardness of these samples were also measured and found to change slightly as the processing conditions were changed.

1. Introduction

Mixed type conducting materials have attracted much attention in recent years because of their potential applications in oxygen separation membranes, solid oxide fuel cells and electrocatalytic reactors. One group of these materials, the perovskite oxides have been extensively investigated due to their high electronic and ionic conductivities at elevated temperatures as well as their structural stability in both oxidizing and reducing atmospheres [1–3]. The oxygen permeation through one particular perovskite material, $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCFO), has been studied by several groups due to its high oxygen permeability [3–8]. The results reported are found to vary considerably, however, the reason for these variations is not yet completely understood. It was suggested that the permeation flux might be affected by differences in the microstructure and the texture generated by the particular sample preparation method [5, 6]. Unfortunately, little has been reported about the microstructural properties of the samples used, which makes it difficult to compare the results obtained in these experiments.

The rate of diffusion at interfaces generally differs from that in the bulk crystal lattices [9], and can be faster or slower depending on the diffusing species and the type of crystalline solids that adjoin the interfaces. Badwal and Drennan investigated the effect of microstructure on the conductivity of yttria-zirconia [10], and found that the grain size had no measurable effect on the lattice resistivities, while the grain boundary resistivity decreased dramatically with the increase of the grain size. An inflection was observed when the grain boundary resistivity was plotted as a function of grain size. No experiments, however, have been conducted to investigate the effect of microstructure on the oxygen permeation properties of perovskite materials. It is thus interesting to investigate whether or not the grain boundaries in $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ membranes have a significant effect on the oxygen permeation properties.

In this paper, the effect of microstructure on the oxygen permeation of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ membranes was studied in order to determine the role of grain boundaries. Also the results of the mechanical characterization of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$, including microstructure, density and microhardness, are reported.

2. Experimental procedure

Disc samples with approximate dimensions of 14 mm in diameter and 2 mm in thickness were fabricated from $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ powders (Praxair Specialty Ceramics) using different processing parameters. Samples used for the oxygen permeation measurements were uniaxially pressed with 220 MPa pressure, while the mechanical characterization samples were uniaxially formed by applying either 280 or 480 MPa pressure. The sintering was conducted in air at temperatures ranging from 950 to 1200 °C for 6 h in order to change the microstructure. To study the effect of sintering time, samples formed at the same pressure were sintered in air at 1100 °C and at holding times of 6, 9, 12 and 18 h. All sinterings were conducted with 60 °C h^{-1} heating and cooling rates. The effect of sintering atmosphere was studied by sintering the samples in 100% argon, combination of argon and O_2, and 100% O_2. After the samples were sintered, mechanical characterization was conducted and the effects of different processing parameters on the properties of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ were studied. The grain size of the samples was determined by measuring the mean linear intercept lengths on micrographs of at least three images. The density of the samples was determined using Archimedes' method, while the Vickers hardness was measured using a Leitz Miniload 2 hardness tester with

a V3177 pyramid diamond indenter. The surfaces of samples used for hardness measurement were ground and then polished using up to 1 μm diamond polishing pastes. The oxygen permeation fluxes were measured using the apparatus described in [6], where the details of the experimental procedure are also given. All tests were conducted at similar conditions, including the sample thickness, surface treatment, data collecting time and flow rate of helium gas.

In these experiments, disc samples ground using 600 grit paper were sealed between two quartz tubes with gold rings. At one end of the sample, a pre-dried mixture of oxygen and nitrogen gases was fed, while helium gas with a flow rate of about 38 cm^3 min^{-1} was swept through the other end. The flow rate was controlled by a MKS 247C mass flow controller. A computer controlled Antek 3000 gas chromatograph was connected to the exit on the sweep side, where both oxygen and nitrogen concentration were measured. The gas chromatograph was calibrated using a standard gas of O_2 in helium. The test temperature was measured by a thermocouple inserted in the quartz tube at the fed gas side with the accuracy of ± 1 °C. All experiments were conducted in the temperature range 800–900 °C. The samples were first heated up to 900 °C and kept at this temperature until a steady state was reached when the oxygen concentration varied less than 1%. The temperature was then dropped to the next measurement point. The oxygen permeation flux at each temperature was monitored periodically and recorded when the steady state was reached. The reported oxygen permeation fluxes are based on the steady-state values.

