The obtaining and properties of asymmetric ion transport membrane for separating of oxygen from air

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Abstract. The bilayer oxygen-permeable membrane, consisting of a thin-film dense composite based on Co$_3$O$_4$ - 36 wt. % Bi$_2$O$_3$, and of a porous ceramic substrate of Co$_2$SiO$_4$, was synthesized and characterized. The way for obtaining of porous ceramic based on cobalt silicate was found, while the microstructure and the mechanical properties of porous ceramic were studied. Layered casting with post-pressing was used to cover the surface of porous support of Co$_2$SiO$_4$ by the Co$_3$O$_4$ - 36 wt. % Bi$_2$O$_3$ - based film. Transport properties of the asymmetric membrane have been studied, the kinetic features of oxygen transport have been established, and the characteristic thickness of the membrane has been estimated. The methods to prevent the high-temperature creep of ion transport membranes based on solid/molten oxides, which are the promising ones for obtaining of pure oxygen from air, are proposed and discussed.

1. Introduction

One of the urgent problems of modern membrane science is the production of high-purity oxygen, which is necessary for needs of nanoelectronics, medicine and pharmaceuticals [1]. For the obtaining of oxygen by using the ion transport membranes many people typically apply inorganic mixed-conducting oxide materials, such as BSCF [2] or LSCF [3], operating at a temperature of above 850 °C. Despite of the many-years investigations, the question of creating of the membrane material, operating in the intermediate-temperature region, with stable transport characteristics during 40,000 hours of exploitation is still remaining the relevant [4]. It is evident that technological efforts for lowering operating temperatures of the membranes to 500-850 °C while maintaining the same values of transport properties as for known for the high-temperature systems are required [5]. One of such decisions is the creating of new more advanced membrane materials, which possess high oxygen permeability and selectivity at separation of an air.

Nowadays the direction, related to the creating of solid/molten composite membrane materials with high mixed oxygen-ion and electron conductivity in the intermediate-temperature range below 850 °C, widely develops and is being investigated [6, 7]. The indisputable advantage of such membranes is the high selectivity of the process of concentrating of oxygen and possibility to generate a product of high purity [8]. It is possible due to the presence of wetting interlayers at grain boundaries of the solid skeleton and forming of so-called "liquid-channel grain-boundary structure" [9]. Predominantly, in
such composites the solid component has an electronic conductivity, while the melt is predominantly an oxygen-ion conductor [10]. Thus, the membrane material of the above-mentioned type based on Co$_3$O$_4$ - 36 wt. % Bi$_2$O$_3$ showed high oxygen permeability with a record selectivity of oxygen over nitrogen (> 100,000) at 790-850 °C [11]. In addition, it was found that the transport of oxygen through the given membrane material of 1.5-3.3 mm thick was carried out in a diffusion regime according to Wagner's mass transfer law (the flux was inversely proportional to the thickness of membrane) [12]. It is assumed that such membrane material may replace the high-temperature membrane materials having the various disadvantages. However, for the practical use of such material in oxygen separators it is necessary to increase its productivity by minimizing the membrane thickness, which may be achieved by creating a thin-film solid/molten oxide membrane onto a porous ceramic substrate. In this case the thin-film ion transport membrane should possess high mixed ionic-electronic conductivity and provide an accelerated ambipolar transport of charge carriers, and the porous substrate should operate as a high-performance track system to penetrate and remove of pure oxygen. When developing the asymmetric "porous substrate / dense ion transport membrane" system, the chemical and thermal compatibility of the membrane material with this substrate, as well as their stability under operating conditions, are required. Besides, the substrate must have big open porosity (about 40 %), but acceptable mechanical properties (strength must be not less than 30-50 MPa), thus the development of such system should take into account all these necessary aspects. In the present work, Co$_3$SiO$_4$ with a structure of olivine [13] has been chosen as the porous substrate because it is chemically and thermally compatible with the solid/molten composite thin-film membrane of Co$_3$O$_4$ - 36 wt. % Bi$_2$O$_3$. This article is devoted to the development of an asymmetric oxygen-permeable membrane based on the above-mentioned materials.

