

Grain growth of LaCoO₃ film dispersed with a second phase prepared by a sol-gel technique

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Porous LaCoO₃ films dispersed with La₂O₃ or Co₃O₄ and porous LaCoO₃ film were prepared by sol-gel dip-coating, their average grain sizes being 40 nm, 160 nm, and 160 nm, respectively. These porous films were heat-treated by 1-15 cycles at a maximum temperature of 1273 K for 3.6 ks with a heating and cooling rate of 0.017 Ks⁻¹. The grain size of LaCoO₃ increased with increasing thermal cycle. The size of LaCoO₃ grain in the La₂O₃-dispersed LaCoO₃ film was smaller than that in LaCoO₃ film and Co₃O₄-dispersed LaCoO₃ film. Abnormal grain growth occurred in the LaCoO₃ film. The grain growth of LaCoO₃ in the films with La₂O₃ or Co₃O₄ obeyed a power-law relationship as given by $d^n - d_0^n = KN$, where d is a grain diameter, N the cycle number, d_0 the grain diameter at 0 cycle, K the grain growth constant, and n the grain growth exponent. The n value was 2.0 for the La₂O₃-dispersed LaCoO₃ film, while the n was 4.2 for the Co₃O₄-dispersed LaCoO₃ film, suggesting different grain growth is operative in these films.

Key words: lanthanum cobaltite, sol-gel dip-coating, grain growth, diffusion

1. INTRODUCTION

Doped-LaCoO₃ is used as a cathode of solid oxide fuel cell (SOFC) [1,2] and a catalyst for NO_x decomposition [3]. For these applications, doped-LaCoO₃ with large surface area and interfaces are desirable. High temperatures in these applications, however, enhance the grain growth of doped-LaCoO₃, resulting in degradation of the properties as the cathode or catalyst during their long-term operations. This study focuses on inhibition of grain growth of LaCoO₃ in porous films by dispersion of a second phase of La₂O₃ or Co₃O₄. It is expected that the dispersed second phase retards motions of grain boundary by a particle drag [4], and controls the diffusion of cations, since the second phase fixes the concentration of the cation vacancy when it is equilibrated with matrix LaCoO₃ [5].

2. EXPERIMENTAL

Precursor solutions were prepared according to Hwang's method [3]. Lanthanum tri-*i*-propoxide powder was dissolved in a solution of 2-methoxyethanol and stirred at room temperature for 1.8 ks. Cobalt acetate powder was put into the La solution and ethyl acetoacetate was added to La-Co solutions heated at 333 K. The La-Co solution thus obtained was refluxed at 403 K for 7.2 ks in a high purity Ar gas (purity: 99.9995 %). A distilled water was added to the refluxed solution to perform a partial hydrolysis and polymerization with a 1:1 molar ratio of water to the alkoxide. Polyethylene glycol with a molecular weight of 2000 was added to the precursor solution, which was further stirred at room temperature for 7.2 ks. The ratio of Lanthanum tri-*i*-propoxide and cobalt acetate was varied to prepare the films of 15 vol% excess La₂O₃ or Co₃O₄ contained LaCoO₃ and LaCoO₃.

Ytria-stabilized zirconia (YSZ) ceramics were obtained from powder (Tosoh, YZ-8YS) by pressing at

an uniaxial pressure of 14 MPa, cold isostatic pressing at 98 MPa, and sintering in air at 1773 K for 7.2 ks. Relative density of the YSZ was determined to be 96% by Archimedes methods.

The precursor solution was diposited on the sintered YSZ substrate by a dip-coating technique. The coated gel film was fired at 1073 K for 3.6 ks in air. This dip-coating and firing procedure was repeated five times.

Grain sizes of LaCoO₃ particles obtained after 1-15 thermal cycles at a maximum temperature of 1273 K for 3.6 ks with a heating and cooling rate of 0.017 Ks⁻¹ were observed by scanning electron microscopy (SEM). Phase identification of the film on the YSZ substrate were carried out by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

3. RESULTS AND DISCUSSION

3.1 LaCoO₃ Films Prepared by Sol-gel Dip-coating

Fig. 1 shows the XRD patterns for LaCoO₃ film with 15 vol% La₂O₃ (a), LaCoO₃ film (b), and LaCoO₃ film with 15 vol% Co₃O₄ (c) prepared by sol-gel dip-coating and firing at 1073 K. The peaks of LaCoO₃ and YSZ appear.