3. Results

3.1. Effect of processing parameters

Among the processing parameters that were varied, sintering temperature was found to have a strong influence on the mechanical properties of the $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ sample, while the sintering atmosphere had no obvious effect. Table I lists the mechanical properties of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ measured for samples fabricated using different processing parameters of temperature and pressures. In this table, the density is represented as the percentage of the theoretical density of the material. When the forming pressure was 220 MPa, the samples sintered at 950, 1100 and 1200 °C, exhibited densities of 94.4, 95.8 and 94.6% of the theoretical value, respectively, and the corresponding grain sizes were 4.1, 11.1 and 14.8 μm.

TABLE I Mechanical properties of SCFO samples sintered at different temperatures

Temperature (°C)	Pressure (MPa)	Density (%)	Microhardness (GPa)	Grain size (μm)
950	280	95.8	5.91	3.9
	480	96.0	6.40	4.1
1000	280	98.4	6.03	4.3
	480	96.4	6.53	4.5
1050	280	95.1	7.31	5.0
	480	97.3	7.86	5.6
1100	280	98.2	7.75	10.0
	480	97.3	7.70	10.8
1150	280	96.7	7.58	11.2
	480	97.8	7.41	10.4
1200	280	98.0	7.87	14.8

From Table I, one can see that the densities of the samples vary little as the sintering temperature is changed between 950 and 1200 °C. Also the applied pressure seems to have little effect on the densification of the samples under these processing conditions. This shows that the $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ powder has high reactivity and sintering is completed at relatively low temperatures and short times. The microstructure and microhardness of the samples, however, were observed to change with sintering temperature. Fig. 1 shows the microstructure and grain size distribution of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ samples sintered at several temperatures, where a bimodal grain size distribution was observed. The grain size is within the range 1–10 μm for samples sintered at 950 °C, and the microstructure is dominated by grains in the 1–4 μm range (about 80%). When sintered at 1100 °C, the grain size ranges from 2 to 28 μm, and most of them are in the range 4–12 μm. Only small amount of grains are less than 2 μm, while some large grains (>20 μm) appear. For samples sintered at 1200 °C, the grain size spans from 3 to 32 μm. Some grains grow even larger (>30 μm), but the majority of the grains is in the range 4–16 μm. The grain size and the microhardness of these samples as a function of sintering temperature is plotted in Fig. 2, and shows that the average grain size of the sample is generally increased with the increase of sintering temperature. It is interesting, however, to see that the microhardness changed slightly in spite of large microstructural changes. Although the grain size increased by a factor of four, from 4.1 to 14.8 μm, the microhardness of the sample changed only by about 20% from 6.40 to 7.78 GPa.

The time dependence of the microhardness and grain size of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ samples sintered at 1100 °C is shown in Fig. 3. It can be seen from this figure that the sintering time has little effect on these properties. Also, limited changes were observed in the density, microstructure and microhardness when the sintering atmosphere was changed.

To investigate the stability of microstructure of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ samples at elevated temperatures, samples sintered at 1100 and 1200 °C were ground and polished, and then placed in a furnace heated in air to 1050 °C for different times. The microstructural evolution with time at this temperature was studied, and no grain growth was observed.

3.2. Effect of microstructure on oxygen permeation

The oxygen permeation rates (mole per second) were calculated from the measured oxygen concentrations at the helium exit end of the permeation assembly assuming the ideal gas law. From the concentration of nitrogen detected in the helium sweep gas, the oxygen leakage was calculated and used to correct for the oxygen permeation rates. The oxygen leakage was found to be about 3% at 900 °C, but increased to around 5% when tested at 800 °C. The permeation fluxes (mole per

