Plasma spray coating with iron oxides for manufacturing of the corrosion-resistant electrodes

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Abstract. Magnetite anodes were manufactured by plasma spray coating of titanium with the iron oxide powder. The powder was obtained by plasma-electrolytic atomization of carbon steel. Porosity, adhesion, specific resistivity of these coatings were measured in relation to size distribution and chemical composition of the powder used for spray coating.

1. Introduction
Magnetite is characterized by relatively high conductivity and corrosion resistance, which makes it suitable for producing anodes for various electrochemical applications. Bulk magnetite anodes are the most common ones. These anodes suffer from significant drawbacks such as brittleness, difficulty of manufacturing, considerable mass and size as well as increased resistivity. By making an anode with plasma spray coating by magnetite on an inert and conducting substrate such as titanium, niobium, zirconium, tantalum or stainless steel, it is possible to create electrodes that are free of these drawbacks [1].

In order to produce high quality magnetite anodes by plasma spray coating it is important to use magnetite powder of particular properties [2, 3]. Low-temperature plasma is a good tool for surface treatment of materials [4 – 11]. One method of creating magnetite powder suitable for plasma spraying is plasma-electrolytic atomization of carbon steel [12 – 14]. This method is easy to implement and it makes it possible to produce spherical particles of magnetite with diameter of 0.01 – 0.50 mm that has low amount of impurities. This study aims to determine operational characteristics of anodes made by plasma spraying of magnetite powder on a titanium substrate. The powder used was obtained by plasma-electrolytic atomization of carbon steel.

2. Materials and methods
Magnetite powder was produced using the plasma-thermic reactor with electrolytic cathode and metal anode [12]. The anode was made of SAE AISI 1120 steel rod 10 millimeters in diameter. Solution of 0.01% sodium chloride in distilled water was used as the electrolyte.

During the atomization process the distance between electrodes has been maintained at 1 mm and voltage of 600 V was applied. This allowed for the current of 1.9 A to pass through the gap between the electrodes. The anode was atomized and thus obtained product was carefully collected, washed and dried under 90 °C until a constant mass was obtained. A number of fractions by size was isolated by sifting through a set of sieves with a mesh of 40 – 160 µm.
The resulting powder consists of two unbound components: one is ferrimagnetic (Fe304) and the other is paramagnetic (FeO), which are easily separable by a magnet. The ratio of these components allows for Fe(II):Fe(III) relation of 0.43 – 0.52 to be achieved.

Plasma spray coating was performed using an UPU-3D device with argon as a working gas at a flow rate of 20-30 liters/min. The arc electrical power was set at 18-30 kW with spraying distance of 100 – 130 mm. A coated electrode formed on a titanium SAE AISI Grade 2 substrate with homogeneous and tough coating having a thickness of about 300 micron was produced for further study.

The coated electrodes were studied using techniques of microscopy analysis on Micromed MET metallographic microscope, Vickers hardness test on PMT-3M hardness tester and adhesive peel strength test on a Elcometer 108 hydraulic tester. Anodic dissolution rate was studied by electrolysis in 5% solution of sodium chloride in distilled water at a current density of 5 A/dm².

3. Results and discussion

Hardness and adhesion strength of the coatings produced are given in Table 1, and microphotograph of a cross section is presented in Figure 1.

![Figure 1. Microphotograph of the magnetite coating, magnification 200x](image)

| Fraction by size, µm | Hardness, HV 0.05 | Adhesive strength, MPa | Porosity, % |
|----------------------|-------------------|------------------------|-------------|
| 40 – 50              | 537               | 11.4                   | 5 – 8       |
| 50 – 71              | 491               | 16.3                   | 6 – 10      |
| 71 – 90              | 471               | 17.2                   | 7 – 10      |
| 90 – 120             | 468               | 15.9                   | 8 – 12      |
| 120 – 160            | 453               | 9.8                    | 12 – 18     |

Using of coarse particles with the diameter of more than 120 µm resulted in deposition of highly porous coatings with poor adhesion. Only a small part (about 50%) of this size fraction took part in coating formation because coarse particles failed to heat through and gain enough momentum in a plasma jet.

Size fraction of 40 – 50 µm forms non-porous coatings with strong adhesion and high coalescence rate. The only downside is that small particles can partially oxidize during the deposition process, which leads to cracking due to the elevated structural stress.
The highest quality coatings were produced by deposition of the size fraction of 50 – 120 µm. Adhesion strength of these coatings is consistent with the known values for coatings of the same type [15].

Measured parameters for coatings with particle size fraction of 72 – 90 µm of various Fe(II):Fe(III) relations used as a spray coating source are given in Table 2. Porosity increases and adhesion strength decreases as the relation increases.

| Fe(II):Fe(III) | Hardness, HV 0.05 | Adhesive strength, MPa | Porosity, % |
|----------------|-------------------|------------------------|-------------|
| 0.43           | 485               | 12.6                   | 9           |
| 0.45           | 471               | 13.8                   | 8           |
| 0.47           | 463               | 14.2                   | 6           |
| 0.49           | 450               | 14.7                   | 6           |
| 0.51           | 446               | 15.0                   | 5           |

The most important parameters of magnetite anodes are specific resistance $\rho$ and anodic dissolution rate $\Delta M_A$. Direct current specific resistance of the coatings in logarithmic scale is plotted versus the Fe(II):Fe(III) relation and shown in Figure 2.

![Figure 2. Specific resistance plotted versus Fe(II):Fe(III) relation.](image)

Anodic dissolution rate in linear scale is plotted versus the Fe(II):Fe(III) relation and shown in Figures 3.

![Figure 3. Anodic dissolution rate (b) plotted versus Fe(II):Fe(III) relation.](image)
Anodic dissolution rate of these coatings is consistent with the known values for bulk magnetite anodes [16]. $\Delta M_A$ increases with the decreasing amount of Fe(II) ions, but specific resistance increases exponentially below stoichiometric point.

4. Conclusion
The study shows that coated electrode formed on a titanium substrate with homogeneous and tough magnetite coating having a thickness of about 300 µm produced through the above-described spray coating treatment has the same electrochemical durability as a bulk magnetite anode, but at the same time has decreased mass, size and brittleness. The best quality coatings can be produced when magnetite powder of size fraction of 50 – 120 µm with Fe(II):Fe(III) relation of 0.495 – 0.510 is used as a spray coating source.

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