Reactionary-solidified oxygen permeable membrane material based on cermet Bi$_{1.6}$Er$_{0.4}$O$_3$ – 26 wt % Ag – 4 wt % In

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Abstract. Using hot uniaxially pressing in argon atmosphere at 800 °C and at a stress of 6 MPa, the high-density reactionary-solidified cermet material based on Bi$_{1.6}$Er$_{0.4}$O$_3$ - 26 wt % Ag - 4 wt % In with total porosity of less than 0.3 % was firstly synthesized. The relationship between phase composition, microstructure, oxygen permeability coefficient, and oxygen selectivity (vs air nitrogen) of this material before and after its long-term (100 hours) operation as an ion transport membrane was established. The dependences of oxygen transport through this cermet material at 650-800 °C were investigated: for example, at 800 °C and at a ratio of oxygen partial pressures on both sides of the membrane of about 20, the oxygen transfer regime changes from diffusion to kinetics while the characteristic thicknesses of membrane were of 0.11 cm. It was shown that at 800 °C the membrane material based on Bi$_{1.6}$Er$_{0.4}$O$_3$ - 26 wt % Ag - 4 wt % In had an oxygen permeability coefficient of $1.1 \times 10^{-8}$ mol/cm/s, while its selectivity for oxygen (over nitrogen) was about 100. The decrease in oxygen flux by 1.3-1.5 times during 100 hours of work at 700-800 °C with a slight change in oxygen selectivity was observed, thus the possible causes of this phenomenon were explained.

1. Introduction

Despite many years of researching, there is still no optimal medium-temperature (600-800 °C) membrane material for separation of oxygen from air, since the currently known single-phase (cobaltites, cobaltite-ferrites and manganites of alkaline-earth or rare-earth cations) or composite (cermets, perovskite-fluorite or spinel-fluorite composites) materials do not completely satisfy all the requirements for long-term stability or performance [1-4]. In some of them (perovskites and cermets), a high level of oxygen permeability has already been achieved, while, unlike perovskites, cermets have better thermal, chemical and mechanical stability. In addition, the indisputable advantage of cermet materials for ion-transport membranes compared to perovskite ones is a lower range of operating temperatures (from 500 °C), and also, when having both percolation of ion-conducting ceramic and electron-conducting metal nets, the much higher oxygen permeability is achieved [5-8]. However, due to the differences of ceramic and metallic components, there is a technological problem of creating high-density, highly oxygen-selective (vs air nitrogen) and oxygen-permeable cermets with percolative ceramic and metal components. This is mainly due to the formation of either scaly (i.e. incoherent, when silver is introduced into cermet in the form of metal with its subsequent pressing, resulting to the formation of a membrane with low oxygen permeability, but with high oxygen selectivity), or porous (i.e. non-gas tight, when silver is introduced in cermet in the form of Ag$_2$O, and the resulting membrane is highly oxygen-permeable, but poorly oxygen-selective) of the structure of the material. In this regard, the question of creating porous-free cermet materials with high selective...
oxygen permeability is very relevant. This problem has been solved in our laboratory by creating the partly molten oxide composite membrane materials [9-11]. However, such membranes have a significant drawback that impedes their practical use - high creep, accompanied by deterioration in transport characteristics. To overcome this problem, in the present work, it is proposed to use a fusible component not at membrane operating temperatures, but in the process of preparation of the material. Metallic indium, known to have a melting point of about 160 °C and oxidation resistance up to 800 °C, will be taken as such a low-melting component [12]. It is assumed that liquid indium, which is a surface-active modifier of the silver particles [13], will provide compaction of the material and will prevent recrystallization of silver particles, and will also interact with silver above 330 °C to form a plastic α-Ag solid solution [12]. The choice of the ceramic component Bi$_{1.6}$Er$_{0.4}$O$_3$ is due to its high oxygen-ion conductivity at 500-800 °C [14].

In this regard, the main aim of this work is to develop a reactionary-solidified membrane material for oxygen separation based on cermet Bi$_{1.6}$Er$_{0.4}$O$_3$ - 26 wt % Ag - 4 wt % In. Its composition has been empirically selected based on the Ag-In phase diagram [12], as well as from considerations of further obtaining the maximum of electronic and ionic conductivity for the membrane material.

2. Experimental

The synthesis of samples was carried out in two stages. At the first stage, Bi$_{1.6}$Er$_{0.4}$O$_3$ powder was obtained by solid-phase synthesis from starting components of bismuth oxide (Bi$_2$O$_3$) and erbium oxide (Er$_2$O$_3$) purity of 99.99 %. The powder mixture of Bi$_2$O$_3$ and Er$_2$O$_3$ was ground in isopropyl alcohol for 30 minutes using a Pulverisette 5 planetary mill (Fritsch, Germany) at room temperature, then was dried in an oven at 120 °C for 4 hours and was annealed at 800 °C for 20 hours with intermediate grinding. Silver oxide (I) was obtained by adding to the aqueous solution of silver nitrate (1 M) a twofold excess of potassium hydroxide (2.5 M) according to reaction: 2AgNO$_3$ + 2KOH (excess) → Ag$_2$O↓ + 2KNO$_3$ + H$_2$O. The resulting black precipitate was filtered using a Buchner funnel, washed thoroughly and dried in an oven at 120 °C for 4 hours.