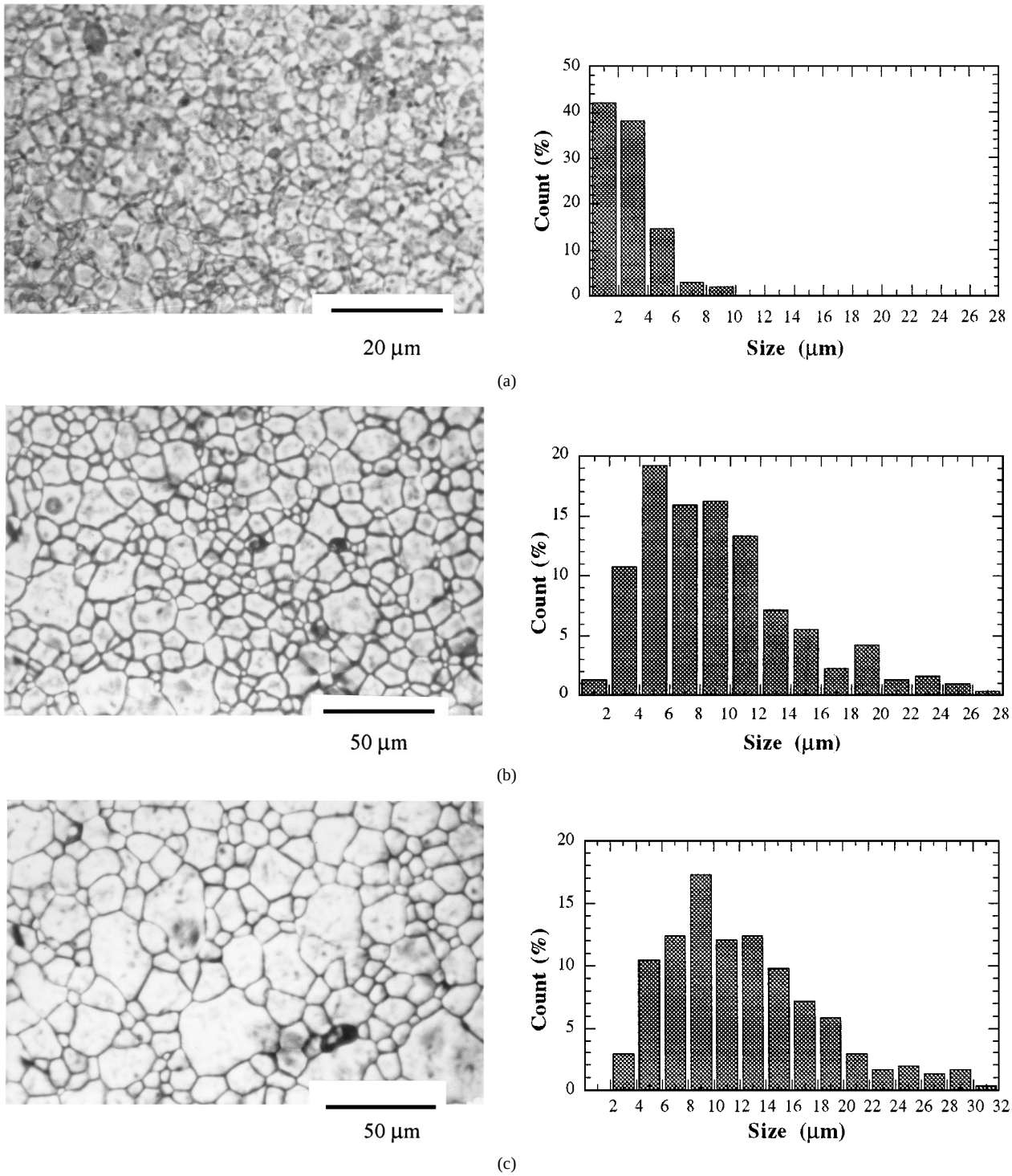

Figure 1 Micrographs and size distribution for samples sintered at different temperatures: (a) 950 °C, (b) 1100 °C, and (c) 1200 °C.

square centimetre per second) were then calculated by dividing the permeation rates by the effective area of the disc samples. Under the experimental conditions used in this study, it took a substantial time for the $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ samples to reach the steady state as shown in Fig. 4, where the oxygen flux approached a steady value after about 94 h.

The variation of the permeation flux with temperature for samples with different grain size of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ is plotted in Fig. 5. Linear relationships between log J_{O_2} and $1000/T$ are observed for all samples. From these plots, it is clear that the oxygen permeation flux depends on the microstructure of the sample. The oxygen permeation flux is generally increased with the decrease of the average grain size of the sample. The microstructure effect on oxygen permeation of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ can also be examined when log J_{O_2} is plotted as a function of the average grain size of the samples as is shown in Fig. 6. The oxygen permeation flux is increased more rapidly as the grain size becomes smaller.

