

Smart Oxygen Membrane

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Abstract. Oxygen selective membrane based on δ -Bi₂O₃/Ag cermet has maximum potential in separating oxygen from air. However, the achieved oxygen flow is inferior to high-temperature membranes. The paper proposes a new approach to creating a smart oxygen membrane with a selective layer from a nanocomposite with a complex architecture, operating at intermediate temperatures (T_{op} ~550-600 °C). At the stage of obtaining nanopowders of membrane components, the potential and features of the mechanochemical ceramic method are taken into account. Mild conditions at the stage of consolidation by hot pressing are provided by the composition of the AgCu-matrix alloy. Achieving a gas-tight selective layer at the stage of reaching T_{op} is ensured by dilatation of some components during the oxidation of copper alloys. The choice of T_{op} for the oxygen membrane is based on the possibility of regeneration while maintaining the nanoscale microstructure. New solutions allow the creation of stable thin membranes with a reduced cost, including due to the silver content near the percolation threshold.

1 Introduction

There are several types of oxygen selective membranes (OSM). Two of them are SOFC (solid oxide fuel cell) membranes made of solid electrolytes with deposited porous electrodes and CMR (catalytic membrane reactor) membranes made of mixed ionic-electronic conducting (MIEC) ceramics for the implementation of processes such as partial oxidation of methane. A huge number of publications have been published on these types of membranes, with no visible commercial success in the market. Oxygen flow through the membranes is provided by a significant difference in oxygen partial pressures due to the reducing gas. The third type is oxygen separators (OS) based on membranes made of MIEC materials - mainly complex oxides with the structure of perovskite or cermets δ -Bi₂O₃/Ag. The oxygen flow is generated by high air pressure, which can be reduced by using a sweep gas. In the case of a cermet membrane, the sweep gas must contain O₂ because Bi₂O₃ is unstable in a reducing atmosphere. Published works on OS are disproportionately small, and on cermet membranes, their number does not exceed 10 [1-4]. In the United States, oxygen transporting membrane technology based on MIEC complex perovskites has been developed for coal combustion in pure oxygen (oxy-fuel combustion) for the subsequent capture and storage of CO₂. Cermet membranes, composed of the best ionic and electronic conductors, have the potential to maximize air separation efficiency. Weak attention to them is associated with the rapid degradation of functional properties and the instability of

bismuth oxide in a reducing atmosphere. Testing stabilized δ -Bi₂O₃ with the fluorite structure showed a rapid deterioration of conducting properties due to the ordering of oxygen vacancies with subsequent phase transformation into stable dielectric phases. Doping with highly charged cations improves the kinetic stabilization of the fluorite structure [4]. With decreasing membrane thickness, the oxygen flux is limited by oxygen exchange reactions at the contact line of three phases δ -Bi₂O₃-Ag-gas [1, 3]. The nanoscale structure of cermet, which can be obtained by the mechanochemical ceramic method [2], should provide a high rate of exchange reactions. However, in this case, the rate of total degradation also increases. The acceleration of the phase degradation of δ -Bi₂O₃ is associated with incorporating silver into the fluorite lattice with the local formation of additional oxygen vacancies, which promote the ordering of oxygen vacancies [4]. Mechanochemical nanopowders of oxide ceramics contain a free volume of up to 9% in the form of vacancy defects, which is five orders of magnitude higher than the equilibrium content of Schottky defects [5]. The high concentration of cation vacancies in the fluorite structure favors the incorporation of Ag⁺. The deposition of a Pd(Pt) catalyst on the cermet surface sharply accelerates the degradation processes, including the recrystallization and segregation of silver. It can be assumed that a highly mobile state Ag-O-Ag \leftrightarrow Ag⁺-O²⁻-Ag⁺ is formed on the silver surface. Taking into account degradation processes [4], we obtained gas-tight nanocermet with an interpenetrating structure 60 δ -Bi₂O₃/40(60Ag@40P) from annealed at 400 °C δ -Bi₂O₃ nanopowder by hot pressing at 350 °C and a pressure of 1 GPa. Prepared nanocermet successfully passed the long-term test for 500 hours at 500 °C with a significant reduction in silver segregation. Instead of silver, the core-shell nanocomposite Ag@P (where P is a perovskite La_{0.5}Y_{0.3}Pr_{0.2}Cr_{0.5}Fe_{0.3}Mn_{0.2}O₃ with a high electronic conductivity [4] and good wettability to Ag) was used. A solid electrolyte of composition Bi_{0.76}Y_{0.06}Er_{0.08}Tb_{0.08}W_{0.02}O_{1.5+x} with a high conductivity and good kinetic stabilization of fluorite structure was found. The obtained nanocermet showed the fundamental feasibility of intermediate temperature (IT) oxygen membranes. However, control samples prepared with small deviations of parameters display degradation. For example, the porosity of cermet after the consolidation of more than 5% promotes degradation because it facilitates the recrystallization and deformation of δ -Bi₂O₃ grains associated with the ordering of oxygen vacancies. Hot pressing parameters are too difficult to commercialize the technology. Further optimization of the parameters for materials, roadmap and architecture are required to fabricate an effective membrane. The challenge is to develop an IT smart OSM for accommodation at all stages of the life cycle.