Microstructures of 15 vol% La₂O₃-LaCoO₃ film (a), LaCoO₃ film (b) and 15 vol% Co₃O₄-LaCoO₃ film (c) were shown in Fig. 2. In Fig. 2(a), uniform particle in size and shape with average grain size of 40 nm and pores between particles were observed. In Fig. 2(b), large and small particles, and pores along particles are seen. Since the XRD peaks of only LaCoO₃ as a product were detected, large particles were LaCoO₃, its average grain size being 160 nm. In Fig. 2(c), large and small particles of 160 nm and 40 nm, respectively, are seen, with pores (70 nm) between particles. Since the amount of smaller particles is less than that of larger ones, smaller particles assume to be Co₃O₄.

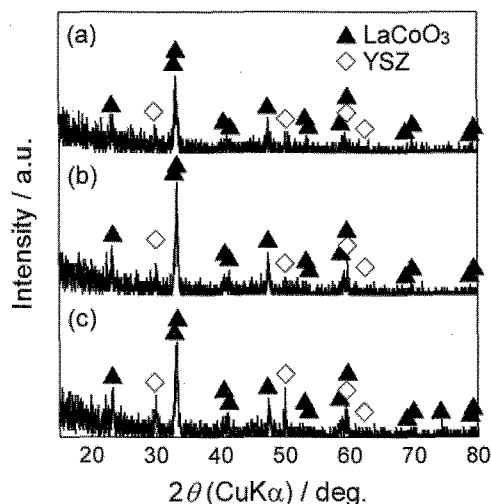


Fig. 1 X-ray diffraction patterns of LaCoO_3 film with 15 vol% La_2O_3 (a), LaCoO_3 film (b), and LaCoO_3 film with 15 vol% Co_3O_4 (c) on YSZ substrate prepared by sol-gel dip-coating and firing at 1073 K.

3.2 Grain growth of LaCoO_3 films

Fig. 3 shows 15 vol% La_2O_3 - LaCoO_3 film (a), LaCoO_3 film (b), and 15 vol% Co_3O_4 - LaCoO_3 film (c), after 15 thermal cycles at a maximum temperature of 1273 K. After 15 thermal cycles, no cracks were observed in these films. Grain formed after the thermal cycles grew compared with those before the cycle treatment. The size of LaCoO_3 grain in the La_2O_3 -dispersed LaCoO_3 film (Fig 3.(a)) was smaller than that in the LaCoO_3 film (Fig 3.(b)) and Co_3O_4 -dispersed LaCoO_3 film (Fig 3.(c)). Small pores still remained in the La_2O_3 -dispersed LaCoO_3 film after 15 cycles in contrast to the LaCoO_3 film and Co_3O_4 -dispersed LaCoO_3 film. In Fig. 3(b), an abnormally grown grain (see an arrow) is seen, while the size of grains obtained in the La_2O_3 -dispersed LaCoO_3 and Co_3O_4 -dispersed LaCoO_3 was relatively uniform. This indicated that a second phase of La_2O_3 or Co_3O_4 prohibit the abnormal growth of matrix LaCoO_3 grain.

Average grain sizes of LaCoO_3 for three kinds of films, d , as a function of thermal cycle N were plotted in Fig. 4. Average grain size increased with increasing cycle number for these films. Average grain size in the LaCoO_3 film showed a sudden increase after 15 cycles, probably because of occurring of abnormal grain growth (Fig. 3(b)).

