Oxygen separating membrane manufactured from $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ perovskite-like material

M GROMADA^{1,*}, J ŚWIDER¹, J TRAWCZYŃSKI², M STĘPIEŃ³ and M WIERZBICKI³

¹Institute of Power Engineering, Ceramic Department CEREL, Research Institute, 36-040 Boguchwała, Poland

²Division of Chemistry and Technology of Fuels, Wrocław University of Technology, 50-370 Wrocław, Poland

³Laboratory of Fuel Cells, Institute of Power Engineering, Research Institute, 02-981 Warszawa, Poland

MS received 30 August 2013; revised 28 November 2013

Abstract. The dense thin membrane for oxygen separation was manufactured from $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) mixed oxide with perovskite-like structure prepared by the solid-state method. Properties of both powder and granulate (chemical and phase compositions, the specific surface area and the porosity) as well as sintered material (the apparent density, the apparent porosity, the water absorbability, the chemical composition, the crystallographic structure and microstructure), that affect the process of ion oxygen permeation through membrane, were determined. Parameters influencing on usable properties of membranes *viz.*, the bending strength and the coefficient of thermal expansion were assessed as well. Effect of the sintering temperature on membrane structure was evaluated. The elaborated fabrication procedure enables one to manufacture membrane, in which microstructure is characterized by the presence of big grains as well as decreased concentration of grain boundaries. Measurements of the oxygen permeation through BSCF membrane revealed that the highest oxygen flux reaching $2.6 \text{ cm}^3 \text{ O}_2 / (\text{cm}^2 \text{ min})$ was obtained at 950°C under air and helium flows equal to $1 \text{ dm}^3 \text{ min}^{-1}$.

Keywords. Oxygen membranes; perovskite-like materials; solid-state method; oxygen permeation flux.

1. Introduction

Mixed oxides revealing perovskite-like structure and both ion and electron conductivities are successfully used for manufacturing the dense membranes separating clean oxygen from air. It follows from the transport properties of these materials and their stability in environments differing in oxygen content. The effectiveness of membrane described by the oxygen flow permeating through it depends, among others, on the chemical composition of perovskite material, the membrane thickness (range controlled by diffusion or surface processes), its microstructure and the operating temperature as well as the gradient of oxygen partial pressures at both sides of membrane.^{1,2}

The fabrication of dense oxygen membrane comprises the perovskite powder synthesis, the forming of membrane and its sintering. The method of perovskite-like mixed oxides preparation strongly influences on the powder grain size and from this reason also on the membrane microstructure. Many methods of perovskite powder synthesis were elaborated in the past beginning from the solid-state method through wet chemical ones (like sol–gel, hydrothermal ones) and finishing on the chemical combustion or pyrolysis of appropriate raw materials solution.^{2,3} Variety of perovskite powder fabrication methods result in materials with various properties (specific surface area, porosity, etc.), influencing on the degree of

membranes densification and thereby their effectiveness in the oxygen separation.^{2,3} Moreover, the technology of membrane forming (extrusion, isostatic pressing) as well as the sintering conditions (rate of heating and cooling, sintering temperature and dwell time, atmosphere of sintering) considerably affect their microstructure. It is well evident that the presence of pores in the membranes microstructure worsens the transport of oxygen ions.² The influence of the microstructure on the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) membrane oxygen permeability was confirmed by measurements of oxygen permeation through samples sintered at various conditions.^{3,4} It was found that the oxygen flow grows up considerable together with the increase in grain size. In turn, increase of grain size lowers the concentration of grain boundaries which block ion oxygen flow and in this way improves the ionic conductivity.

Gromada *et al*⁵ have found that BSCF perovskite-like powders, possessing properties suitable for manufacturing of oxygen permeating membranes, can be prepared by the solid-state method. The membranes manufactured from powders prepared in this way show the low resistance of oxygen transport on grain boundaries and therefore they reveal greater effectiveness.^{3,6} The additional advantage of this method is its greater efficiency in comparison with other ones, which will have huge importance on membranes manufacturing cost at commercial scale.⁷ Moreover, it was stated that the BSCF mixed oxide prepared by the solid-state method and exhibiting perovskite-like structure is the most promising

*Author for correspondence (gromada@cerel.pl)

material for membrane fabrication among other studied ones.⁵

In this paper, outcomes of membranes manufactured from BSCF perovskite material are described. The physicochemical properties of the membrane at each stage of its preparation (powder, granulate, sintered material) are determined. The main aim of this work was to determine the influence of sintering temperature on the membrane microstructure and thereby the oxygen permeation flux. On the basis of obtained results, the procedure of thermal treatment enabling manufacturing of effective membrane has been elaborated. In the paper by Sunarso *et al.*,³ oxygen permeation flux of at least 1 ml O₂/(cm² min) has been specified for membranes from the economic point of view, although a value of 3.5 ml O₂/(cm² min) is considered to satisfy the present technological application.