4. Discussion

The results of mechanical properties of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ given in Section 3.1 demonstrate that variations in the sample processing parameters have little effect on the density of the material as is shown in

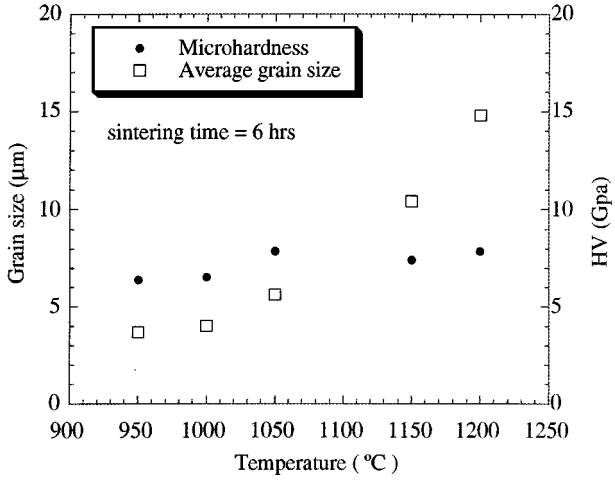

Figure 2 The effect of sintering temperature on hardness and grain size of SCFO.

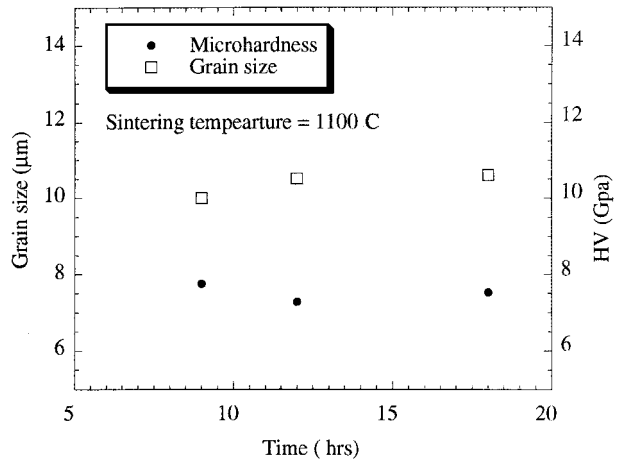

Figure 3 The effect of sintering time on the hardness and grain size of SCFO.

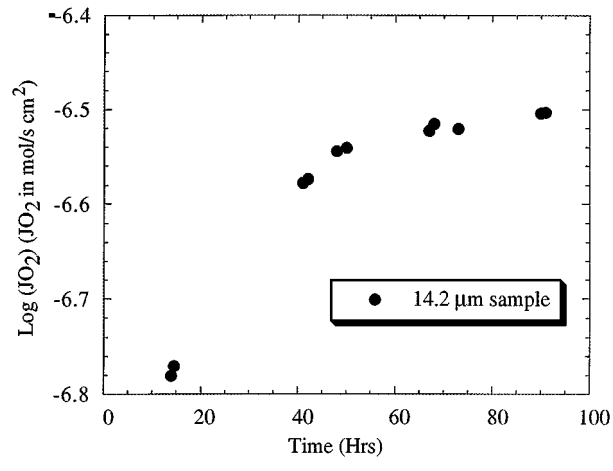

Figure 4 Time dependence of oxygen permeation flux, J_{O_2}, in SCFO at 900 °C.

Table I. The density of the sample is typically greater than 94% of the theoretical value and indicates that the sample became dense at the lowest processing parameters used. This was verified by the small amount of pores present after sintering, as can be seen in Fig. 1. The microhardness of the sample increased slightly when the sintering temperature changed from

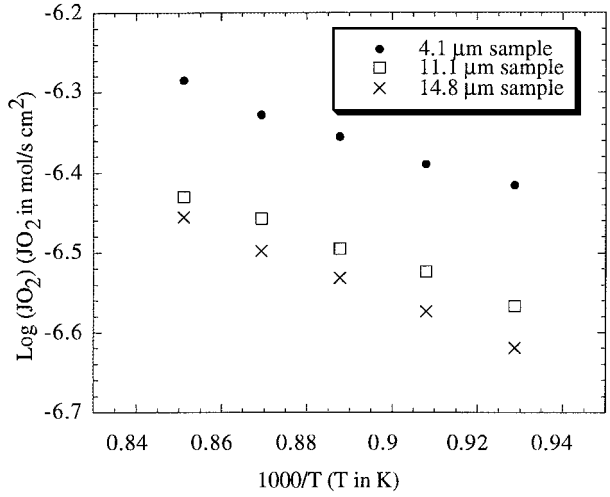

Figure 5 The oxygen permeation flux, J_{O_2}, in SCFO as a function of temperature for different grain size samples.

