Article ID: 1000-324X(2010)02-0221-04 **DOI**: 10.3724/SP.J.1077.2009.09474

Improving the Oxygen Permeability of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ Membranes by Laser Ablation

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Abstract: The surfaces of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCFO) membranes were decorated by laser ablation treatment in order to increase the specific surface of the membrane surface, and laser ablation treatment could improve the ability of oxygen surface exchange and enhance the oxygen permeation flux of the membranes. The arc shape stripes with width about 150μm and depth about 25μm increase the specific surface of the membrane surface significantly, which were made by laser ablation treatment. XRD patterns showed that the BSCFO phase structure was kept after laser ablation treatment. The oxygen permeation fluxes through the membranes after laser ablation treatment were enhanced, and laser ablation treatment with cross stripes pattern on both sides of the membranes had a signification impact on the oxygen permeation flux. The oxygen permeation flux through the membrane with cross stripes pattern on both sides was 34% higher than that through membranes without laser ablation treatment.

Key words: oxygen permeation membrane; laser ablation; specific surface; oxygen permeation flux

In recent years, oxygen permeation membranes made by mixed conducting oxides have attracted a lot of attentions due to their potential applications in fields such as oxygen separation, solid oxide fuel cells and the partial oxidation of methane to syngas[1-4]. A high oxygen permeability of the membranes is desirable in actual applications. It is well known that there are two factors which affect the oxygen permeability of the membranes mainly. One is the bulk diffusion rate of oxygen ions in such membranes, and another is the solid-gas phase exchange rate (surface exchange rate) of oxygen at the surface of the membranes[5]. Pursuing materials which have a high bulk diffusion rate and simultaneously a high surface exchange rate of oxygen is a constant aim in the research field.

Mixed conducting oxides, such as $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCFO)[6], $SrFeCo_{0.5}O_{3-\delta}$ (SFCO)[7] and $La_{0.2}Sr_{0.8}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCFO)[8], may be the most promising materials for oxygen permeation membranes at present. These materials have oxygen permeation flux about or over 1mL/(cm^2·min) for membranes with thickness 1-2mm at temperature about 900℃. As is well known, reducing the thickness of the membrane is feasible to enhance the oxygen permeation flux of such membranes. When thickness reduces to a critical value, a transition from oxygen bulk diffusion limited to surface exchange rate limited will occur and the oxygen surface exchange rate will play a key role in the process of oxygen permeation. In such case, further reducing the thickness will be useless[9]. Therefore, the surface modification technology becomes important. The common method of the surface modification technology is to coat the membrane surface by a catalytic thin layer (such as metals or other ceramic materials) which has a faster surface exchange rate of oxygen than the substrate material, and/or has a larger specific surface area. Such coating layers can improve the surface oxygen exchange rate of the membrane and increase the oxygen permeation flux of the membranes[10-11].

In the present study, a new method was used to increase the specific surface of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCFO) membrane. Laser beam was used to modify the membrane surface and created a pattern of stripe on the surface of the membranes. Due to the increase of the specific surface, a higher oxygen permeation flux can be obtained.

1 Experimental

$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCFO) samples were prepared by the common solid state reaction method. The stoichiometric mixture of $BaCO_3$, $SrCO_3$, Fe_2O_3, and Co_3O_4 were ground in an agate mortar. After decarbonation at 950℃ for 5h, the powders were pressed into

Received date: 2009-07-07, **Modified date**: 2009-09-17, **Published online**: 2009-09-25
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disks with ϕ22mm under a pressure of 120MPa and heated to 1100℃ and held for 5h in air at a heating and cooling rate of 2℃/min. The thickness of the membranes which polished using fine sandpaper was controlled to 1.5mm in order to compare their oxygen flux at the same thickness.

In ambient air, stripes on the surface of the BSCFO membranes were made by a commercial Nd:YAG laser writing system (JBJ-IID, China Daheng) with wave length 1064nm. The laser fluence was about 1.0 J/cm^2 and the scanning speed was 900μm/s. After parallel stripes were made, the sample was turned a right angle and another group of parallel stripes were made, thus a cross shaped pattern on the membrane surface was obtained. Four kinds of samples were made: parallel stripes on the surface of low P_{O_2} side or on both surfaces of the membrane (labeled as SS-BSCFO or SD-BSCFO), cross-shaped pattern on the surface of low P_{O_2} side or on both surfaces of the membrane (labeled as CS-BSCFO or CD-BSCFO).

The phase structures of the samples were identified by X-ray diffraction (XRD) using an X'Pert Pro diffractometer (PANalytical, Holand). The microstructures of the membrane surfaces were observed using a scanning electron microscope (SEM, Model JSM-5610LV, JEOL, Japan).

