Development of a protective coating against high-temperature oxidation for fuel cell current collectors

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The main requirements for the characteristics of bipolar plates and current collectors are stability in a corrosive-carbonate atmosphere at high temperature, good electrical conductivity and low contact resistance with electrodes. Bipolar plates are exposed to different atmospheres on the anode and cathode sides, so the material for bipolar plate current collectors must have acceptable corrosion resistance for all these atmospheres. Stainless steels such as 310S (24-26 wt% Cr) and 316L (16-18 wt% Cr) have become the materials of choice for MCFC equipment [Frangini S. et al. 2010]. However, hot corrosion in the presence of carbonate melt is a critical problem for these materials for long-term service.

The approach of coating stainless steel with conductive nitrides such as CrN, AlCrN, TiN is a promising alternative to improve corrosion resistance. For current collectors with high corrosion resistance, a minimum contact resistance between the electrodes and the metal is desirable, especially on the cathode side, where scale formation increases the contact resistance between the metal and the cathode [Kuprin A.S. et al. 2015]. The review of the literature clearly suggests that at present substantial R&D, opportunity exists for the development of stable and cost-effective alloys for MCFC hardware applications.

The aim of this work is to develop effective functional layers on stainless steel, obtained by the physical vapor deposition (PVD) method, with high electrical conductivity and oxidation resistance. Continuous and uniform PVD coatings can effectively prevent further electrochemical corrosion and dissolution of stainless steel. Cr_2N and Cr_2N/Ni coatings are considered as promising coating materials due to their excellent corrosion resistance and high metal-like electrical conductivity. Such functional layers on stainless steel substrate provide good electrochemical performance in the fuel cell environment.

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 [Kuprin A.S. et al. 2015]. 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. The phase composition, texture and substructural characteristics of the coatings were studied by X-ray structural analysis on a DRON-3 diffractometer in filtered Cu-Kα radiation (λCu-Kα = 0.154178 nm). Diffractograms were taken in the θ-2θ scanning scheme with Brague-Brentano focusing in the

range of 2θ angles from 20 to 100 degrees. The database of the International Center for Diffraction Data (JCPDS) was used to identify the phases.

Table 1. Technological parameters 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

X-ray diffractograms of coatings of the Cr-N system No. 1 and No. 2, deposited under nitrogen pressure in a vacuum chamber of 2 and 0.2 Pa, respectively, are shown in Fig.1. Samples No. 3 and No. 4 were deposited under similar parameters, however, before their application to the substrate, a sublayer of Cu was applied. X-ray diffractograms of coatings No. 3 and No. 4 are shown in Fig.2. The results of X-ray structural analysis are shown in Table 2.
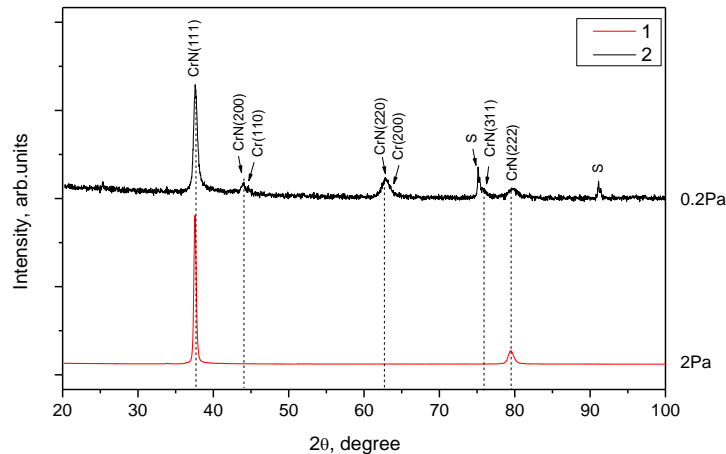

Fig.1. Diffractograms of samples #1 and # 2 with coatings of the Cr-N system deposited on a steel substrate at nitrogen pressure in a vacuum chamber of 2 and 0.2 Pa, respectively.

The main phase in the coatings is CrN nitride, which has a cubic structure of the NaCl type (structural type B1). On the diffractograms of all investigated samples, the lines of this phase are detected, the angular position of which is indicated by dashed lines. In addition to the nitride lines, most of the diffractograms show narrow lines of the steel substrate (γ-Fe), marked with the letter S. The diffractograms of coatings # 3 and #4 show lines of the copper sublayer - Cu with an fcc structure. The thinner the coating, the more intense the substrate and sublayer lines and the weaker the nitride lines. It can be seen that for coating #4, which has a thickness of only 1.6 μm, the lines of the sublayer and the substrate are more intense than the lines of the nitride. On the diffractogram of the thickest coating No. 1, which has a thickness of 16.6 μm, the lines of the substrate are not detected at all due to the absorption of X-ray radiation in the coating.