3.3 Grain Growth Kinetics

The normal grain growth kinetics obeys a power-law relationship as given by

$$d^n - d_0^n = Kt \quad (1)$$

where d is a grain diameter, t time, d_0 the grain diameter at time $t=0$, K the grain growth constant, and n the grain growth exponent [4,6]. In two-phase ceramics, the grain growth exponent varying from $n = 2$ to 4 has been used to analyze the growth kinetics. There is a general tendency based on the models that the grain growth

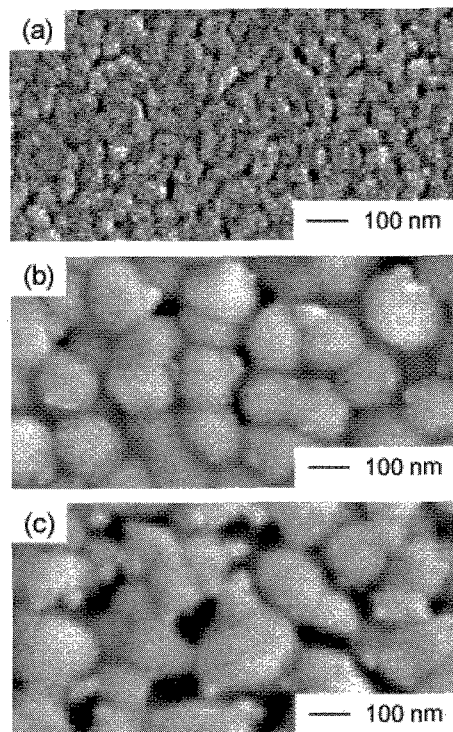


Fig. 2 SEM images of microstructures of LaCoO_3 film with 15 vol% La_2O_3 (a), LaCoO_3 film (b), and LaCoO_3 film with 15 vol% Co_3O_4 (c) prepared by a sol-gel dip-coating and firing at 1073 K.

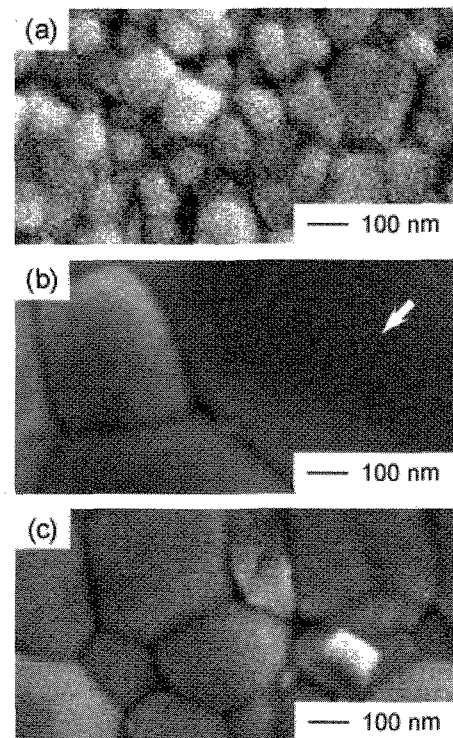


Fig. 3 SEM images of microstructures of LaCoO_3 film with 15 vol% La_2O_3 (a), LaCoO_3 film (b), and LaCoO_3 film with 15 vol% Co_3O_4 (c) after 15 thermal cycles at a maximum temperature of 1273 K and a dwell time of 3.6 ks.

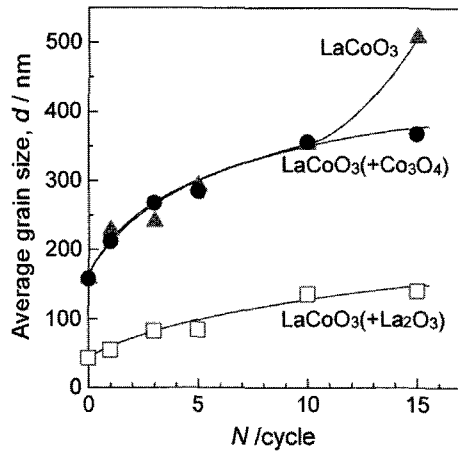


Fig. 4 Average grain size of LaCoO₃ films as a function of thermal cycle N .

LaCoO₃: LaCoO₃

LaCoO₃(+La₂O₃): LaCoO₃ with 15 vol% La₂O₃.