2. Experimental

The powder of BSCF perovskite was manufactured from the appropriate metal oxides: Co₂O₃ (minimal content of Co 70%, Sigma), Fe₂O₃ (99% of purity, Sigma-Aldrich) and metal carbonates: BaCO₃ (99.5% of purity, Chempur), SrCO₃ (99% of purity, Chempur). The raw materials were mixed with ethyl alcohol and milled in the mixer mill for 2 h. The obtained powder was calcined in the electrical furnace for 5 h at 950°C. The triple milling and calcinations were necessary to obtain monophase material. The chemical composition was determined by the ICP method (Liberty 220 Varian), the X-ray powder diffraction (XRD) patterns were recorded by X'PertPROX diffractometer equipped with PIXcel detector (Cu K α radiation). The specific surface area and the pore size of fabricated powder were determined by the low-temperature nitrogen adsorption method (77 K, Quantachrome Autosorb-1).

In order to improve the mouldability, the obtained perovskite-like powder was granulated. The powder was mixed with deionized water in mixer mill for 30 min and then dispex, oil emulsion F15 and polyvinyl alcohol were added. The granulation process was performed in spray drier (Niro) at the inlet temperature of 220°C, the outlet temperature of 80°C and the spray pressure was equal to 40 mm water column. The basic properties of received granulate: chemical and phase compositions, the specific surface area and pore size were determined.

Pellets from BSCF granulate were manufactured by combined uniaxial and isostatic pressing. Then the green pellets were sintered in the electrical furnace according to the curve ensuring high density of sintered disc. The highest temperature of sintering was 1000°C, the dwell time was 1 h and the rate of heating and cooling was equal to 100°C h⁻¹.

The basic properties of sintered pellets *viz.*, the apparent density, the apparent porosity, the water absorbability, the chemical composition and crystallographic structure as well as its microstructure were determined. Parameters characterizing the extent of material sintering: the apparent density,

the apparent porosity, the water absorbability were estimated by method taking advantages of Archimedes law. The chemical composition of material was determined by the ICP method (Liberty 220 Varian). XRD patterns were obtained using X'PertPROX diffractometer. The surface microstructure of material was evaluated by means of scanning electron microscopy (SEM) SEM/HITACHI S-3400N/2007. Bars produced according to the same procedure as pellets were used for determining the bending strength and the coefficient of thermal expansion. The bending strength of BSCF material was determined by three-point method on the sintered, not polished, samples of the cross-section of 54 mm². The strength testing machine ZDM-5 from VEB Werkzeugmaschinenkombinat company was applied. The speed of cross-bar movement was equal to 6 mm min⁻¹ and the applied distance of supports was 50 mm. The coefficient of linear expansion in the range of temperature from 20 to 900°C was determined using high temperature dilatometer from BÄHR-Gerätebau GmbH company.

The oxygen permeating membrane from BSCF perovskite was made according to the same procedure used for pellets preparation and was denoted as BSCF_0. With the aim of determining the effect of sintering temperature on the membrane properties, four green membranes were sintered in the electrical furnace according to different sintering curves. The rate of both heating and cooling was 100°C h⁻¹, the highest temperature of sintering was 1000, 1050, 1100 and 1150°C, while the dwell time was 5 h. Sintered membranes were denoted, respectively, as BSCF_1, BSCF_2, BSCF_3 and BSCF_4. Finally, membranes were grinded with abrasive papers of the gradation of 40 as well as 80. This procedure removed contaminations gathered on the membrane's surface during sintering and enabled development of external surface of membranes and thereby increased the rate of both adsorption and desorption processes on the surfaces. Moreover, as a result of grinding, the thickness of membranes was lowered below 1.05 mm. It is known³ that in the range controlled by diffusion processes, the oxygen flux through membranes depends on the membrane thickness. It means that the membrane thickness has to be decreased to the minimum in order to maximize the oxygen flow. However, the requirement of the membrane appropriate mechanical strength restricts decreasing of its thickness. The usability of the BSCF_0 membrane for oxygen separation in the temperature range from 700 to 950°C was determined. Measurements of oxygen permeation were performed using home-made experimental set-up (figure 1), in which the sweep gas (helium) flows with 50 ml min⁻¹ through quartz tube ($d = 50$ mm) while synthetic air flows with the capacity of 100 ml min⁻¹ through inner alumina tube ($d = 28$ mm) fastened inside of quartz one. On the top of smaller tube, the membrane was fixed with the use of the ceramic glaze. The active area of membrane was 450 mm². In the first turn, the measurement of background was performed in each test temperature—in this case nitrogen instead of air was fed into inner tube. Then nitrogen flow was changed to the air flow and oxygen permeation was measured. The oxygen