2. Experimental

The initial components to synthesize Co$_3$SiO$_4$ phase were Co$_3$O$_4$ (99,9% purity) and amorphous SiO$_2$ with a specific surface area of 350 m$^2$/g. Amorphous SiO$_2$ was taken in excess (3%) due to removal of water during the crystallization, while Co$_3$O$_4$ was taken in excess (7%) due to decomposition to CoO at heating of above 900 °C. The powder was premixed in a planetary mill (Pulverisette 5, rotation speed of 200 rpm, duration of 5 hours) with additive of ethyl alcohol (1:1 by volume) and held for 3 hours at 120 °C in a drying camera for removal alcohol, then was sintered on zirconia crucible in air at 1200 °C for 40 hours with an intermediate grinding and homogenization. The resulting single-phased product was grinded and used as a starting component to obtain the porous ceramics.

To obtain the porous ceramics of Co$_3$SiO$_4$, the powder mixture of particles size of 20-30 μm (60%), of 0.1-1 μm (25%), and of 1-10 μm (15%) was used. Such size distribution, as shown on a Figure 1, was chosen a priori for production of porous but strong enough ceramics, since it is known that the growth of average grains and the formation of isthmuses in the porous skeleton are due to dissolution of small particles with the recrystallization of average particles. A carbon black of 5-10 μm was used as a technological burning out additive. The Co$_3$SiO$_4$: carbon black (mass ratio of 3:1) composition was obtained by mixing in ethyl alcohol (1:1 by volume) in a planetary mill for 30 minutes at a rotation speed of 120 rpm with drying to remove an alcohol. The resulting powder was then cold uniaxially pressed (100 MPa) into tablets (diameter of 30 mm, height 4 mm for the subsequent studying of transport properties, and diameter of 6 mm, height of 20 mm for the strength measurements). These tablets were sintered in air on zirconia substrates at 1200 °C for 20 hours with a slow heating of the furnace (2 °C/min) to burn out the carbon black and to form pores in ceramics.

The forming of a thin-film material based on Co$_3$O$_4$ - 36 wt. % Bi$_2$O$_3$ onto a porous substrate of Co$_3$SiO$_4$ was carried out by layered (100 μm) covering by the suspension, which was prepared in an agate mortar by homogenization and was consisted of Co$_3$O$_4$ (99.9% purity), Bi$_2$O$_3$ (99.9% purity) and 5% polyvinyl alcohol aqueous solution (10% by weight). The suspension was covered onto a pre-polished porous Co$_3$SiO$_4$ substrate with a Teflon spatula, then was dried at 120 °C to remove water. Then the next layer was applied, and the procedure was repeated to form the controlled coatings with the thickness of 0.7 mm, 0.5 mm and 0.3 mm. The finish forming of the coatings was carried out by its
cold uniaxially pressing (10 MPa) using vacuum-tight rubber, protected with a Teflon film. The obtaining material was annealed at 750 °C for 5 hours with a slow heating of the furnace (2 °C/min).

Figure 1. Chosen particle size distribution of Co$_2$SiO$_4$ powder

X-ray analysis (XRD) was performed on Shimadzu XRD-6000 diffractometer, the interval of angles was 10-90 ° with the steps of 0.1 ° (CuKα radiation, wavelength λ = 1.54178 Å). The decoding of the initial X-ray diffraction patterns was carried out using ICDD PDF-2.

The manufacturing of polished samples for the subsequent studying of their microstructure was carried out with using STRUERS equipment. The samples were placed in automatic hot press on the bottom of a cylindrical shape (diameter of 30 mm, depth of 10 mm). Then the shape was filled by a conductive resin, which solidified after heat treatment. Both SiC papers (grades of 80 to 4000) and diamond pastes of various granularity were used to polish the samples. The microstructure of polished sections was studied on Olympus GX-51 optical microscope.

The studying of burn-up of carbon black from the initial powder for synthesis of porous ceramics was carried out by thermogravimetry (TG) and differential thermal analysis (DTA) using NETZSCH STA 449 F3 Jupiter thermal analyzer. The powder of Co$_2$SiO$_4$ + C was placed in a YSZ crucible and heated in an air atmosphere at a rate of 20 °C/min from room temperature to 1300 °C.

