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Combustion synthesis and characterization of porous Ni-Al materials for metal-supported solid oxide fuel cells application

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Combustion synthesis (CS) in thermal explosion mode under conditions of controlled heat loss is used for synthesis of thin Ni-Al porous plates. In the present work, compacted Ni-Al elemental powder mixtures placed between heat-removing clamp plates are heated in a furnace at 25 K/min up to 1000 K under the uniaxial load up to 1.2 MPa with further heat treatment at the temperature of 1100 K. The effects of the Ni/Al mass ratio, reagent powders size, porosity and thickness of the reacting samples as well as conditions of heat-exchange during the CS on the reaction parameters have been studied. Based on the thermocouple measurements, the temperature and timing characteristics of the CS process have been calculated. The phase composition evolution during the process has been analyzed using X-ray diffraction and energy-dispersive X-ray spectroscopy. Special attention has been paid to the study of the following characteristics of synthesized materials: porosity parameters, gas permeability and mechanical properties. Due to the high strength of synthesized materials and formation of relatively homogenous structure with proper pores size and gas permeability, the synthesized porous Ni-Al plates can be considered as good supporting substrate for application in metal-supported solid oxide fuel cells.

1. Introduction

Solid oxide fuel cells (SOFC) are classified as electrochemical devices that can effectively convert the chemical energy of hydrogen oxidation into electric one. Architecturally, a SOFC is a multilayer system that is an assembly of thin layers of different materials functioning as the anode, electrolyte, cathode, and the supporting substrate. The anode is normally a composite porous Ni-YSZ (YSZ – yttria stabilized zirconia), electrolyte – YSZ, cathode – $La_{1-x}Sr_xMnO_3$, and the supporting substrate, in various embodiments – the anode, cathode, electrolyte or additional porous layers.

Since ceramic SOFC components are prone to brittle fracture, it is highly promising to use so-called metal-supported SOFC (MS-SOFC) [1], where the layers of the anode, cathode and electrolyte are applied onto a porous plate made of a corrosion-resistant metal material: Fe-Cr alloy or stainless Ni-Cr steel. Due to the high ductility and thermal conductivity parameters of the metals, MS-SOFC are notable for the quick starting procedure, lower sensitivity to thermal cycling, greater resistance to mechanical shock and vibration loads [2,3]. According to [4], the performance of Fe-Cr-based MS-SOFC during long-term tests (1000 h at 1000 K) may be comparable and even superior to Ni-YSZ anode-supported cells.

A significant problem in the application of steels is the diffusion transfer of chromium from the substrate to the surfaces of the anode and cathode layers, which leads to deterioration of the electrical characteristics of cells during their operation [5]. To some extent, the diffusion can be reduced by applying special barrier layers [6] or adjustment of the chemical and phase composition of the alloy [7]. However, the process is not fully terminated. Another solution is the use of materials that do not contain chromium [5]. For this purpose, Ni-Al alloys are usable [8,9], as they are distinguished among other heat resistant alloys for low density, high thermal and electrical conductivity and long operation in an oxidizing atmosphere of up to 1400 K [10,11].

To manufacture a porous metal SOFC support, various methods of thermo-mechanical processing of the finished alloy (having a predetermined phase composition) are applicable, such as strain hardening of foam [8], punching non-porous blanks [12], extrusion

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and sintering of a powder sample [13]. However, for Ni-Al alloys more economical technologies are combining the formation of chemical and phase composition and of the pore structure of the material within one work cycle [14]. These technologies include the reaction sintering method [15] and the combustion synthesis [16]. The former is implemented by slowly heating a powder sample from nickel and aluminum powders in a vacuum furnace followed by soaking at high temperature [17]. The latter is done through the organization of a self-sustaining exothermic reaction between the components of the powder mixture in self-propagating mode (propagation of thin combustion wave through the sample) [18] or thermal explosion mode (instant reaction in whole volume of the sample) [19]. The advantages of CS are high performance and energy-saving effect.

This paper is devoted to studying the capacities of combustion synthesized Ni-Al materials intended for use as a supporting substrate in MS-SOFC. The problem to be solved in the study was the synthesis of Ni-Al materials with low roughness of the outer surface (pore size below 10 μm), which is suitable for applying a thin layer of anode using vacuum deposition or thermal spray techniques [20]. In the self-propagating mode of CS Ni-Al materials with pore size of 20 μm are usually formed [21], and the organization of thermal explosion mode often leads to the fusion of the sample with a loss of shape [22]. Therefore, an upgraded process was used in the work – thermal explosion with organization of purposive heat loss during the synthesis. This way of organizing the CS, previously approved in Ref. [9] for the synthesis of porous materials composed of Ni + 10% Al, can be called a soft thermal explosion (STE). In comparison with the conventional thermal explosion mode STE can significantly reduce the temperature of the process and, consequently, provide conditions for obtaining materials with microporous structure.

Given the lack of knowledge about STE, the complex research in the laws of thermal and structure-phase dynamics of the Ni-Al system in the process of thermal explosion with intense heat loss has been carried out. We have studied the influence of the initial state of parameters of the system on the morphology of pores, gas permeability and mechanical properties of the final product. The research appears to be important to determine ways of the directed synthesis of microporous Ni-Al materials with desired functional characteristics.

