Manufacturing of Metal Supported BSCF Membranes by Spark Plasma Sintering

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Abstract

Spark plasma sintering (SPS), also known as field assisted sintering technique (FAST), is a relatively new method for rapid consolidation of metallic or ceramic powders. In the present work, its suitability for the manufacturing of metal supported $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) based membrane by co-sintering of functional ceramic BSCF layer and porous metallic support has been investigated. The BSCF based membranes are highly attractive for oxygen separation from air due to mixed ionic and electronic conductivity (MIEC) at temperatures around 800°C. Metallic substrate is introduced to enhance mechanical stability of the membrane and to ease joining of membrane modules. Processing conditions were investigated regarding full densification of the BSCF while maintaining open porosity of the substrate. Membrane characterization comprises of microstructure investigation by SEM/EDX, phase analysis by X-ray diffraction, gas tightness by helium leakage measurements as well as oxygen transport behavior.

1. Introduction

The combustion of fossil fuels in an oxygen rich atmosphere is a promising way to increase of efficiency of modern power plants. The application of membranes separating oxygen from air is energy and cost saving alternative to commonly used cryogenic technique. Ceramic materials possessing a perovskite ABO_3 type structure are promising candidates for manufacturing of oxygen separating membranes due to their ionic conductivity rising with temperature. The perovskite $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ was synthesized to increase both ionic conductivity and stability of structure [1, 2]. The oxygen permeability of BSCF membranes grows with decrease of their thickness. Therefore the modern membranes have a double layered structure including thin dense BSCF functional and highly porous supporting layers [3]. The supporting layer is usually made from BSCF powder by space holder technique. This excludes a mismatch in thermal expansion of layers and consequently formation of cracks during sintering. From the other side purely ceramic membranes cannot be easily assembled in modules. The possible solution may be an application of metallic instead of ceramic supporting layer. Thereat a metallic support must be oxidation resistant at operation temperatures which are around 800°C. The nickel based alloy NiCoCrAlY has been investigated as a possible candidate for metallic support. Free co-sintering of BSCF and NiCoCrAlY was till now not fully successful because of diffusion of alloying elements into BSCF and as consequence drastically decrease in oxidation resistance of NiCoCrAlY. In the present paper the applicability of relatively new spark plasma sintering technique for manufacturing of metal supported BSCF membranes was investigated. This technique is based on a rapid heating of samples by current flowing through the electrically conductive tool and conductive sample. The powder consolidation is supported by an external mechanical loading. Due to high heating rates and short consolidation time the minimization of diffusion interaction near contact area of BSCF and NiCoCrAlY was expected. The advantage of SPS application and appearing challenges are highlighted.

2. Experimental

2.1 Samples preparation

The BSCF powder was supplied by Treibacher Industrie AG (Althofen, Austria). It was synthesized by solid state reaction of carbonates following by impact milling. The resulting powder consisted of dense particles with mean specific surface area of 1.6 m^2/g.The particle size distribution is characterized by d_{10}=0.8 μm, d_{50}=2.0 μm and d_{90}=3.7 μm. For manufacturing of metallic support a gas atomized spherical NiCoCrAlY powder (BCM 319, Praxair, USA) was used. The chemical composition of this powder is presented in Table 1. The particle size distribution of starting powder is characterized by d_{10}=15.5 μm, d_{50}=24.0 μm and d_{90}=36.8 μm. The fraction larger then 25 μm was separated from this powder by sieving. This relatively coarse fraction was used in all further sintering experiments to decrease shrinkage of NiCoCrAlY powder at higher temperatures of co-sintering with BSCF powder and thus to increase a permeability of metallic support by maintaining interconnected porosity.

Table 1. Nominal chemical composition of NiCoCrAlY powder used for support manufacturing (wt. %)

Ni	Co	Cr	Al	Y	Hf	Si	Other
Bal.	18.0-26.0	13.0-21.0	10-15.0	0.1-1.0	0.1-1.0	0.1-0.7	$\leq$ 5.0