The strength on three-point bending was studied using Instron 3382 testing machine. The measurements were carried out at a room temperature using five cylindrical samples (the length of 15 mm, the diameter of 5 mm, the load of 0 - 100 kg, the distance between supports of 12 mm). The obtained strength results were averaged, and the error of measurements was evaluated.

The oxygen permeation of the composite membranes was measured using gas chromatography. The testing samples were polished to the diameter of 25 mm, and their edges were covered by silver paste with the average grain size of Ag of 1 μm. Then the samples were annealed at 700 °C for 5 hours to form a dense edge coatings and to eliminate of possible air leaks. The resulting samples of 3-4 mm thick (the thicknesses of dense coating of Co$_3$O$_4$ - 36 wt. % Bi$_2$O$_3$ were of 0.2 mm, of 0.4 mm, and of 0.6 mm) were hermetically sealed at the end of the quartz tube, while the other end of this tube was connected to inlet of a gas chromatograph. The collected cells were placed in a tube furnace and heated to the temperature of 790-850 °C. The samples were in contact with air in the furnace from the one side, while the other side of samples was blown by sweep gas (helium) to removal a penetrated oxygen. The obtaining gas mixture (oxygen and helium) was directed to a chromatograph to determine the concentration of oxygen. The rate of helium was fixed to be 5-20 mL/min.
3. Results and discussion

According to X-ray analysis data, it was shown that the yield of Co$_2$SiO$_4$ olivine (JCPDS No. 84-1298) was 100%. Basing to Zhuravlev’s model [14], the full transformation of amorphous SiO$_2$ to crystalline tridymite completes at 1200 °C, after that, according to CoO - SiO$_2$ phase diagram [15], the Co$_2$SiO$_4$ formation is taken place. Phase analysis of the coating deposited on the surface of a porous ceramic based on Co$_2$SiO$_4$ showed the formation of two phases - Co$_3$O$_4$ with a spinel structure (JCPDS No. 42-1467) and Bi$_{88}$Co$_3$O$_{136}$, which was isostructural to sillenite $\gamma$-Bi$_2$O$_3$ (JCPDS No. 45-1344). This is in a good agreement to phase diagram of Co$_3$O$_4$ - Bi$_2$O$_3$ system [16]. The quantitative composition of the coating corresponds to Co$_3$O$_4$ - 36 wt. % Bi$_2$O$_3$, all peaks have been indexed and determined.

The thermal analysis data for Co$_2$SiO$_4$ + C powder indicates slight increasing in mass up to 850 °C, which is apparently due to the sorption of air oxygen by carbon black. At the temperature range of 850 °C to 970 °C the significant decrease in mass is observed, which is probably due to the desorption of CO$_2$. Since the mass value does not change up to a temperature of 1300 °C, one can be spoken about the full burning out the carbon black at 970 °C. Such a high burning out temperature corresponds to about 0.7 of melting temperature of Co$_2$SiO$_4$ (1415 °C). One may conclude about the good choice of technological burning out additive, because, according to the Tamman’s semi-empirical rule, the ability of the sintering of particles and of the formation of a strong skeleton in porous ceramics appears near the temperature of 0.6-0.7 by a melting point. Basing on this conclusion, the partial sintering of skeleton firstly appears, then the pores formation becomes due to burning out the technological additive, so the porous but strong ceramics may be obtained. The microstructure studies, then confirmed by hydrostatic weighting, indicated that ceramics with an open porosity of about 40 % was formed. The mechanical strength on the three-point bending of porous ceramic was 35±6 MPa, which was a good and predictable result. One can be concluded that such porous ceramic should be used as a substrate for an asymmetric ion transport membrane for air oxygen separation.