2. Research methods

As initial reagents three grades of nickel powder and two grades of aluminium powder were used. Their particle size and chemical compositions are shown in Table 1. According to the electron microscopy, aluminium powders are composed of smooth spherical particles, and powders of nickel have developed surface (Fig. 1).

A Turbula shaker-mixer was used to prepare powder mixtures with the mass concentration of aluminum: $C_{Al} = 0.07–0.315$. In order to provide the quality of mixing the following procedure was matched. The mixing chamber was filled in with the powder reagents and steel balls with a diameter of 4 mm (the ratio of mass of balls to mass of powder is 1:1). The powders were saturated with ethanol in an amount necessary to obtain the nonseparating slurry. Filling degree of the batch did not exceed 0.2. Mixing of powders was carried out at a rotation speed of the mixer chosen to provide Froude number Fr = 1 (equality of flow inertia to the gravity. See, for example [24]). After mixing, the powders were dried in a vacuum desiccator. The mixing quality was controlled with a microscope. It was found that the mixing during 4 h is sufficient to obtain a homogeneous mixture at any powder particle size under consideration.

The mixtures were pressed into flat cylindrical samples with diameter $D = 20$ mm, thickness $h = 0.3–4.0$ mm, pressing pressure of $P_C = 30–250$ MPa. The porosity of the compacted samples was determined by the ratio:

$$\Pi_0 = 1 - \frac{m}{V}\left(\frac{C_{Al}}{\rho_{Al}} + \frac{1-C_{Al}}{\rho_{Ni}}\right), \qquad (1)$$

where m, V are the mass and volume of the sample, C_{Al} – mass concentration of aluminum, ρ_{Al} and ρ_{Ni} – density of nickel and aluminum. The structure of the initial reaction samples is shown in Fig. 2. It is seen that the nickel particles retained their shape and size, whereas the more plastic component Aluminium (Yield stress $\sigma_{0.2} = 30$ MPa for annealed Al with purity 99.95% [25]) had changed its form by interaction with more rigid particles of Nickel ($\sigma_{0.2} = 80$ MPa for annealed Ni) and the steel surface of press mold ($\sigma_{0.2} = 800$ MPa for 40H steel grade, analog of AISI 5135 steel).

Synthesis of porous Ni-Al alloys was carried out according to the following procedure (Fig. 3). The initial compacted sample was placed between two flat heat-removing clamp plates – 6 mm thick parallel-sided stainless steel discs having the same diameter with the samples. The disc surfaces were smoothed by plane-parallel grinding to surface roughness of less than 1 μm. The contact pressure of the plates to the sample was adjusted using a special press within the range of $P_F = 0–1.2$ MPa ($P_F = 0$ means pressure only by the weight of the clamp plate and the sample). The press is designed so that the bending deformation of the sample can be neglected. Sandwiched between the plates, the sample was placed in an electric furnace chamber in argon atmosphere (purity 99.8%, gaseous medium pressure 0.1 MPa), and heated at a constant rate of 25 K/min. The power to the heaters was carried out by a DC voltage source. The sample temperature was monitored using a K-type thermocouple (junction diameter 0.1 mm) embedded in the sample near its surface. The thermocouple signal through an analog-digital converter was recorded on a PC at a data acquisition rate of 200 Hz.

The porosity of the materials after synthesis Π_P is determined by the formula:

$$\Pi_P = \frac{\Pi_0 + \Delta_V + \Delta_\rho(1-\Pi_0)}{1+\Delta_V}, \qquad (2)$$

where $\Delta_V = V_P/V_0 - 1$ is the volume change, V_0 and V_P – the sample volume before and after the synthesis, $\Delta_\rho = 1 - \sum_j \frac{C_j}{\rho_j} / \sum_i \frac{C_i}{\rho_i}$ – the change in the material volume and density as a result of chemical transformations, where C and ρ are concentrations and densities of the phase components of the material before (i indices) and after (j indices) the STE.

In order to stabilize the phase composition and porous structure, after the STE the samples were subjected to heat treatment in a vacuum furnace under conditions of heating and cooling at a rate of 10 K/min and kept at a temperature of 1100 K for 1 h; the residual air pressure in the furnace was 10^{-2} Pa.

The morphology of the materials was studied with a Philips SEM 515 scanning electron microscope. The elemental composition was determined by Energy-dispersive X-ray spectroscopy (EDS) using a dual-beam scanning electron microscope (SEM) and focused ion beam (FIB) instrument QUANTA 200 3D. The latter was also used for visualization of compositional variations of samples by back-scattered electron (BSE) technique. The phase composition of the material was determined by X-ray diffraction analysis using a Shimadzu XRD 600 diffractometer, PCPDFWIN and PDF + databases, and PowderCell 2.4 full-profile analysis software.

The materials strength was studied by three-point bending using the Instron Testing Machine, Model # 3369 at the crosshead rate of 0.4 mm/s and the distance between supports l = 30 mm.