2 Experimental

Reagent grade powders of metal oxides and metals with a purity >99.9% from Reachim, Russia, and other manufacturers were used. Nanopowders were obtained by the solid state method using mechanical activation (MA) in the high-energy planetary mill AGO-2, Russia. MA of the powders was carried out in the most intensive mode 60g with stainless steel balls 4 mm in diameter. The mass ratio of material and balls was (20-30g)/200g, time of milling 5-30 min (supplied energy $E_s = 15-100$ MJ/kg). A standard procedure of milling for ceramic powders was used [5]. According to this procedure, continuous mechanical treatment of ceramic powder was 60 s in a pre-coated steel medium with the same material. After stopping the mill, the powders and balls were remixed to avoid the accumulation of material in the dead zone of the milling jars. The operations of milling and firing at 500-800°C were repeated three times for ceramics. CuMn₂ alloy with FCC structure was obtained by MA of metal powders after firing at 900 °C in nitrogen atmosphere with subsequent milling of sintered powder. The used procedure provides simultaneously high powder uniformity and drastically reduced iron contamination of materials. The

characterization of powders and materials was carried out by a combination of methods. XRD data were collected on a D8-Advance (Bruker, Germany) using $\text{CuK}\alpha$ -radiation. The full-profile Rietveld analysis of the obtained data was done using TOPAS and PowderCell-2.1 programs. SEM studies with EDS were carried out on the microscope TM-1000 (Hitachi, Japan). The selection of ceramic fillers was done after studies of conducting properties of sintered at 800 °C ceramics by the 4-electrode scheme in installation IPU-1, Russia). Sintering of MA ceramic powders after pressing at 200 MPa was carried out at relatively low temperatures in order to prevent phase transformations and preserve the nanostructure.

3 Results and discussion

Designed to implement the principles of a smart OSM, the general architecture consists of a support made of modified stainless steel grid, filled by ceramic composite, a gas-tight nanocermet layer 10 μm thick, porous protective, and catalytic layers 1-2 μm thick [4]. For improving the kinetic stability of $\delta\text{-Bi}_2\text{O}_3$ with fluorite structure (F) we study conducting properties and long-term stability of solid electrolytes family on the base $\text{Bi}_{0.8}\text{Dy}_{0.12}\text{Er}_{0.08}\text{O}_{1.5}$, doped by 2% molar of W^{6+} , Ta^{5+} , Me^{4+} (including a mix of cations). Doped by W^{6+} samples display relatively good phase stability and conductivity. The structure of the key component of the selective layer in a smart OSM, Ag-based nanocomposite, is shown in Fig. 1.

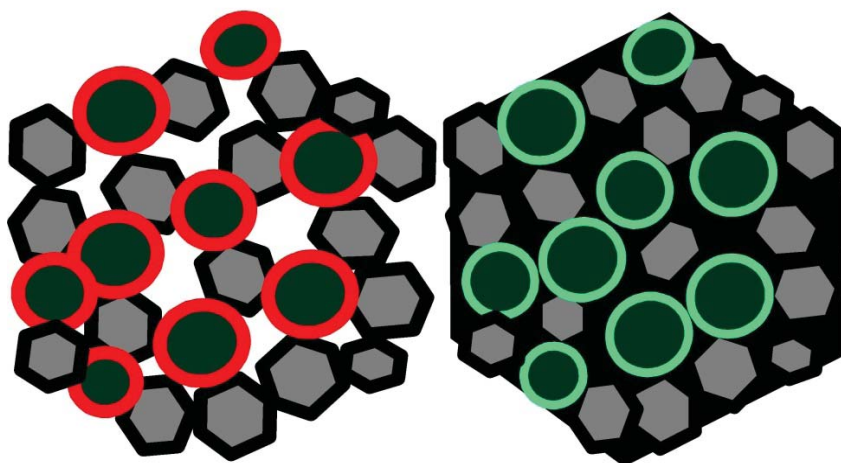


Fig. 1. Schematic representation of Ag-based nanocomposite after the consolidation of mixed nanopowders by hot pressing (left), and after oxidation and sintering at T_{op} (right). Black – Ag-based matrix, red – CuMn_2 .

