Fabrication and ionic conductivity of apatite-type Mg doped lanthanum silicate films by DC plasma spraying

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Dense films of Mg doped lanthanum silicate were deposited on Fe, stainless steel and lanthanum chromite substrates by atmospheric DC plasma spraying with an input energy of 44–21 kW. Scanning electron microscopic observation showed that microstructure of the films on these substrates consists of densely piled up particles with a disk-like shape. The film deposited with the lowest input energy of 21 kW includes a larger amount of smaller particles. Bulk ionic conduction was observed in the film deposited on lanthanum chromite substrates with an input energy of 38 kW and annealed at above 1073 K. On annealing at above 1173 K the ionic conductivity measured at 973 K rapidly increased up to 2 mS cm^{-1} , while the grain boundary resistance disappeared on annealing at above 1273 K and the electrode interface resistance gradually increased with the annealing temperature. A mixture of amorphous and apatite phase in the as-deposited films turned to a single apatite phase after the annealing at 1273 K.

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1. Introduction

Oxide ion conductors with an apatite-type structure have been developed by a pioneering work by Nakayama et al.^{1)–3)} The apatite-type ionic conductors have attracted great interests because of their promising potential, high ionic conductivity at relatively low temperatures³⁾ and pure oxide ion conduction over a wide oxygen partial pressure range,⁴⁾ as an electrolyte for solid oxide fuel cells (SOFCs) working at intermediate temperatures (773–1073 K). Recently, it has been found that the ionic conductivity is further increased by Mg doping on the Si site^{5)–8)} and by containing excess oxide ions at the same time; $\text{La}_{9.8}\text{Si}_{5.7}\text{Mg}_{0.3}\text{O}_{26.4}$ shows ionic conductivity comparable with Sr and Mg doped lanthanum gallate below 823 K.⁹⁾ Fuel cell properties of the SOFCs using apatite-type ionic conductors as electrolytes have shown reasonable power densities,^{6),9),10)} exhibiting phase stability in both reduced and oxidized atmospheres and compatibility with typical electrode materials such as Pt,^{6),10)} $\text{Ni-Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ cermet and $\text{La}_{0.9}\text{Sr}_{0.1}\text{CoO}_{2.95}$ perovskite.⁹⁾

The remaining issue of the apatite-type electrolytes is the fabrication of dense sintered ceramic membranes since the sintering temperature of the apatite-type lanthanum silicates is generally as high as 1973–2023 K. The high sintering temperature causes serious problems such as size reproducibility, reaction with a setter and the manufacturing cost. One of the breakthroughs for these problems is a use of thin film fabrication process. Apatite-type lanthanum silicate films have been prepared by the sol-gel process using alc oxide-hydrolysis and heating the gels at 1273 K.¹¹⁾ The film, however, was porous and the electrical properties were not reported. In this study the apatite-type films of Mg doped lanthanum silicates are prepared by atmospheric DC plasma spraying; plasma spray methods are easily applied to large area coating and generally cost-efficient. This paper reports the fabrication and ionic conductivity of dense apatite-type films by DC plasma spraying and heat treatments after the spraying.

2. Experimental procedures

Plasma spray deposition was conducted in Thermal Spraying Technology R&D Laboratories, Tocalo Co., Ltd., using a Sulzer Metco atmospheric DC plasma sprayer. Starting powder of Mg doped lanthanum silicate was prepared by heating the mixture of La_2O_3 , MgO and SiO_2 at 1973 K in N_2 , annealed at 1573 K in air and then pulverized to 10–45 μm in Powlex Co., Ltd. Deposition was carried out on Fe, stainless steel (SS430) and lanthanum chromite ceramic substrates. The surface of the substrates was blasted with silicon carbide powder prior to the deposition. Input energy to the plasma gun was controlled to 21, 29, 38 and 44 kW by changing the ratio of H_2 and Ar supplied to the gun. The powder was then delivered to the gun by Ar carrier gas to start the coating. The distance between the substrates and the gun was 120 mm. During the deposition, the gun was scanned over the substrates to achieve uniform thickness. Deposition rate changed with the scanning area and the input energy; typically, the deposition time of 5 min gave the film thickness of 100–150 μm .

Phases in the film were investigated by X-ray powder diffraction (XRD) with $\text{Cu K}\alpha$ radiation (RINT2000, Rigaku Corp.). Microstructures of the films were examined by scanning electron microscope (SEM) with a field emission type electron source (Sirion, FEI Co.). Ionic conductivity was evaluated for the films deposited on lanthanum chromite ceramic substrates. AC impedance between the substrates and Pt electrodes pasted on the surface was evaluated at temperatures between room temperature and 973 K using an impedance analyzer (model 1260, Solartron) with an applied voltage of 30 mV and frequencies from 10 MHz to 0.1 Hz.