The sintering experiments have been carried out in a HP D 25/3 spark plasma sintering machine (FCT Systeme GmbH, Rauenstein, Germany). Through all experiments a temperature control mode, no direct current pulsing and a vacuum of 0.05 mbar have been applied. The tool set-up used in experiments is shown in Fig. 1. The tool consists of an upper and a lower cylindrical punch with a diameter of 15 mm and a length of 35 mm, two conical protection plates with diameters of 34 and 80 mm and an axial height of 45 mm and a die with a wall thickness of 12.5 mm and a height of 48 mm. In the case of sintering of NiCoCrAlY samples the diameter of punches and the internal diameter of die were increased to 20 mm. All tool components were machined from isostatically pressed Ringsdorff® graphite bars (grade R 7710, SGL Carbon GmbH, Bonn, Germany). In order to minimize the radiation heat losses and to enhance the temperature homogeneity, the graphite die was insulated from ambient by a Sigratherm® carbon felt with thickness of 10 mm (type KFA 10, SGL Carbon GmbH, Meitingen, Germany). Sigraflex® graphite foil (SGL Carbon GmbH, Meitingen, Germany) with a thickness of 0.35 mm was inserted between the punches and the die to enhance the electric and thermal conductivity of the contact. During the experiments, the temperature was measured by a central pyrometer focusing on the bottom of the central borehole in the upper protection plate and punch (Fig. 1). The distance between the focusing point and the top of the sample was around 4 mm. The pyrometer reading was used as an input signal for a PID temperature controller. The small distance between the point of temperature measurement and the top of a sample insured accurate temperature control.

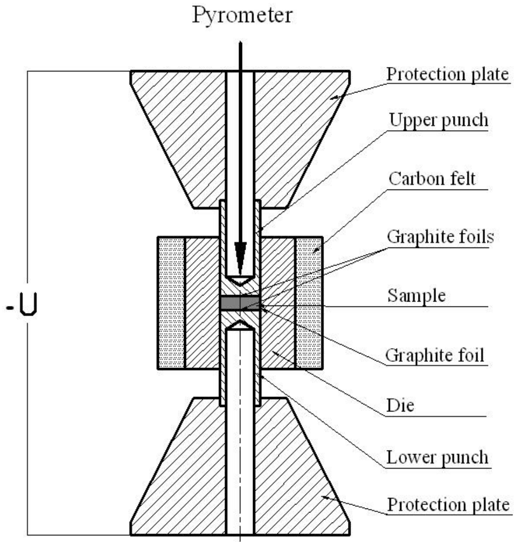

Figure 1. Schematic representation of the graphite tool used in spark plasma sintering experiments

Three types of experiments were carried out. Firstly the sintering behavior of NiCoCrAlY powder has been investigated to determine SPS parameters providing manufacturing of a sufficiently porous and strong metallic support. Then the sintering of BSCF powder has been studied to get SPS conditions needed for its full densification. In the third set of experiments the co-sintering of NiCoCrAlY and BSCF powders has been explored. The heating rate in all experiments has been maintained as 100°C min^{-1}. In all cases a constant load of 5 kN has been applied at the beginning of a sintering cycle to create proper contacts between the components of the machine, tool and sample. This load corresponds to pressure of 28.3 MPa applied to a powder loaded in a 15 mm die and to 15 MPa if a 20 mm die was used. Before filling the vertical Sigraflex$^{®}$ graphite foil has been inserted in the die and the disc cut from this foil has been placed on the top of the lower punch as shown in Fig. 1. After that a fixed amount of powder has been poured into the die. In the case of plain NiCoCrAlY powder the mass of powder was 6 g, and in the case of plain BSCF powder the mass was 2 g. For manufacturing of double layer samples 2 g of NiCoCrAlY powder and then 1.5 g of BSCF powder have been poured into the die. The Sigraflex$^{®}$ graphite disc has been placed on the top of a powder column to create a proper contact with the upper punch (Fig. 1). All graphite foils elements were treated by a BN spray to avoid a possible interaction of BSCF material with graphite.

The temperature profile of all SPS cycles consisted of a heating stage, dwell and a cooling stage. The initial minimal load of 5 kN was maintained constant during whole SPS cycle or continuously increased to certain maximal value after temperature of 600°C was reached. The maximal value of load has been maintained constant during a dwell period. All SPS cycles used in the present work are summarized in Table 2.