Oxygen permeability experiments were carried out on a vertical high-temperature gas permeation measuring system. This system has been illuminated in Ref. [11]. The BSCFO membrane disks were sealed on one end of an alumina tube by using high temperature ceramic glass glue which can provide a perfect sealing[12]. High purity helium stream was introduced to the inner of the alumina tube at a flow rate of 50mL/min, and the outside surface of the membrane was exposed to static ambience air. The composition of the effluent helium stream was analyzed with an Agilent T1790 gas chromatograph and the oxygen partial pressure was calculated based on the oxygen content in helium stream. The oxygen permeation experiments were performed in the temperature range of 500-850℃ with a temperature interval 50℃.

2 Results and discussion

The X-ray diffraction patterns of the BSCFO membrane surfaces before and after laser ablation are shown in Fig. 1. After laser ablation, additional diffraction peaks appear at $2\theta = 35.12°$, $51.10°$ and $58.98°$, which can be ascribed to the characteristic diffraction peak of $BaFeO_{3-x}$ and $Fe_{0.95}O$ phase, respectively. These impurities should be generated in the laser ablation process. But the main structure of the samples is still BSCFO phase, which indicates that the laser ablation has no serious effect on the sample phase. Similar result can be found in others work[13].

Figure 2 shows the SEM micrographs of the BSCFO membrane surface after laser ablation. The straight stripes on the BSCFO membrane surface can be seen clearly in Fig. 2(a). The distinction between the regions with and without laser ablation is clear. Many thin cracks were formed due to the material melting and shrinking in the laser ablation process, which had been discussed by Linde, et al[14]. The distance between the adjacent stripes is about 50μm. Figure 2(b) shows the cross section of a stripe. The width of the stripe is about 150μm and the depth is about 25μm. Figure 2(c) shows a top view of the surface with cross shaped pattern. In the second process of laser ablation, the material melted and shrunk again, the cracks were reduced and many large pores were formed. Since the profile of the stripes was arc form and many large pores were formed, it could effectively increase the specific surface of the membrane which was beneficial for improving the surface exchange rate of oxygen.

Figure 3 gives the variation of the oxygen permeation flux of the membranes with temperature, and each membrane thickness is 1.5mm. The value of oxygen permeation flux through BSCFO membrane without laser ablation is about 0.91mL/(cm^2·min) at 850℃. But the

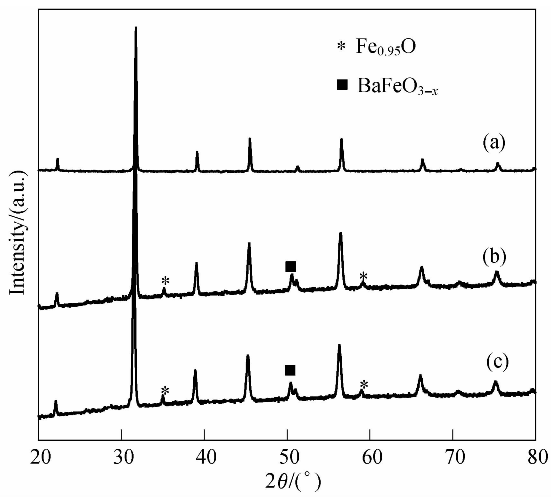

Fig. 1 XRD patterns of (a) BSCFO powder, (b) BSCFO membrane surface after laser ablation (parallel stripes pattern) and (c) BSCFO membrane surface after laser ablation (cross-shaped pattern)

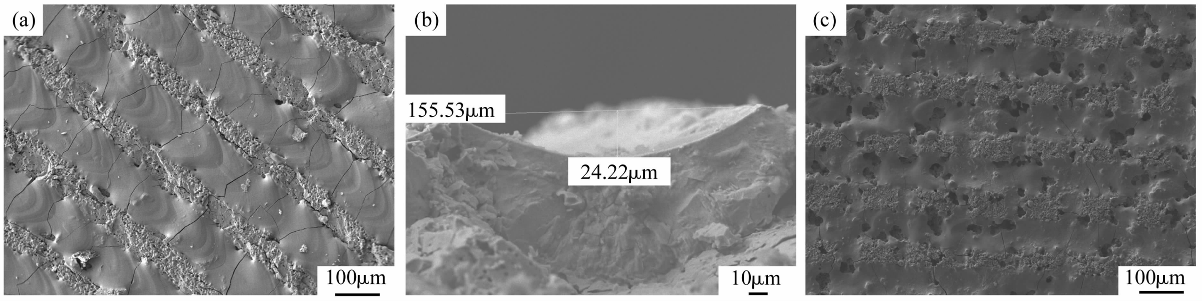

Fig. 2　SEM micrographs of BSCFO membrane surface after laser ablation

(a) Surface with stripes pattern; (b) Cross section of a stripe; (c) Top view of cross-shaped pattern

