DEVELOPMENT OF PROTECTIVE COATING FOR MOLTEN CARBONATE FUEL CELL CURRENT COLLECTOR

VIKTORIYA PODHURSKA[1], PAVEL SHUHAYEU[1], OLEKSANDER KUPRIN[2], JAROSLAV MILEWSKI[3]

1. Karpenko Physico-Mechanical Institute of NAS of Ukraine
2. National Science Center "Kharkiv Institute of Physics and Technology"
3. Warsaw University of Technology

A coating based on chromium nitride is applied to the stainless steel substrates. The microstructure and properties of coatings in their initial state and after long-term oxidation in the air at 600°C were studied. It has been found that the textured chromium nitride coating has better oxidation resistance and can be proposed as a protective coating for the molten carbonate fuel cell current collector.

Keywords: current collector, fuel cell, oxidation resistance

Introduction. Bipolar plates and current collectors are critical metallic components for commercial MCFC stacks. In fact, for commercial MCFC systems, up to 55 % of the material content could be the metallic hardware (for the complete system) which includes cell, stack, and balance-of-plant materials. The stability in a corrosive carbonate atmosphere at high temperature, good electrical conductivity and low contact resistance with the electrodes are desired characteristics of bipolar plates and current collectors. The bipolar plates are exposed to different atmospheres on the anode side, cathode side, and wet seal area of MCFC, and hence the ideal material for bipolar plate current collectors should have acceptable corrosion resistance for all of these atmospheres. Stainless steels like 310 S (24–26 wt. % Cr) and 304 L (16–18 wt. % Cr) have emerged as materials of choice for MCFC hardware [1]. However, the hot corrosion in the presence of the carbonate melt is a critical issue with these materials for long-term operation. During the period of initial operation, the mechanism of corrosion in these steels is normal corrosion involving scaling via the formation of a layer of iron oxides on the chromium-rich oxide layer.

One of the methods of protecting and improving the corrosion properties of steels is the application of coatings based on nitrides. The corrosion resistance of Cr-N coatings is better than that of the stainless steel and other nitride coatings in the high temperature pressurized water and the oxidation rate in air at 600/800°C is low.

Experimental. 304L stainless steel specimens of sizes $0.4 \times 25 \times 25$ mm^3 were used as substrates. The substrates were polished using abrasive silicon carbide paper to a roughness Ra of about 0.02 μm, then chemically degreased and ultrasonically cleaned in a hot alkaline bath for 10 min and dried in warm air. After cleaning, they were mounted on a rotating holder of a chamber (rotation speed of about 30 rpm). The distance between substrates and a cathode was about 300 mm. The chamber was evacuated to a pressure of 1×10^{-3} Pa. Argon gas was introduced into the vacuum chamber up to pressure 5×10^{-2} Pa for stable burning of the arc discharge [2]. During the deposition of the chromium nitride layer, the nitrogen filling pressure was 2 Pa (variant #1 and #3 Table 1) and 0.2 Pa (variant #2 and #4 Table 1). To ensure better electrical conductivity and prevent the diffusion of chromium from the substrate, a thin layer of copper was applied to samples #3 and #4.

Table 1. Technological parametres coating obtaining

# specimen	Nitrogen pressure P, Pa	Bias voltage U, V	Thickness CrN, μm
1	2	150	16.6
2	0.2	120	6.9
3	2	150	4.1
4	0.2	120	2.2

The structures and phase composition of the materials were investigated by X-ray diffraction (XRD) with refined according to Rietveld's full profile approach using the PowderCell 2.4 software. The XRD study was performed in monochromatic Cu Kα radiation using STOE powder diffraction system in a focusing Bragg-Brentano geometry.

The material microstructure was studied with a Carl Zeiss EVO-40XVP scanning electron microscope (SEM). The chemical homogeneity evaluation of materials was based on an energydispersive X-ray (EDX) microanalysis performed using an INCA Energy 350 system.

The oxidation resistance tests were divided into four stages, and each of them has duration of 250 h. Each stage consisted of heating to 600°C in air, exposition for a certain time, and cooling to room temperature. The weight of the specimens was measured before the test and after each stage by an analytical balance. The accuracy of the weight measuring was $\pm\ 10^{-4}$ g. The oxidation resistance of materials was characterized by weight gain per unit surface area $\Delta m/S$.

Results and discussion. Microstructural analysis of the obtained coatings showed that they are uniform and their chemical composition corresponds to stoichiometric chromium nitride (Fig. 1). X-ray structural analysis showed that the coating is single-phase, only variants 2 and 4 contain traces of chromium, which may be caused by the deposition of cathode particles, and under conditions of low nitrogen pressure, by the inability to form nitride (Table 2).