Table 2. Characteristic parameters of SPS cycles used for sintering of samples

Sample	Temperature, °C	Pressure, MPa	Dwell, s
NiCoCrAlY	800	15	30
	900	20	0; 15; 30
BSCF	900; 1000; 1010; 1020; 1030; 1040; 1050	28	15
	950	50	120
	1000	50	120; 240; 360
	1000; 1050; 1070; 1080; 1090	50	240
NiCoCrAlY / BSCF	900	28	15
	1000	28	15
		50	240

2.2 Characterization procedures

The Archimedes method has been applied for density measurements of sintered BSCF samples. The porosity of NiCoCrAlY layer in a prototype of membrane and porosity of plain NiCoCrAlY sintered samples have been determined by an image analysis using AnalySIS pro 5.0 software (Olympus Soft Imaging Solution GmbH, Münster, Germany). The microstructure of samples has been investigated by a light microscope PMG 3 (Olympus Corp., Tokyo, Japan) and by a scanning electron microscope Ultra 55 (Carl Zeiss AG, Oberkochen, Germany). The chemical composition of phases has been studied by EDX spectrometer Inca Energy 355 (Oxford Instruments, UK). The retention of a perovskite structure of BSCF after spark plasma sintering has been checked by a Bruker XRD apparatus type D4 (Bruker AXS GmbH, Karlsruhe, Germany) and monochromatic Cu-K_{α} radiation. The helium leakage tests of BSCF samples and membrane prototypes have been carried out by HLT260 instrument (Pfeiffer Vacuum GmbH, Asslar, Germany). The oxygen permeation of monolayer BSCF samples and BSCF based membrane prototype has been evaluated at temperatures up to 1000°C using air as a feed gas by home made equipment as described elsewhere [3,4].

3. Results and Discussion

3.1. Densification

The values of porosity of NiCoCrAlY samples after spark plasma sintering at different conditions are summarized in Table 3. Porosity clearly decreases with increase in temperature and soak period. At the same time mechanical strength of samples grows with decrease in porosity and increase in temperature, pressure and dwell duration time sintering. Interconnected porosity over 40% was discussed as acceptable for air transport in the substrate, which supports the BSCF layer. Therefore temperature of 900°C, pressure around 20 MPa and dwell of 15 s has been taken as optimal set of SPS conditions of NiCoCrAlY sintering for the particle size fraction used in this study.

The porosities of BSCF samples spark plasma sintered at different conditions are presented in Table 4. As evident from this table, the pressure of 28 MPa and dwell of 5 s are insufficient for obtaining closed porosity (usually below 5%) even at 1050°C sintering. Therefore the pressure was increased to 50 MPa and soak time to 120 s and more. As a result the samples with porosity under 4% were manufactured at temperatures of 1000-1080°C. These conditions are in good agreement with data reported by Darab et al. [5]. The resulting microstructures (cross section) of porous NiCoCrAlY and dense BSCF samples are presented in Fig. 2.

Table 3. Porosity of NiCoCrAlY samples after spark plasma sintering at different conditions

Temperature, °C	Pressure, MPa	Dwell, s	Porosity, %
800	15	30	45
900	20	0	48
		15	42
		30	37

Table 4. Porosity of BSCF samples after spark plasma sintering at different conditions

Temperature,°C	Pressure, MPa	Dwell, s	Porosity, %
1050	28	15	16
1000	50	120	3.4
		240	2.1
		360	2.0
1050	50	240	1.7
1070			1.5
1080			1.0

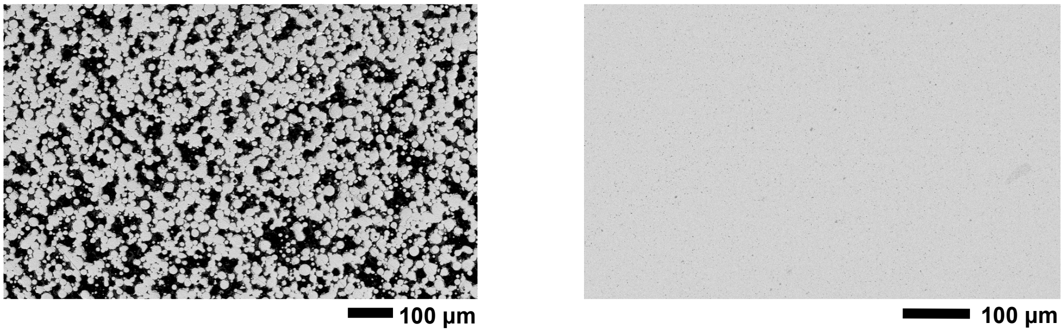

Figure 2. Microstructure of porous NiCoCrAlY sample (left) and dense BSCF sample (right) spark plasma sintered at 900°C, 20 MPa, 15 s and 1070°C, 50 MPa, 240 s.