LaCoO₃(+Co₃O₄): LaCoO₃ with 15 vol% Co₃O₄.

exponent n is 2 for interface-controlled grain growth, 3 for bulk-diffusion controlled grain growth, and 4 for grain-boundary-diffusion controlled grain growth [4], although there are several reports that exponent n determined experimentally deviates from the value from 2 to 4 [6].

Ignoring the grain growth on heating and cooling because the grain growth rate decreases exponentially with decreasing temperature, eq. (1) can be rearranged as the following equation:

$$d^n - d_0^n = KN \quad (2)$$

where N is the cycle number, d_0 the grain diameter at 0 cycle.

Fig. 5 shows the plots of $\log(d^n - d_0^n)$ vs $\log(N)$ in the various integers n . For the correct grain growth exponent, the slope of this plot is equal to unity. As shown in Fig. 5, the growth of grains in LaCoO₃ film dispersed with La₂O₃ or Co₃O₄ obeys a power-law relationship. The n value for the LaCoO₃ film with La₂O₃ was 2.0 and that for the LaCoO₃ with Co₃O₄ was 4.2, suggesting that the different grain growth occurred in these films.

3.4 Grain Growth Mechanism and Rate Determining Species

LaCoO₃ is known to be a mixed conductor of a thermally activated p-type small polaron hopping conduction [7] and oxygen ionic conduction through vacancies [8]. One can assume that either lanthanum ion or cobalt ion is the rate determining species in grain growth, since the slowest conducting species in the fastest grain growth mode is the rate determining species. Although the diffusivities of cations in LaCoO₃ are not well known, one can suggest that lanthanum ion diffuses faster than cobalt ion by referring to the report that the diffusion of lanthanum ion in LaCoO₃ could be the rate-controlling step of the solid state reaction between La₂O₃ and Co₃O₄ [9]. This is similar to the report that lanthanum ion diffuses faster than chromium ion in LaCrO₃ [10] with the same perovskite structure as LaCoO₃.

It is known that there are mainly two mechanisms in grain growth of two-phase material, the coalescence

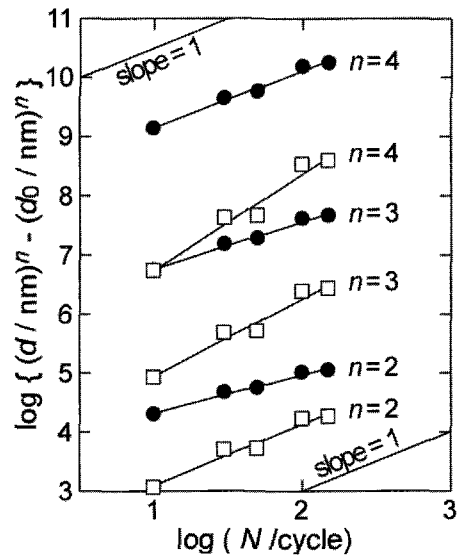


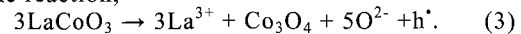
Fig. 5 The slope of $\log(d^n - d_0^n)$ vs $\log(N)$ in various integer n .

□: LaCoO₃ dispersed with 15 vol% La₂O₃.

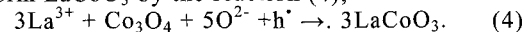
●: LaCoO₃ dispersed with 15 vol% Co₃O₄.

process involving particle drag and the Ostwald ripening process resulting in the creation of new grain boundary [4].

Fig. 6 illustrates the schematics of the two grain-growth mechanisms for LaCoO₃ matrix dispersed with Co₃O₄ particles on the basis of the mechanism described above. When Co₃O₄ particles are dragged by the movement of grain boundaries of LaCoO₃ (Fig. 6(a)), lanthanum ion, oxide ion, and Co₃O₄ form at the right side of the left Co₃O₄ particle (at interface I) in Fig. 6(a) by the reaction,

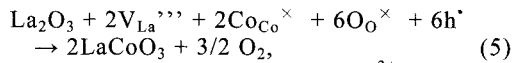


The lanthanum and oxide ions formed at the right side of Co₃O₄ particle (interface I) diffuses to the left side (interface II), and react with Co₃O₄ to form LaCoO₃ by the reaction (4);