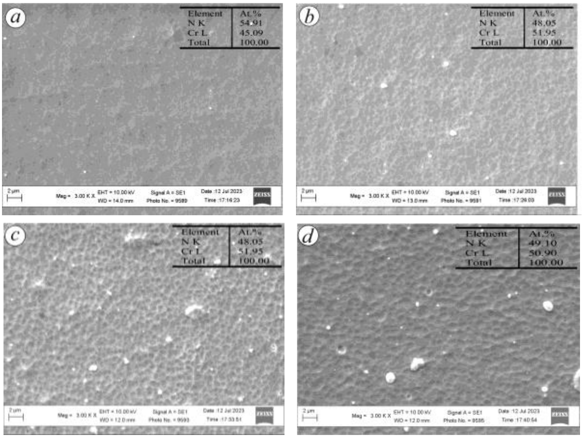

Fig. 1. The investigated coatings in the initial state.

Table 2. Results of X-ray structural analysis of the Cr-N system coatings.

# specimen	Phases	Structural type	Lattice parameter *a*, nм	*L*, nм
1	CrN	NaCl (B1)	0.4173	38
2	CrN	NaCl (B1)	0.4166	19
	Cr	BCC (A2)		
3	CrN	NaCl (B1)	0.4180	21
	Cu - sublayer	HCC (A1)		
4	CrN	NaCl (B1)	0.4177	12
	Cr	BCC (A2)		
	Cu - sublayer	HCC (A1)		

Coatings based on chromium nitride #2, #3 and #4 have high oxidation resistance but are inferior to steel substrate (Fig. 2). In coatings #2 and #3, we observe microcracking, which may be caused by the difference in the coefficients of thermal expansion of the substrate and the resulting coatings (Fig. 3, *b*, *c*). The single-phase structure of coating No. 1 with the textured orientation of CrN crystallites (Table 2, #1) to some extent prevents the opposite migration of N and O atoms in the transverse direction, which ensures the stability of the phase composition after long-term oxidation. No cracks are observed in coating # 4 (Fig. 3*d*), but its oxidation resistance is at the level of coatings 2 and 3, which may be due to the too-small thickness of the coating (Table 1).

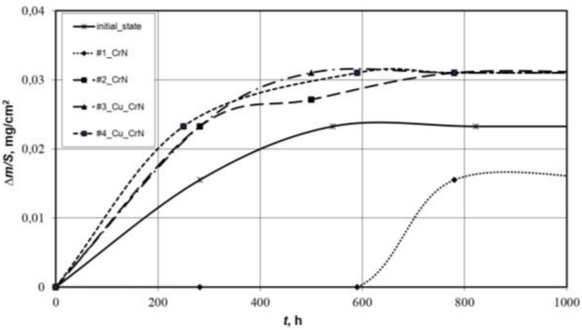

Fig. 2. Oxidation kinetic curves of studied coatings.

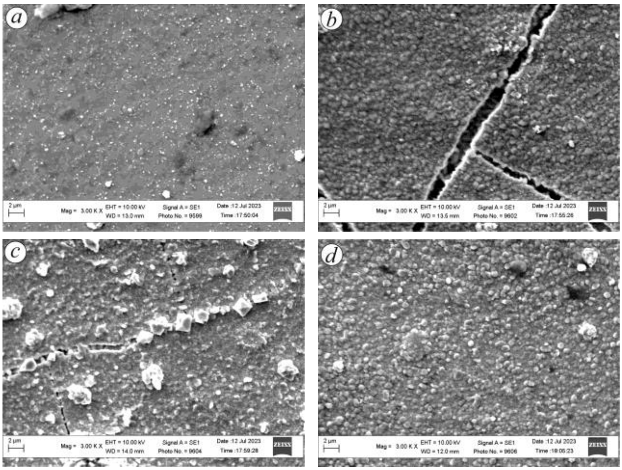

Fig. 3. The investigated coatings after holding for 1000 h at 600C in the air.

Conclusions. The studied coatings have high resistance to high-temperature oxidation. Regardless of the nitrogen pressure, the chemical composition of the coatings corresponds to the stoichiometric composition of chromium nitride. It has been found that a textured coating based on chromium nitride has much higher oxidation resistance and could be proposed as a protective coating for molten carbonate fuel cell current collector.

1. *Frangini S, Moreno A, Zaza F*. Solutions for material corrosion problems in MCFC // Adv. Sci. Tech. – 2010. – 72. – P. 291–298.
2. *Kuprin A.S., Belous V.A., Voyevodin V.N., Bryk V.V., Vasilenko R.L., Ovcharenko V.D., Reshetnyak E.N., Tolmachova G.N. and Yugov P.N.* Vacuum-arc chromium-based coatings for protection of zirconium alloys from the high-temperature oxidation in air // J. Nucl. Mater. – 2015. – 465. – P. 400–406.