3.2. Microstructure

The microstructure of spark plasma sintered BSCF sample (1040C, 50 MPa, 15 s) at higher magnification is shown in Fig. 3. The chemical compositions of phases were investigated by SEM/EDX elemental analysis. The composition of bright phase corresponds to the basic material $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and the dark spots show increased content of cobalt. This phase can be attributed to the cobalt oxide frequently observed in sintered BSCF.

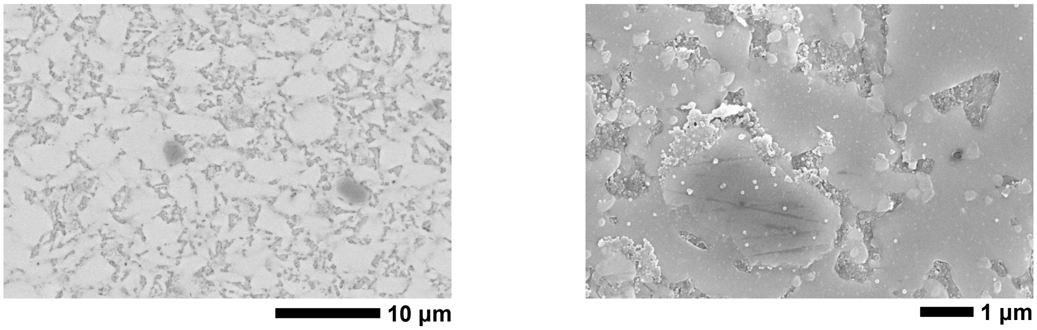

Figure 3. Cobalt rich regions (dark phase) observed in the microstructure BSCF samples

Nevertheless, an X-ray diffraction analysis of BSCF samples spark plasma sintered at 1000°C during 120-360 s and samples sintered during 240 s at 1050°C, 1070°C and 1080°C has shown that the initial perovskite structure of BSCF remains in general unaltered. Therefore a reasonable oxygen permeability of spark plasma sintered BSCF samples can be expected.

3.3. Co-sintering

The BSCF and NiCoCrAlY powders were spark plasma co-sintered at 900°C, 28 MPa, 15 s to maintain porosity of metallic layer. One pellet was spark plasma sintered at 1000°C, 28 MPa, 15 s. Another pellet was spark plasma consolidated at 1000°C, 50 MPa, 240 s and then additionally sintered in air at 1000°C for 12 hours. The pellets were optically of good quality (Fig. 5). No delamination of metal and ceramic layers was observed. The porosity of metallic layer was evaluated by image analysis as 25.5% for samples sintered at 1000°C, 28 MPa, 15 s and as 34.0% for sample sintered at 900°C, 28 MPa, 15 s. Thus both these samples had relatively dense metallic layer.

Figure 5. Double layer samples manufactured by SPS co-sintering of BSCF and NiCoCrAlY powders

The contact surface of metal and ceramic joint after SPS was free of any transient phases. The transient phases have been appeared after additional sintering in air due to diffusion of Ni and Al atoms from NiCoCrAlY into BSCF as shown in Fig. 6. The generation of a transient layer leads to a decrease in oxygen conductivity of contact surface. Besides this after additional sintering a number of cracks appear.

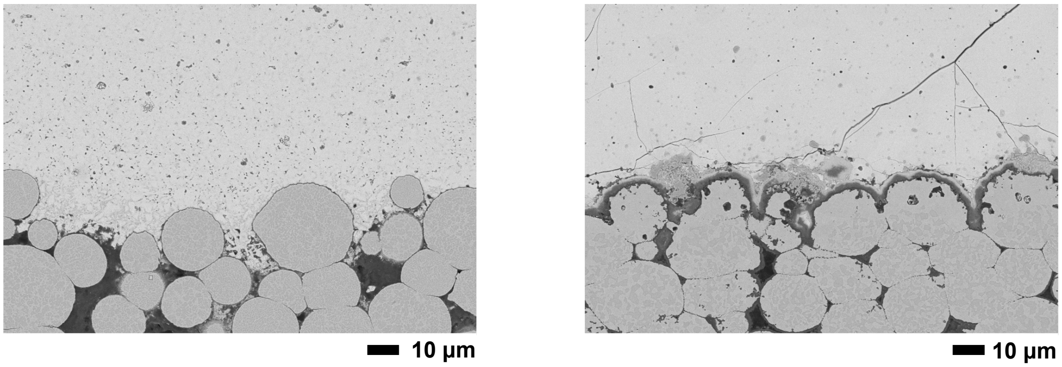

Figure 5. Contact surface between BSCF and NiCoCrAlY layers after spark plasma sintering (left) and after additional free sintering (right)