Figure 1. Scheme of apparatus for testing oxygen membranes with disk shape.

concentration in the outlet gas was determined by gas chromatograph (Varian CP-4900). The volume flow of outlet gas was estimated on the basis of results of measurements by pellicular electronic flow meter and then recalculated to the standard conditions. The scheme of apparatus for determining the oxygen permeation flux through membranes is presented in figure 1.

3. Results

The results of chemical analysis of the prepared BSCF powder confirmed that it possesses assumed content of Ba, Sr, Co and Fe. Differences in content of particular components are very small and neglected. However, extent in which these components were built into perovskite lattice sites is not clear. On the XRD pattern of BSCF powder (figure 2), only peaks corresponding to $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ perovskite-type phase are visible (PDF: 055–0563). However, this pattern does not fully fit to the reference one because of the small shifts of peaks suggesting the imperfection of BSCF structure as well as the lattice tension. The ratio of noise to diffractive peaks of crystalline phase indicates relatively slight content of amorphous contaminations.

The BSCF powder revealed very small specific surface area equal $1.1 \text{ m}^2 \text{ g}^{-1}$. Moreover, the measurements of low-temperature nitrogen sorption showed that this material exhibited only trace porosity, which confirms insignificant value of pore volumes reaching $0.001 \text{ cm}^3 \text{ g}^{-1}$.

XRD patterns of BSCF powder and BSCF granulate are very similar and the observed differences in value of the lattice constants fits in limit of measurement error of method. The specific surface area of granulate ($1.5 \text{ m}^2 \text{ g}^{-1}$) is higher than corresponding one of the powder, as a result of the powder fragmentation during homogenization in the mixer mill.

The basic requirement of the material usability for oxygen membrane fabrication is that its apparent density was at least 90% of theoretical one.⁸ For BSCF pellets the apparent

Figure 2. XRD pattern of BSCF powder.

density was found to be 5.13 g cm^{-3} , water absorbability 0.02% while apparent porosity 0.09%. The theoretical density calculated on the base of value of lattice constant⁴ is 5.81 g cm^{-3} . Therefore, the ratio of the apparent density to the theoretical one was equal only 88.3%, which is the value slightly lower than this one suggested in the literature.⁸

Moreover, as it was found in the case of powder and granulate, the chemical composition of manufactured pellets corresponds to the expected one. The XRD pattern of BSCF pellet (figure 3) presents sharp and intense peaks corresponding to the presence of crystalline BSCF perovskite (PDF: 055–0563) phase with no contaminants. It seems that the additional treatments (pressing and sintering of the sample) improved the phase composition by incorporation of residual raw metal oxides—the amorphous components—into the crystal structure of perovskite.

As mentioned above, the membrane microstructure strongly affects the process of the oxygen separation occurring in this membrane. The SEM micrograph of BSCF pellet

(figure 4) reveals large grains separated by narrow grain boundaries. Such type of microstructure profitably influences on the process of oxygen permeation.³

The mechanical strength and the thermal expansion of perovskite material belong to essential parameters determining its usability for manufacturing of device for oxygen separation, therefore they were also evaluated. The bending strength of BSCF bars achieved value was 57 MPa. It is relatively high value and one can suppose that membranes in the shape of tube, can be formed from this material. Moreover, BSCF bar exhibits relatively low value of thermal expansion coefficient $18.8 \times 10^{-6} 1/K$, which should ensure the reliable membranes sealing in the device for oxygen separation.

Figure 3. XRD pattern of BSCF pellet.

Figure 4. SEM micrograph of BSCF pellet surface.

Figure 5. SEM micrographs of (a) BSCF_1, (b) BSCF_2, (c) BSCF_3 and (d) BSCF_4 membrane surfaces.

However, the most important parameter characterizing usability of oxygen separating membrane is the value of oxygen flux through membrane. For BSCF_0 membrane, the highest value of the oxygen permeation flow ($0.822 \text{ cm}^3 \text{ O}_2/(\text{cm}^2 \text{ min})$) was obtained at 950°C for the air flow 100 ml min^{-1} and the helium flow on the level of 50 ml min^{-1} .