3. Results and discussion

A photograph of DC plasma sprayed films deposited on Fe substrates with different input energy is shown in Fig. 1. The color of the film deposited with an input energy of 21 kW is

white, while the films deposited with a higher input energy show greenish color. This suggests that the chemical composition of the films slightly changed during the coating probably due to the volatilization of Si in the high temperature plasma. SEM photographs of surfaces and fractured cross sections of the films deposited on Fe substrates with a different input energy are shown in Fig. 2. Microstructures consisting of densely piled-up particles with a disk-like shape were observed for these films, which reveal rapid quenching from the melts on the substrate surfaces. A slight change in the microstructure with an input energy was noticed; the film deposited with the lowest input energy of 21 kW includes a larger amount of small particles as shown in Figs. 2(d) and (h). On the other hand, no significant change in the microstructure with substrate material was observed. Note that no through-hole from the substrate to the top surface was observed in the cross sections (Figs. 2(e)–(h)).

XRD patterns of as-deposited films with a different input energy along with that of the starting powder are shown in Fig. 3. The as-deposited films show the patterns of diffraction peaks attributable to the apatite-type structure, which are denoted by A and agree with that of the starting powder. In addition, broad halos around $25\text{--}30^\circ$ are observed in all as-deposited films, showing the existence of an amorphous phase. The amorphous

phase content increases with increasing the input energy because of the large quenching rate on the substrate surface.

Ionic conduction in these as-deposited films was not observed by AC impedance measurements. This is probably due to the amorphous phase existing between apatite crystals or in the grain boundary and blocking the ionic conduction. Thus we tried to crystallize the amorphous phase by heat treatments. AC impedance of the films deposited with 38 kW on lanthanum chromite substrates and annealed at 1073 or 1273 K was measured at 973 K; complex impedance plots of the AC measurements are shown in Figs. 4(a) and (b), respectively. The film annealed at 1073 K shows two semicircles in the plot. As the higher frequency semicircle does not pass the origin, the equivalent circuit is shown in Fig. 4(c), in which R_c , R_b and R_e are bulk resistance in grain, amorphous or grain boundary resistance and electrode interface resistance, respectively. In Fig. 4(a) the resistance value A corresponds to R_c , whereas B and C correspond to $(R_c + R_b)$ and $(R_c + R_b + R_e)$, respectively.

The film annealed at 1273 K shows only one semicircle in the plot (Fig. 4(b)). This indicates that the annealing at 1273 K caused crystallization of the amorphous or grain boundary phase and R_b disappears. The thorough crystallization of the amorphous phase was confirmed by XRD on the annealed films. In Fig. 5 broad halos from the amorphous phase exist in the as-deposited film and the film annealed at 1073 K, whereas a single apatite phase without amorphous or any second phase is observed when annealed at 1273 K.

Bulk resistance, amorphous or grain boundary resistance and electrode interface resistance measured at 973 K with a Pt top electrode are shown in Fig. 6 as a function of annealing temperature, T_a . Bulk resistance is constant at $\sim 20\ \Omega$ as T_a is more than 1173 K. This corresponds to the ionic conductivity of $2\ \text{mS cm}^{-1}$ when calculated from the thickness and electrode sizes. The conductivity is considerably lower than that of the sintered $\text{La}_{9.8}(\text{Si}_{5.7}\text{Mg}_{0.3})\text{O}_{26.4}$ sample ($43\ \text{mS cm}^{-1}$).⁹⁾ Amorphous or grain boundary resistance decreases significantly with annealing at 1173 K and disappears above 1273 K. On the other hand, the electrode interface resistance slightly increases with increasing annealing temperature, which is probably due to the reaction

Fig. 1. A photograph of the plasma sprayed films deposited on Fe substrates with input energies of 44, 38, 29 and 21 kW.

Fig. 2. SEM images of (a)–(d) surfaces and (e)–(h) fractured cross sections of the as-deposited films on Fe substrates with input energies of 44, 38, 29 and 21 kW.

Fig. 3. XRD patterns of the sintered powder and the as-deposited films on stainless steel substrates by DC plasma spraying with a different input energy.

Fig. 4. Complex impedance plots measured at 973 K of the films deposited on lanthanum chromite substrates with an input energy of 38 kW and annealed at (a) 1073 K and (b) 1273 K and (c) their equivalent circuit.

between electrolyte and electrode or a defect in the interface caused by thermal expansion.

In conclusion, dense thin films of Mg doped lanthanum silicate were prepared by atmospheric DC plasma spraying. The films showed apatite-type structure and ionic conduction on annealing at above 1073 K. The bulk ionic conductivity of 2 mS cm^{-1} was obtained by annealing at above 1173 K.

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Fig. 5. XRD patterns of the as-deposited film on a lanthanum chromite substrate with an input energy of 38 kW and films annealed at 1073 and 1273 K.

Fig. 6. Values of the (a) bulk and (b) amorphous or grain boundary and (c) electrode interface resistance measured at 973 K of the films deposited on lanthanum chromite substrates with an input energy of 38 kW as a function of annealing temperature.

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