Figure 2 illustrates the dependences of oxygen flux j(O$_2$) of Co$_3$O$_4$ - 36 wt. % Bi$_2$O$_3$ membranes deposited on a porous substrate vs their inverse thicknesses L$^{-1}$ at the temperatures of 790-850 °C (log P'(O$_2$)/P''(O$_2$) = 0.5). The first four series of points located in the lower left corner of the Figure 2 are the data taken from [11], while the second three series of points are the experimental data obtained by us on membranes with covered thicknesses of 0.6 mm, 0.4 mm, and 0.2 mm, respectively. It is shown...
that the oxygen flux rises at an increase in the temperature and in inverse thickness, but the tendency of such rising describes according to Burggraaf’s model [17]. If the oxygen transport was described by the Wagner’s model [12], the values of oxygen flux would be much higher, as shown in Figure 2 (the hypothetic values are marked as hollow geometric figures). Because the oxygen transport through the investigated composite system satisfies the Burggraaf’s law, the process is carried out in a mixed diffusion-kinetic regime. Hence, the estimations of the characteristic membrane thicknesses indicate the values of 0.9 mm at 790 °C, of 0.85 mm at 810 °C, of 0.8 mm at 830 °C, and of 0.75 mm at 850 °C, respectively. These values are in good agreement with the literature data, since for the known SCF membranes the values of characteristic thickness are of 0.7 to 2 mm [18]. A similar characteristic thickness of 0.5 mm is known for BSCF membrane material [19]. At an increase in the temperature, the characteristic thickness of the membrane decreases, which is quite logical, since the rate of the oxygen surface exchange processes on interfaces is accelerated. It can be concluded that the optimal thickness of membrane material of Co₃O₄ - 36 wt. % Bi₂O₃ is approximately of 0.8 - 1 mm.

![Figure 3. The micrograph of asymmetric membrane after oxygen transport tests](image)

Figure 3 shows the microstructure of polished section of asymmetric "dense Co₃O₄ - 36 wt. % Bi₂O₃ / porous Co₂SiO₄" membrane after 10 hours of oxygen transport investigations at 850 ºC. The microstructure indicates good adhesion of dense membrane to a porous support. But, unfortunately, one can be seen the penetration of Bi₂O₃ - based melt (light-grey fraction) on the depth of 50 μm into a porous support. Sadly, we can conclude that such melt interpenetration and its spreading along the membrane body will may subsequently lead to a decrease in the transport properties of the membrane. However, at now this conclusion is difficult to make, more long-term tests of oxygen transport of this membrane are needed. In our opinion, the solving of the problem of impregnation a porous membrane body by a melt can be a decrease in the surface energy of the substrate. In addition, the solving of the problem of impregnation a porous body by a melt can be a decrease in the surface energy of the substrate. It may be achieved by partial amorphization of support and by reduction of its average particle size to submicron, since it is known that surface energy of the material decreases at a decrease in particle size. Perhaps the dramatic creep problem solution which will also allowed to improve the mechanical properties of the substrate is to form the hierarchical porous microstructure of the substrate without a lot of mechanical stress concentrators. The solving of above-mentioned problems is not an easy task, since in our case we are dealing with a bismuth oxide-based melt that interacts with most oxide materials having good mechanical properties (Al₂O₃, ZrO₂, etc.). Possibly it is worthwhile to develop of the membrane material of other composition, operating at lower temperatures and not reacting with known constructional oxide materials, this may be a follow-up of our current researches.
4. Conclusions
As can be seen from all the presented results, the main goal of the research is solved. However, it should be noted that a significant increase in the oxygen flux of composite membranes is difficult because of the rather large value of the characteristic thickness of the membrane, which describes the rate of surface-exchange processes at the interfaces. It should also be understood that the increase in specific oxygen fluxes is difficult to realize due to a significant difference in the total pressure on both sides of the membrane because of the possible creep of membrane and interpenetrating of melt into the porous substrate.
In addition, it is known that Co$_3$O$_4$ is not enough thermodynamically stable at a low partial oxygen pressure [20], it is also no possibility of significantly increase in the oxygen flux due to the large oxygen partial pressure difference on both sides of the membrane. Therefore, the record oxygen selectivity with a comparable oxygen permeability of Co$_3$O$_4$ - 36 wt. % Bi$_2$O$_3$ [11], apparently, entails the subsequently lower membrane productivity, which is the dramatically restraining and hindering factor for the large-scale use of such materials in ion transport membranes.

Acknowledgements
This work was supported by the Russian Science Foundation (Project No. 16-19-10608).

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