The SEM micrographs of membrane surface (figure 5) enables one to evaluate an effect of sintering temperature on BSCF grain sizes as well as on grains boundaries. The SEM micrograph of BSCF_1 surface (figure 5a) shows the presence of big grains of irregular shapes. The grain boundaries are narrow and many molten insets are visible on the whole surface. In the case of BSCF_2 sample sintered at 1050°C (figure 5b), grains are bigger and the grain

Figure 6. XRD patterns of (a) BSCF_1, (b) BSCF_2, (c) BSCF_3 and (d) BSCF_4 pellets.

Figure 7. Oxygen permeation flux through BSCF_1, BSCF_2, BSCF_3 and BSCF_4 membranes vs. temperature.

Figure 8. Oxygen permeation flux at 950°C through BSCF_1, BSCF_2, BSCF_3 and BSCF_4 membranes vs. an average crystallite size.

boundaries are even less drawn. However, the surface of membranes in the neighbourhood of grain boundaries is rugose. The molten insets have greater size but are less numerous. On the surface of BSCF_3 membrane (sintered at 1100°C) the grain boundaries are almost invisible; however, surface seems to be more rugose (figure 5c). Moreover, the insets, which were presented on the surface of samples sintered at lower temperatures, are almost invisible. The surface of BSCF_4 material (figure 5d) sintered at the highest temperature of 1150°C possesses totally different appearance than sinters discussed up to now. Grains are invisible and along the grains border lines bulges are visible creating numerous rugosity. These quantitative observations are confirmed by

estimations of an average grains size: from 20 to 50 μm ; from 50 to 100 μm ; from 100 to 150 μm and from 120 to 200 μm , respectively, for BSCF_1; BSCF_2; BSCF_3 and BSCF_4.

Summarizing results of SEM analysis, it can be stated that increase of sintering temperature enlarges an average grain size while the grain boundaries become less visible. Moreover, no pores have been found on the surface of studied membranes. The XRD patterns (figure 6) of all membranes reveal the almost ideal BSCF perovskite structure. It is worth noticing that the value of lattice constant ' a ' of studied membranes BSCF is not affected by increase of sintering temperature and is equal to 3.9830(3) $\text{\AA}$ for all samples, while mean size of BSCF crystallites (d_{XRD} , calculated from the

Scherrer equation) increases from 60 nm calculated for BSCF_1 to 130 nm in case of BSCF_4. One can conclude that crystallographic structure of membrane does not change due to sintering procedure used here.

Measurements of oxygen permeation flux through membranes sintered at different temperatures were carried out for constant flows of helium and air of 500 ml min⁻¹. Results are presented in figure 7, from which clearly follows that membrane sintered at the highest temperature possesses the best properties as the oxygen separating device. The oxygen permeation flux at 950°C for membrane BSCF_4 is nearly 35% higher than corresponding one determined for BSCF_1. Increase of both air and helium flows up to 1000 ml min⁻¹ (figure 7, greater marks) enlarges oxygen flow through BSCF_4 membrane up to 2.61 cm³/(cm² min) at 950°C. As it is presented in figure 8, clear correlation between oxygen flux and average size of BSCF crystallites exists. One can conclude that increase of sintering temperature enhances oxygen flux. Unfortunately, sintering of BSCF membrane at higher temperature (1200°C) results in melting of its material.

4. Conclusions

An effect of the sintering temperature on the microstructure and oxygen permeability of dense membrane manufactured from BSCF powder prepared by the solid-state method was determined. It was found that increase of sintering temperature from 1000 to 1150°C leads to material characterized by better-ordered microstructure composed of large grains with lower share of grain boundaries and bigger mean size of BSCF crystallites. Relative amount of insets contaminating membrane surface lowers with the increase in sintering

temperature. All these effects result in improving of membrane effectiveness, which is evident by increase of oxygen-permeation flux at 950°C from 1.69 cm³/(cm² min) (membrane sintered at 1000°C) to 2.28 cm³/(cm² min) in case of membrane sintered at 1150°C.

Acknowledgements

This scientific work was supported by the National Centre for Research and Development, within the confines of Research and Development Strategic Program 'Advanced Technologies for Energy Generation' project no. 2 'Oxy-combustion technology for PC and FBC boilers with CO₂ capture', Agreement no. SP/E/2/66420/10. The support is gratefully acknowledged.

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