At the second stage, powder mixture of Bi$_{1.6}$Er$_{0.4}$O$_3$ - 26 wt % Ag - 4 wt % In composition was prepared, taking into account the reduction of Ag$_2$O to Ag, and then it was thoroughly mixed in a planetary mill for 1 h in isopropyl alcohol and was dried in oven at 120 °C for 4 hours. Then, the powder was placed in a corundum mold (diameter of 1.5 cm) and calcined in an HP20-3560-20 hot uniaxial pressing machine (Thermal Technology Inc., USA) at a temperature of 800 °C for 1 hour in an argon atmosphere at a pressure of 6 MPa. To relieve mechanical stresses, the obtained samples were calcined at 800 °C for 24 hours in a vacuum furnace in argon atmosphere. The obtained samples were in the form of tablets with a diameter of 1.5 cm and a height of 1.5-2.0 cm, from which the samples of 0.1-0.5 cm thick were made on a cutting machine (STRUERS, Denmark).

Phase composition of both oxide powders of Bi$_{1.6}$Er$_{0.4}$O$_3$, Ag$_2$O and cermet membranes was characterized by X-ray phase analysis on an XRD-6000 diffractometer (Shimadzu, Japan) using CuKα - radiation. The decoding of X-ray diffraction patterns was performed using ICDD PDF-2 database. Microstructure of polished cross section for the cermets before and after long-term tests, which had been prepared by STRUERS equipment, was investigated by Olympus GX-51 optical microscope. Open, closed and total porosity of the composite was measured by hydrostatic weighing.

The measurements of oxygen fluxes for cermet membranes (tablet of Ø = 1.5 cm, h = 0.1-0.4 cm) were performed by gas chromatography technique at 650 °C, 700 °C, 750 °C and 800 °C on Crystallux-4000M (Russia) gas chromatograph. To do this, the polished tablet was tightly connected to the end of the measuring cell, which was placed into a tube furnace and heated to the temperature of 650-800 °C. From the outside face, the tablet was in contact with air, and from the inner face it was connected to a gas chromatograph, while the sweep gas (helium) was blown through the measuring cell to remove the gas mixture penetrated through the sample. The selectivity of composite membrane was evaluated by the ratio of concentrations of oxygen over nitrogen in the analyzing gas mixture (consisted of oxygen, nitrogen, and helium). The rate of sweep gas flow was 5-20 ml/min. Oxygen
fluxes, oxygen permeability coefficients, and characteristic thicknesses of membranes were measured according to methods, fully described earlier in our previous papers [9, 15].

3. Results and discussion
Figure 1 illustrates the dependences of oxygen flux for 0.1 cm thick cermet membrane on oxygen partial pressure differences and on inverse temperature. The oxygen fluxes rise at an increase in the temperature and oxygen partial pressure differences, and evaluated activation energy of oxygen mass transfer is about 0.8 eV. To establish the regime of oxygen mass transfer through cermet membranes, oxygen permeation tests for some membranes with different thickness have been examined (Figure 2). The values of characteristic thicknesses of all the membranes at every temperatures, according to Burggraaf’s model of mass transfer [16], were close to 0.11 cm. Such values are in good agreements with literature data [5] for the same membrane materials at the same temperatures, but without indium.

**Figure 3a.** Micrograph of polished cross section for as-sintered initial cermet membrane material of Bi$_{1.6}$Er$_{0.4}$O$_3$ - $\alpha$-Ag

**Figure 3b.** Micrograph of polished cross section for the same cermet membrane material after gas chromatographic tests at 700 °C during 100 hours

**Figure 4.** X-rays patterns of initial cermet membrane material (upper graph) and that of the same material after gas chromatographic tests at 700 °C during 100 hours (lower graph)

**Figure 5.** Time (τ) dependences of oxygen flux (j) for 0.1 cm thick cermet membrane at 700 °C and at 800 °C when oxygen partial pressure difference $\ln \frac{P}{P^*} = 3$
The calculated value of oxygen permeability coefficient was close to $1.1 \times 10^{-8}$ mol/cm/s at 800 °C, which is also close to literature data [5], but in our case the content of expensive silver is 25 % lower. The estimated value of selectivity for oxygen (over nitrogen) was about 100 (the value of total porosity was less than 0.3 %), that is definitely very outstanding result for such cermet membrane material. But, the key factor for such membrane material with different components (metal and ceramics) is its long-term stability. Figures 3-5 indicate the problems of instability for membrane material, like agglomeration of silver (Figure 3) or formation of low conductive indium oxide (Figure 4), and, as the result, decreasing of oxygen fluxes during 100 hours of exploitation at 700 °C and at 800 °C by 1.3 and 1.5 times, accordingly. One more problem is the migration of oxygen-conductive silver [17-18] onto the opposite side of membrane, which is the main hindering factor, besides the cost of silver-containing cermets, overcoming their future application in oxygen membrane technology.

4. Conclusions
A new cermet membrane material based on Bi$_{1.6}$Er$_{0.4}$O$_3$ - 26 wt % Ag - 4 wt % In has been firstly synthesized and characterized. The idea of forming the reactionary-solidified oxygen-selective and oxygen-permeable membrane material is quiet workable and applicable. The evaluated selectivity of oxygen over nitrogen is outstanding, but in fact the instability of transport properties, phase composition, and microstructure of investigated cermet membrane material during long-term tests gives us no chance to the future application of such material in oxygen membrane technology.

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