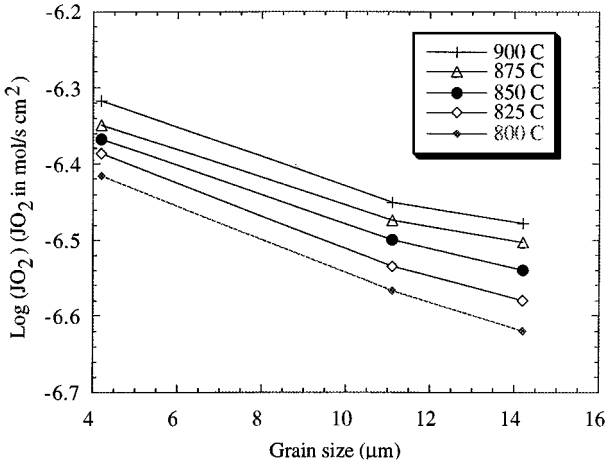

Figure 6 The oxygen permeation flux, J_{O_2}, in SCFO versus grain size at several temperatures.

950 to 1200 °C, while it was not affected by the forming pressure or the sintering atmosphere. These results indicate that the mechanical behaviour of these samples was stable and was little changed through changing the processing parameters.

The microstructure of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ is found to be the property most affected by processing parameters, especially the sintering temperature. As shown in Fig. 2, the average grain size increased from 4.1 to 14.8 μm when the temperature was increased from 950 to 1200 °C. Also, the bimodal grain size distribution of this material is highly affected by the sintering temperature, as indicated in Fig. 1. However, the microstructure is changed only slightly by increasing the sintering time when sintered at 1100 °C, as can be seen in Fig. 3, which indicates that the microstructure of this material becomes relatively stable after the densification process is completed. Furthermore, the microstructure of the sample remains fairly stable at elevated temperature as long as it is below the sintering temperature. The stability of the microstructure of this material has been further confirmed by observing the microstructure of the samples after they were exposed to an oxygen chemical potential gradient at high temperature. Fig. 7