Instead of Ag, we propose to use a two-level nanocomposite of «core-shell» structure with metal-matrix alloy $\text{Ag}_{0.7}\text{Cu}_{0.3}@\text{(P)}(\text{CuMn}_2@\text{S})$, where P – selected perovskite ceramics $\text{La}_{0.7}\text{Y}_{0.3}\text{Co}_{0.5}\text{Fe}_{0.3}\text{Mn}_{0.2}\text{O}_3$ with high conducting properties [6] (Fig. 2), S – spinel CuMn_2O_4 . The general formula of cermet with stabilized fluorite for the selective layer of membrane can be presented in the form $60\text{F}/40[\text{A}@\text{(P)}(\text{M}@\text{S})]$. At a ratio of 60:40, the interpenetrating structure of composites is formed reliably [1, 4]. Metal-matrix alloy A with

closed to optimal composition $\text{Ag}_{0.7}\text{Cu}_{0.3}$ has a melting point $T_m = 820^\circ\text{C}$ (140 K lower than silver). $\text{M} = \text{CuMn}_2$ plays the role of metal-matrix alloy in the stage of powder preparation and consolidation by hot pressing, but after heating up to T_{op} metal is oxidized to spinel CuMn_2O_4 with dilatation effect. An increase in the plasticity of the matrix and the introduction of dilatation centers make it possible to controllably soften the conditions of hot pressing to ~ 200 MPa instead of 1 GPa, because the relative density of the cermet of ~ 0.80 will be quite sufficient.

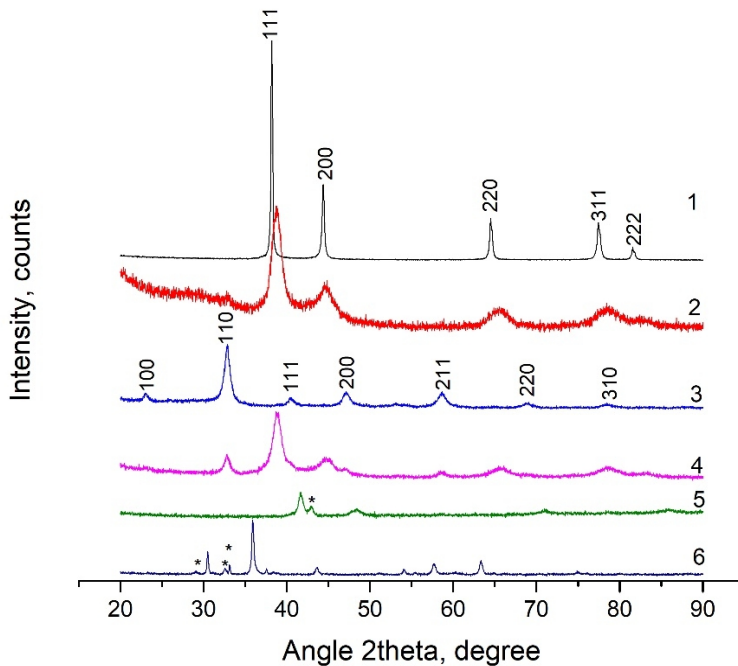


Fig. 2. Powder XRD patterns: 1- Ag and 2- $\text{Ag}_{0.7}\text{Cu}_{0.3}$, 10 min MA, size of crystallites $d=11.3$ nm, with FCC structure, 3- P, 10 min MA ($d=16.6$ nm), 4- nanocomposite $\text{Ag}_{0.7}\text{Cu}_{0.7}@0.5\text{P}$, 10 min MA (for Ag, $d=11.1$ nm, for P, $d=16.6$ nm), 5- CuMn_2 , 5 min MA (FCC structure, peak * belongs to $\alpha\text{-Mn}$ and grows upon mechanical activation), 6- sample 5 after oxidation at 750°C , spinel structure, * belongs to low symmetry phase CuMn_2O_4 .

The alloy CuMn_2 and ceramics CuMn_2O_4 should have good wettability with silver due to high electronic conductivity, according to [4]. After oxidation of the alloy with the formation of nanoscale ceramic grains (Fig. 2), the silver matrix acquires a rigid framework that inhibits recrystallization and segregation. Moreover, spinel CuMn_2O_4 absorbs CuO after oxidation of Cu in AgCu -alloy with a formation of more conducting ceramics $\text{Cu}_{1.3}\text{Mn}_{1.7}\text{O}_4$. The choice of T_{op} about 600°C is associated with the long-term stability of modified metal support and the possibility of membrane regeneration by a short-term temperature rise to $650\text{-}700^\circ\text{C}$, at which disordering of oxygen vacancies in the fluorite structure can be expected. This operation will have little effect on the microstructure of nanocomposites and will prevent irreversible phase transformation of metastable fluorite into stable dielectric phases. In addition, heating up to $750\text{-}800^\circ\text{C}$ completely eliminates dielectric phases.

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References

1. C.S. Chen, A.J.J. Burggraaf, *J. Appl. Electrochem.* **29**, 355 (1999)
2. V.V. Zyryanov, A.A. Matvienko, *Inorgan. Mater.* **51**, 415 (2015)
3. S.V. Fedorov, A.S. Lysenkov, I.V. Kulbakin, 2020 IOP Conf. Ser.: Mater. Sci. Eng. 848 0120191
4. V.V. Zyryanov, *Materials Today: Proceedings* **25**, 416 (2020)
5. V.V. Zyryanov, *Russian Chemical Reviews*, **77**, 105 (2008)
6. V.V. Zyryanov, S.A. Petrov, A.S. Ulihin, *Ceram. Int.* (to be published)