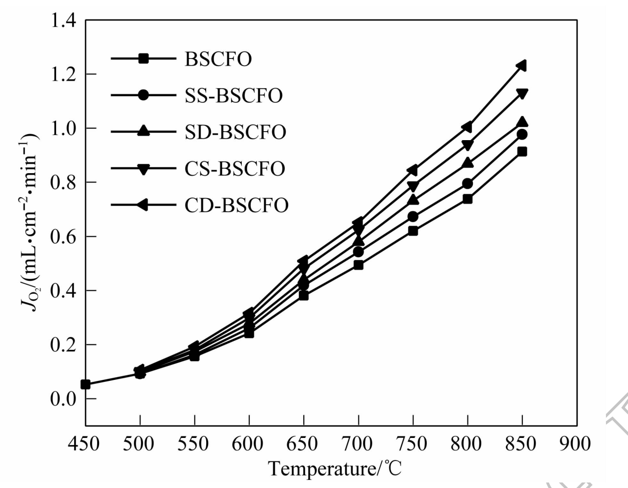

Fig. 3　Oxygen permeation fluxes of different membranes as a function of temperature

Membranes thickness: 1.5mm

values through SS-BSCFO, SD-BSCFO, CS-BSCFO and CD-BSCFO membranes are 0.98, 1.02, 1.13 and 1.23mL/(cm^2·min) at the same temperature, respectively. These values were 7.00%, 11.72%, 23.7% and 34.7% higher than that of the BSCFO membrane without laser ablation. Therefore, the effect of laser ablation on the oxygen permeation flux is obvious and the membrane with cross shaped pattern on both sides is more effective.

Kusaba, *et al*, have indicated that the increase of the specific surface area (roughness) of membrane can improve the oxygen surface exchange property and enhance the oxygen permeation flux[15]. The pores and the arc shape stripes after laser ablation made the surface of the membranes rough, thus they increase the specific surfaces of the membranes surface. As a result, there was more area for the oxygen adsorption on the air side and for oxygen desorption on the helium side, thus theability of gas-solid oxygen exchange was improved.

Shao, *et al*, have pointed that the process of oxygen permeating through BSCFO with thickness about 1.5mm is rate-limited by a combined effect of surface exchange and oxygen bulk diffusion[16]. Therefore, the improvement of surface oxygen exchange can enhance the oxygen permeation flux in our experiments in the experiments. The laser ablation treatment only changed the morphology of the membrane surface and should have no effect on oxygen bulk diffusion. The fluxes increased in according with the order of BSCFO, SS-BSCFO, SD-BSCFO, CS-BSCFO, CD-BSCFO and this order consisted with the order of the increase of the specific surface area of the membranes. Therefore, the increase of the specific surface of the membrane, which was caused by the formation of stripes and pores after laser ablation, should be the main reason for the increasing of the oxygen permeation flux of the membranes in our experiments.

3　Conclusion

The parallel stripes or cross-shaped pattern on the BSCFO membrane surface can be made by laser ablation treatment. Due to the increasing of the specific surface area, the oxygen permeation fluxes through BSCFO membranes can be enhanced. The cross-shaped pattern on both sides of membrane was more effective and resulted in an increase of 34.7% in the oxygen permeation flux. Therefore, laser ablation treatment is a potential way to decorate the membranes surfaces and improves their oxygen permeation flux.

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利用激光刻蚀技术提高 $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ 膜的透氧能力

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摘 要: 利用激光刻图机对 $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$(BSCFO)透氧膜表面进行刻蚀,以提高膜表面的比表面积,改善膜的氧表面交换能力,从而达到提高透氧量的目的. 研究结果表明,激光刻蚀在膜表面形成宽 150μm,深 25μm 的条纹,可以显著提高膜表面的比表面积. XRD 图谱显示,激光刻蚀不会引起 BSCFO 相结构的变化. 透氧量测试表明,激光刻蚀可以增大透氧量,十字交叉双面刻蚀效果更加显著. 十字交叉双面刻蚀后,其透氧量比未用激光处理的样品提高了大约 34%.

关 键 词: 透氧膜; 激光刻蚀; 比表面积; 透氧量
中图分类号: TQ174 **文献标识码**: A