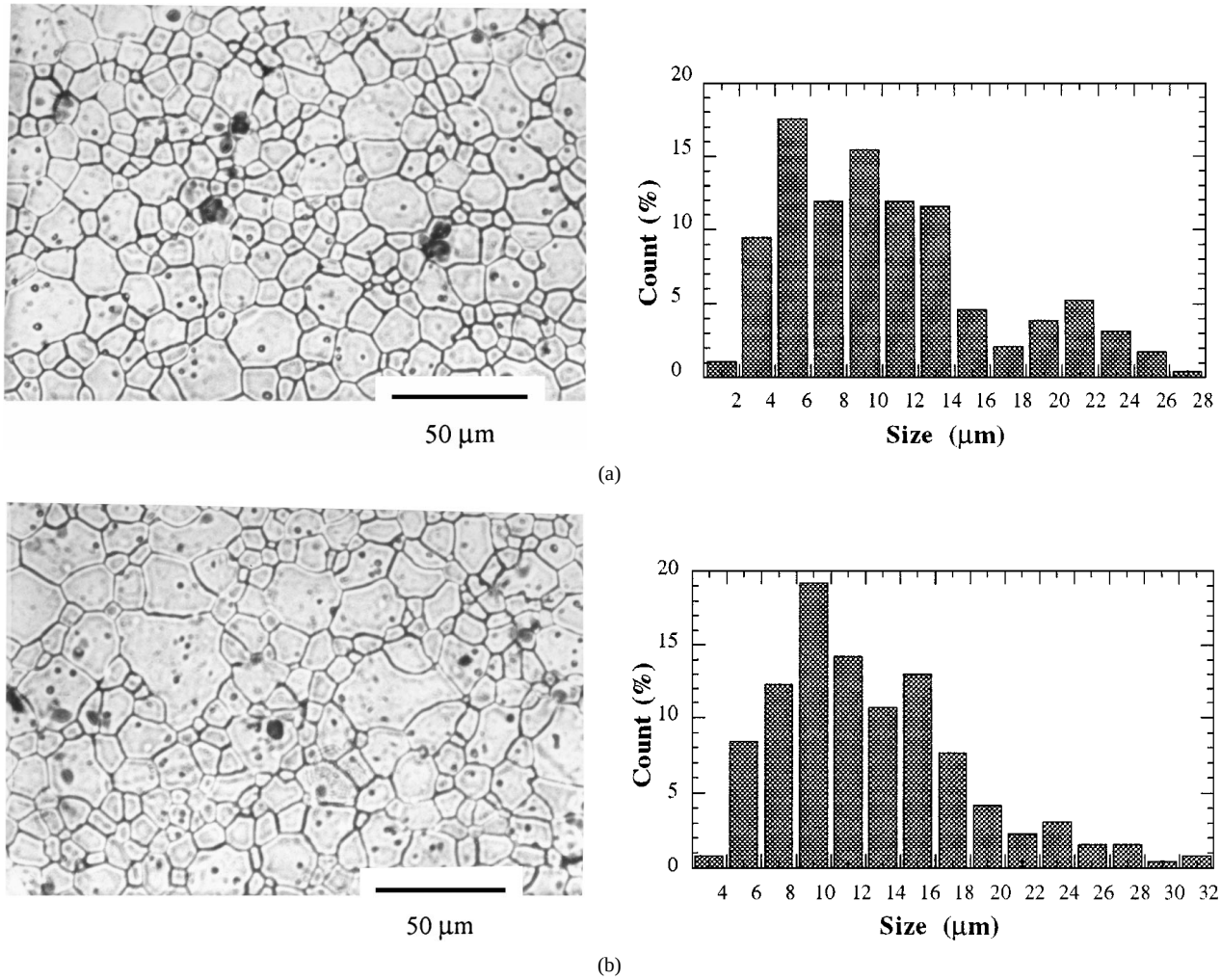

Figure 7 The micrographs and size distribution of thermally etched SCFO specimens after exposed to oxygen permeation experiments: (a) 1100 °C sample, and (b) 1200 °C sample.

shows micrographs of the samples retrieved after the oxygen permeation experiments at temperatures ranging from 800 to 900 °C for about one week. Comparing Figs 7 and 1, it is clear that after the sample was tested at elevated temperature, there is little change in the microstructure, including the average grain sizes and size distribution.

The results of the oxygen permeation flux measurements of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ as shown in Figs 5 and 6 reveal that the electrochemical process can be affected by the sample preparation conditions. Since the densities of the samples used for oxygen permeation are similar, the observed difference in oxygen permeation flux is believed to be caused by the microstructure difference. As in Fig. 5, the oxygen permeation flux through $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ was increased with the decrease of the average grain size, indicating that grain boundaries provide a faster path for oxygen penetration. Although the exact mechanism of this effect is not clear at this point, it is possible that the increase of grain boundaries may affect both the surface exchange and the diffusion processes. Previous studies suggested that both of these processes play rate-limiting roles in the oxygen permeation through SCFO membranes [8]. Thus, the increase of the oxygen permeation flux through SCFO membrane can be due to the faster diffusion path of grain boundaries, which have higher defect concentrations and/or higher defect jump rates than in the bulk. It may also be due to the enhancement of the surface exchange rate by introducing more interfaces on the sample surface. Furthermore, the change of the characteristics of the pores resulting from grain growth may contribute to the effect of microstructure on the oxygen permeation in the sample. When examining Fig. 5, one can see that the slopes of log J_{O_2} versus $1000/T$ decrease with the decrease of the average grain size in the sample, indicating that the apparent activation energy decreases with the decrease of the grain size. However, further studies are needed to understand the mechanisms involved fully.

5. Conclusions

The microstructural and mechanical properties of the $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ samples fabricated using different processing parameters have been investigated in order to determine the effect of microstructure on the oxygen permeation of this material. The microstructure of the material is affected significantly by sintering temperature, such that the average grain size of the sample is considerably increased with the increase of sintering temperature. However, the density and hardness are changed little by variations in the processing parameters. The effect of microstructure on the

oxygen permeation flux through $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ was observed by measuring the flux using samples sintered at different temperatures. The flux increased considerably with the decrease of the average grain size, indicating that the grain boundaries in the sample provided a faster path for oxygen diffusion and/or enhancement of the surface exchange rate.

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