One of the effective methods of improving the efficiency of fuel consumption is to transform the thermal energy into electrical energy by means of magnetohydrodynamic (MHD) generators. The technical solution of this problem poses a series of complex tasks associated with the extremal conditions under which the material has to serve in many of the units of the MHD generators. One of the most complex and difficult tasks was to develop a material for the high-temperature electrodes.

The main service conditions of such a material in open-cycle MHD generators operating on natural gas [1, pp. 463-473] are: a temperature of the plasma containing the ionizing additive (K₂CO₃) up to 3000°K; temperature on the working surface of the electrode, 2000–2200°K; rate of flow of the plasma, up to 1000–2500 m/sec; and the current density at the electrodes of up to 1-2 A/cm². These conditions determine the main technical specifications for the electrode material: refractoriness 2400–2500°; excellent resistance to corrosion, erosion, and evaporation at the above temperatures and flow rates; adequate electrical conductivity in the working range of temperatures; and stable properties.

Materials based on ZrO₂ fully meet these specifications [2, 3]. The main difficulties in the industrial use of this oxide which has the necessary high refractoriness (melting temperature >2700°C) and electrical conductivity at high temperatures are associated with its monoclinic–tetragonal reversible transformation in the 1000-1200°C interval which is accompanied by a change of ~7% in its volume.

The stabilization of ZrO₂ in the cubic form is done by adding MgO, CaO, or Y₂O₃ and this simultaneously helps to improve the electrical conductivity of the material at high temperatures. The solid solutions, ZrO₂–MgO and ZrO₂–CaO, decompose at 1000–1400°C, leading to the destabilization of ZrO₂. The solid solution ZrO₂–Y₂O₃ is very stable and no signs of decomposition can be observed after a dwell of 500 h at 1200°C. Moreover, such a solid solution is significantly more resistant to evaporation than the ZrO₂–MgO and ZrO₂–CaO solutions from which the alkaline-earth oxides begin to evaporate off even at 1800-2000°C.

It has been established in [4] that small additions of Y₂O₃ (mole fraction ~3%) to the ZrO₂–MgO and ZrO₂–CaO solid solutions sharply increase their thermal stability for a relatively small increase in cost. Such materials can be widely used in high-temperature engineering.

Some studies on the stabilization of ZrO₂ by rare-earth oxides and by combinations with MgO, CaO, and Y₂O₃ have been carried out [5–10]. Simultaneously, the electrical properties of synthesized materials have been studied by physicochemical methods and some of them have been tested in experimental MHD generators.

It was found that materials with a purely ionic conductivity (solid solutions of ZrO₂–MgO, ZrO₂–CaO, and ZrO₂–Y₂O₃) are electrolyzed under the action of dc; the stoichiometry in...
relation to oxygen is damaged; and in the final count this leads to the destruction of the materials. It was therefore necessary to look for some way of providing the electrode material with electron conductivity without degrading the other good qualities of the material.

Studies showed that the replacement of $Y_2O_3$ in the solid solutions by oxides of rare-earth elements does not impair the excellent thermal stability of the material. Moreover, such a substitution is suitable from the economic point of view because of the significantly lower cost of the rare-earth oxides of the cerium subgroup than of $Y_2O_3$.

On the basis of a detailed study of the electrical properties of ternary solid solutions, $ZrO_2-Y_2O_3-R_2O_3$ (where $R_2O_3$ is a rare-earth element) over a wide range of compositions, temperatures, and gas media, solid solutions of two compositions (I and II) were finally selected; these had a significant electron conductivity.

The solid solution of composition I contained: $ZrO_2$, 85%; $Y_2O_3$, 3%; and $CeO_2$, 12%; the proportion of electron conductivity was 10-15%. Solid solution of composition II contained: $ZrO_2$, 91%; $Y_2O_3$, 4%; and $Nd_2O_3$, 5%. The proportion of electron conductivity was 7-10%. The electron conductivity was determined using an emf method.

Both solid solutions were thermally stable at medium (1000-1400°C) temperatures. The solid solution containing $Nd_2O_3$ was more resistant to evaporation; in relation to this characteristic, it is as good as the $ZrO_2-Y_2O_3$ solid solution and can be used for a prolonged period at 2000-2100°C. The solid solution containing $CeO_2$ was less resistant to evaporation and, as a result, its working temperature must be limited to ~1900°C.

On the basis of these studies, we have developed an electrode ceramic from these two compositions.

Prolonged working of the electrode ceramic in the channels of MHD generators can only be realized by ensuring that the ceramic is very thermally stable and thermal-shock resistant. Therefore, we paid particular attention to the methods of making the solid solutions. Normally, a ceramic is obtained by a solid-phase sintering of a mixture of oxides. However, in order to complete the reactions in which the solid solutions are formed, it is necessary to use high temperatures (>1700°C); have prolonged dwells at the final-heat treatment temperatures; and to use highly dispersed oxides. The use of chemical codeposition or combined fusion methods makes it possible to obtain sufficiently perfect solid solutions and, where the codeposition method is used, at lower temperatures.

In the preparation of the electrode ceramic, we tested all three methods of synthesis: solid-phase sintering at 1700°C for 7-10 h of a mixture of <5-μm oxide powders after preliminary mixing and pressing (method a);
combined deposition of the components in the form of hydroxides followed by calcining (method b);
fusion of mixtures of oxides by a high-frequency field in a water-cooled crucible which eliminates contamination of the original materials by alien impurities (method c).

The x-ray studies showed that there is a nonuniform distribution of the stabilizing additive in specimens of composition I made by normal ceramic technology. This is shown in the diffuseness of the diffraction maxima in the region of angles of ~40°. In specimens of the same composition obtained by codeposition, the distribution is more uniform. In the fused material, the degree of order in the solid solution is even better. In the case of composition II, these differences were less marked but a more perfect crystal structure is also characteristic of the codeposited and fused specimens.

An increase in the thermal resistance of the ceramic of a grainy structure was achieved by creating a microcracked structure using broken fractions of the material. The thermal-shock resistance was evaluated using a heat-cycle method (1300°C — air). The tested ceramic specimens had a porosity of 18-21% and were virtually without shrinkage (the development of a ceramic with minimal shrinkage helps the operational techniques when it is used for the electrodes of MHD generators).

The tests showed that the most thermal-shock resistant is the ceramic made of fused

*Here and elsewhere, mole fractions are indicated.