These processes make the Co₃O₄ particle move to the right direction and coalesce into a neighboring Co₃O₄ particle. In this case, lanthanum ion is the rate determining species. In the Ostwald ripening process as in Fig 6(b), both cobalt ion and oxide ion diffuse from the left smaller particle to the right larger particle, and the smaller Co₃O₄ particle shrinks and disappears. In this case, cobalt ion is the rate determining species. These two mechanisms can simultaneously occur in LaCoO₃ films dispersed with Co₃O₄ particles. If diffusion of lanthanum ion is faster than that of cobalt ion, the coalescence process is most likely.

For LaCoO₃ film dispersed with La₂O₃, the coalescence process by bulk diffusion of Co³⁺ ion and O²⁻ ion and the Ostwald ripening process by grain boundary ambipolar diffusion of La³⁺ ion and O²⁻ ion are possible from the similar discussion in Fig. 6. Because the activity of La₂O₃ is high (1 in equilibrium state) in LaCoO₃, the concentration of lanthanum vacancy decreases by the following defect reaction:



and the diffusion coefficient of La^{3+} ion is also decreases, which it is proportional to the concentration of lanthanum vacancy [10]. The decrease in the diffusion coefficient of La^{3+} could be one of the reasons for the slower grain growth of LaCoO_3 films with La_2O_3 . However, the experimental exponent $n=2.0$ may support interface-controlled grain growth. Supposing that diffusion barrier layer formed at grain boundaries as shown in Fig. 7, the interface-controlled mass transport across the grain boundary can be proposed. Further investigation is needed to arrive at firm conclusions.

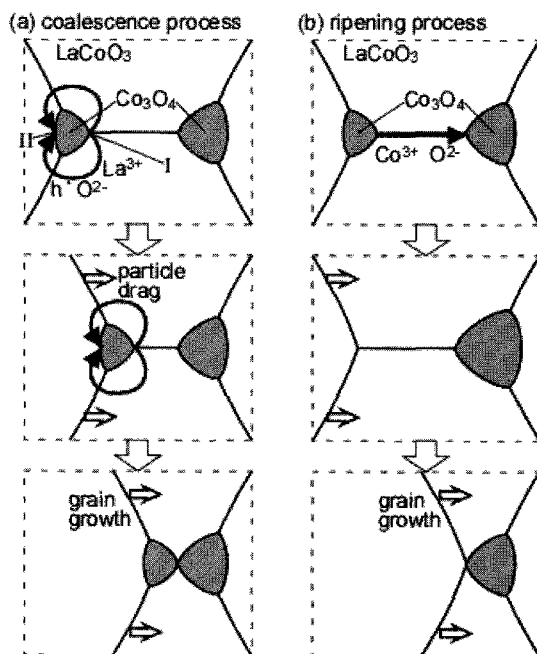


Fig. 6 Schematic of coalescence process (a) and Ostwald ripening process in LaCoO_3 matrix dispersed with Co_3O_4 particles.

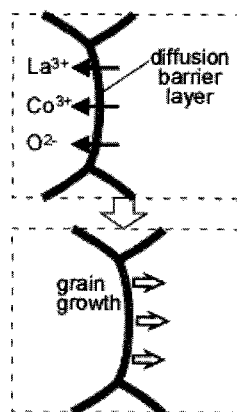


Fig. 7 Schematic of mass transport across a diffusion barrier layer at grain boundary and grain growth of LaCoO_3 .

4. CONCLUSION

Porous LaCoO_3 films dispersed with La_2O_3 or Co_3O_4 and porous LaCoO_3 film were prepared by sol-gel

dip-coating. Grain growth in LaCoO_3 porous films with a second phase obeyed a power-law relationship, while abnormal grain growth occurred in the LaCoO_3 film without a second phase. Grain size of LaCoO_3 in the La_2O_3 -dispersed LaCoO_3 film was smaller than that in the Co_3O_4 -dispersed LaCoO_3 film after the thermal cycles. The different grain growth were operative in these films.

5. REFERENCES

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