At a low nitrogen pressure during deposition, which was used in the synthesis of coatings #2 and #4, in addition to CrN nitride, a metallic Cr phase with a bcc lattice is detected. The lines of this phase are quite weak, which indicates its small amount. It is most likely that such a structure has macroparticles of the cathode material, which are present as defects in the coatings, and were unable to form the nitride phase under conditions of nitrogen deficiency. The Cr_2N phase is not detected.
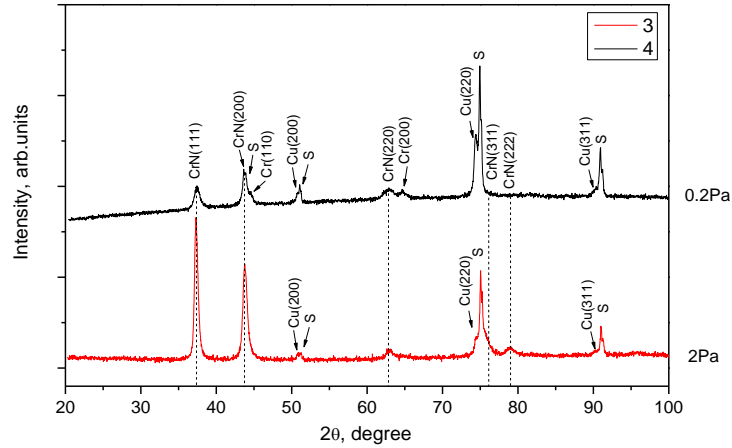
Fig. 2. Diffractograms of samples #3 and #4 with coatings of the Cr-N system deposited on a steel substrate with a copper sublayer under nitrogen pressure in a vacuum chamber of 2 and 0.2 Pa, respectively.

The crystal lattice parameter of CrN in coatings is within 0.4166-0.4180 nm. These values are higher than the parameter of 0.4156 nm, which has CrN of stoichiometric composition, which is due to the presence of compressive stresses in the coatings. The size of the nitride crystallites in the coatings varies from 12 to 38 nm. The detected difference is due to differences in the characteristics of the plasma flows that are deposited on the substrate. It is largely related not only to the change in nitrogen pressure (P), but also to the displacement potential (U), which affects the energy of the ions and the temperature of the substrate (see Table 1).

The intensity ratio of the CrN peaks on the diffractograms deviates from the values given in the powder diffraction database (JCPDS No. 11-0065), according to which the (200) line has the highest intensity. On the diffractograms of the obtained coatings, the (111) line is the most intense, which is associated with the formation of an axial-type texture with the [111] axis in the direction normal to the surface. The greater the thickness of the coating, the more perfect the texture, which is evidenced by a significant increase in the relative intensity of reflections of type (hhh) compared to others. On the diffractogram of coating No. 1 with the strongest texture, in general, only two very intense reflections of CrN nitride are visible - (111) and (222), and other reflections of this phase are not detected.

It should be noted that the copper sublayer also has a predominant crystallite orientation and is characterized by an axial texture with an axis [110]. The Cu (220) diffraction line is much more intense than other reflections of this phase, although the (111) line has the highest intensity for the untextured material (JCPDS No. 04-0836).

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

№ specimen	Phases	Structural type	Lattice parameter a, нм	L, нм
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)		

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 ± 10^{-4} g. The oxidation resistance of materials was characterized by weight gain per unit surface area Δm/S.

Since the tests last 1000 hours, not all coating options have passed the full test base. Fig.3 shows the results of the long-term oxidation resistance of the first batch of coatings. It was established that the coating based on CrN (#1) with a thickness of 16.6 μm has the best oxidation resistance.
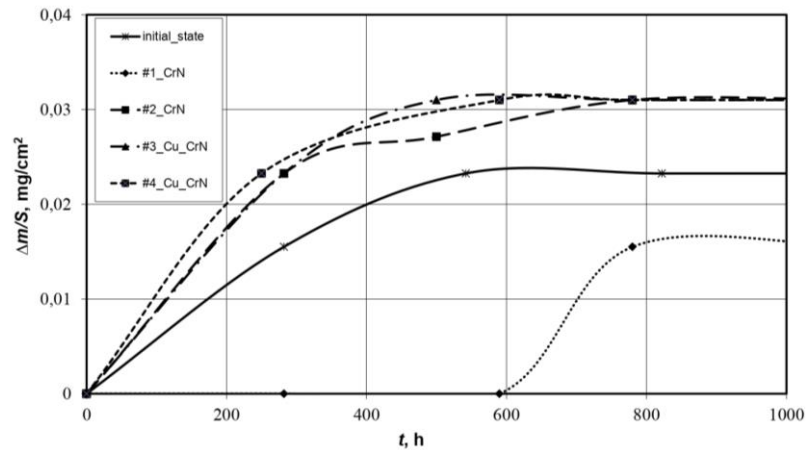

Fig. 3. Oxidation kinetic curves of studied coatings.

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.

Key words: molten carbonate fuel cell, current collector, CrN coating, oxidation resistance,

References

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