3.4. Oxygen permeation

The oxygen permeation rate of two dense monolayer BSCF samples sintered at 1070°C and 1080°C and one double layer sample sintered at 900°C (see Table 1) was investigated. The obtained results are presented in Fig. 7. The comparison with oxygen permeation rate of free sintered BSCF samples of similar thickness shows slightly lower permeability of monolayer samples produced by SPS. The oxygen permeation rate of double layer spark plasma sintered sample is far below of values of free sintered samples. This can be attributed to low porosity of metallic layer and insufficient density and microcracks in BSCF layer. The low porosity of metallic layer reduces whole permeation through the sample. The insufficient density and microcracks in BSCF layer result from the decrease of oxygen partial pressure gradient over the sample thickness. Thus its oxygen permeation rate is significantly diminished.

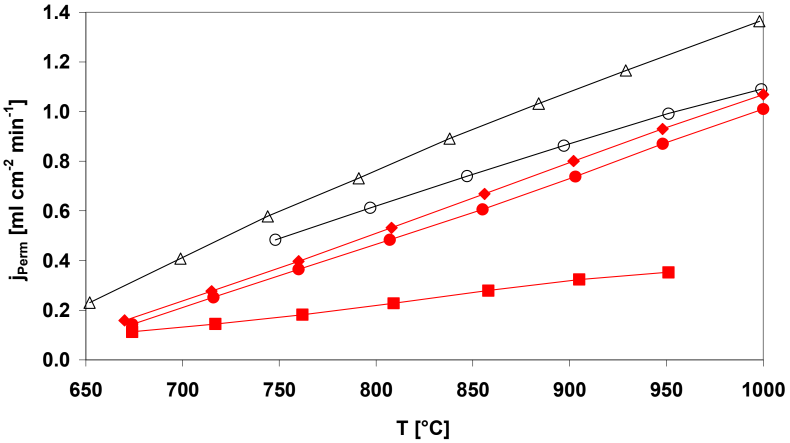

Figure 7. Oxygen permeation rate of: 2 mm (△) and 2.5 mm (○) thick free sintered BSCF samples; 2 mm thick spark plasma sintered at 1070°C, 50 MPa, 240 s (●) and at 1080°C, 50 MPa, 240 s (◆) BSCF samples; double layer BSCF/NiCoCrAlY sample spark plasma sintered at 900°C, 28 MPa, 15 s (■).

4. Conclusions and Outlook

The present work has shown that both porous NiCoCrAlY and fully dense BSCF elements of a metal supported BSCF membrane can be successfully manufactured by Spark Plasma Sintering as two separate parts. Essentially different sintering conditions (temperature, pressure and soak time) are needed to maintain a sufficient porosity of NiCoCrAlY element and to obtain a fully dense BSCF element. The spark plasma co-sintering of BSCF and NiCoCrAlY at condition providing porosity of 34% for metallic support allowed producing of an optically qualitative prototype of membrane, but its evaluated oxygen permeation rate was low comparing to sintered monolayer BSCF samples. In our opinion the reasons for that are insufficient porosity of metallic layer and insufficient density and microcracks in BSCF layer. The low porosity of metallic support leads to decrease in general permeability of membrane. The insufficient density of BSCF results in reduction of oxygen partial pressure difference on functional layer and thus in diminishing the driving force for oxygen conduction. Therefore the further work is needed to bring closer the conditions of successful spark plasma sintering of metallic and ceramic powders for instance by using coarser NiCoCrAlY powder or by application of metal with higher sintering temperature.

Besides this, other BSCF spark plasma sintering peculiarities were found. A direct contact with graphite foil leads to embrittlement of BSCF during SPS. Therefore such contact must be avoided for example by coating of foil surface by BN spray. The starting perovskite structure of BSCF remains unaltered after SPS up to 1080°C and during dwell up to 240 s. This is a prerequisite of the high oxygen permeability of dense spark plasma sintered BSCF samples, which is close to the permeability of samples free sintered at optimized conditions. From the other side spark plasma sintered BSCF possess higher density and therefore is impermeable for air. Thus application of spark plasma sintered BSCF can be potentially more effective. Moreover, the spark plasma co-sintering of BSCF and NiCoCrAlY powders has shown a reasonable joint of ceramic and metallic layers without formation of diffusion layer reducing oxygen permeation and sufficiently decreasing oxidation resistance of NiCoCrAlY support.

5. References

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