Erosion of rod electrodes of the air AC plasma torch

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Abstract. Depending on the plasma-forming mixture, various types of electrode materials are used. If air, carbon dioxide and steam are used, it is optimal to use copper electrodes, since copper has a high thermal conductivity. Copper rod electrodes of an air AC plasma torch are considered. In the binding zone of the electric arc, the electrode material melts and boils, which leads to physical erosion of the electrode. Scanning electron microscopy with elemental analysis, X-ray phase analysis and IR Fourier spectroscopy were used to analyze the products of electrode erosion. The erosion products content copper, iron, nitrogen, oxygen, and other metals from the plasma torch case.

1. Introduction

Air plasma can be used as an oxidizer in the process of plasma gasification, a heat carrier for heating gases or liquids. The greatest load during operation of the plasma torch is tested by electrodes, therefore the electrode material must have good electrical conductivity and thermal conductivity, as well as a high melting point. Tungsten, molybdenum, zirconium, hafnium, yttrium, aluminum, copper, iron and their alloys are used as electrode materials. The choice of material depends on the nature of the working gas [1]. Tungsten is used only in the case of working on non-oxidizing gases, since in the presence of oxygen at high temperatures it is oxidized to oxides. Electrodes are made of zirconium or hafnium, the most stable materials when plasma torches operate in oxidizing environments. On the surface of these materials an oxide film is formed, on the one hand, it conducts electric current well at high temperatures, and on the other hand, protects the metal from further rapid oxidation. For gases containing oxygen, it is more rational to use copper-based alloys. Copper provides a high level of thermal conductivity, which provides low temperatures on the surface of the cooled electrode, and also has a low cost compared to hafnium and zirconium. To increase the melting and boiling point, copper alloys with components that reduce the intensity of evaporation of electrode material during the creation of plasma are often used. For example, iron, chromium, and nickel can serve as such substances [2].

When using in the experimental plasma chemical plants in the IEE RAS, high-voltage AC plasma torches with electric arcs that burn in individual cylindrical channels have proved to be well established. In the power range up to 50 kW three-phase plasma torch with rod water-cooled...
electrodes are designed. The duration of continuous operation of these devices reaches 200 hours and is limited by the resource of the electrodes. The flow rate of plasma-forming air is up to 35 g/s, the thermal efficiency is up to 95% [3]. Further increase in power due to an increase in current on rod electrodes leads to their more intensive wear. As a result, a high-voltage AC plasma torch with power up to 500 kW with cylindrical hollow electrodes was created (Fig. 1) [4].

The principle of operation of such a plasma torch is similar to the above described high-voltage plasma torches stabilized by a swirling gas flow of an arc also burn in separate cylindrical channels, closing one another at the exit from the body. The difference lies in the fact that arc bindings are not installed on a small-sized end face of the rod electrodes, but continuously rotate along the inner surface of the hollow electrodes. The thermal efficiency of such a plasma torch is about 92%. Resource tests have shown that such a plasma torch can work continuously for 2,000 hours [5].

2. Experimental section
Sampling is carried out on a water-cooled stainless steel surface (Tab. 1). After cooling the erosion products were mechanically separated from the cooled surface.

| Sample   | 1     | 2     |
|----------|-------|-------|
| Electrode| Copper, hollow |       |
| Plasma torch power, kW | 200 | 450   |
| The mean temperature, 10$^\circ$K | 2.8 | 3.2-3.3 |

The following physicochemical methods were used to study the compositions and structures of the erosion products of plasma torch electrodes: elemental analysis (EDAX); scanning electron microscopy (SEM); IR spectral analysis (FTIR); X-ray phase analysis (XRD); differential thermal analysis (DTA).

2.1 Elemental analysis and scanning electron microscopy
Element analysis (energy dispersive X-ray spectral analysis) was carried out using the EDAX FP 2012/12 microprobe attachment on a Quanta 200 FEG Environmental Scanning Electron Microscope (ESEM) device to determine the percentage of chemical elements included in the samples. The error in determining the content of elements by this method varies depending on the atomic number of the element and on the average is ± 0.3 mass. %. Table 2 shows the conditions for obtaining microphotographs of the structure of the samples with an increase of 2500.

| Sample   | 1 | 2   |
|----------|---|-----|
| Voltage, kV | 20 |     |
| Working distance, mm | 9.6 | 10.3 |
| Scanning speed, sec | 91.19 | 36.48 |
| Temperature | room indoor temperature |     |
| Pressure | vacuum |     |
2.2 IR spectral analysis
To determine the groups of atoms and the structure of the samples, IR spectral analysis was performed on a SHIMADZU IRTracer-100 IR-Fourier spectrometer under vacuum at room temperature. IR transmission spectra were measured in the range from 350 to 4000 cm\(^{-1}\) with a resolution of 2 cm\(^{-1}\), the moving speed of the moving mirror of the interferometer was 2.8 mm / s. To conduct IR spectral measurements, the solid samples and powder of dry potassium bromide in the ratio 1: 200 were triturated together.

2.3 X-ray phase analysis
To determine the composition of the crystalline phase, an X-ray diffraction analysis was performed on a powder X-ray diffractometer SHIMADZU XRD-7000 on Cu K\(\alpha\) radiation (\(\lambda = 1.5046 \text{ Å}\)). The parameters for the analysis are shown in Table 3.

| Table 3 - Analysis parameters |
|-------------------------------|
| Sample | 1 | 2 |
| Voltage, kV | 35 | |
| Current, A | 30 | |
| Temperature | room indoor temperature | |
| Measurement step, deg. | 0.02 | |
| Range of Bragg angle, 2\(\Theta\), deg. | 10 – 80 | |
| Holding time at point, s | 3 | 8 |

The data obtained were processed in the PDWin 4.0 software package with a PDF2 powder diffraction database. The Rietveld method was used to determine the crystal phase ratios in the samples.

2.4 Differential-thermal analysis
To determine endothermal and exothermic transitions as a function of temperature, a differential thermal analysis was carried out using the SHIMADZU DTG-60A. The analysis was carried out under an air atmosphere. As a reference sample, aluminum oxide was used. The samples were heated from room temperature. Table 4 shows the measurement conditions and the end-of-analysis temperature.

| Table 4 - Data of differential thermal analysis |
|-------------------------------|
| Sample | 1 | 2 |
| Weight of sample, mg | 16,097 | 19,944 |
| Temperature of the end of heating, °C | 1100 | |

Heating of samples 1 and 2 at 200-300°C and 300-1100°C was carried out at a rate of 3 deg/min. and 10 deg/min, respectively.

3. Results and discussion
Samples 1 and 2 are light green powders with particles of different sizes. Table 5 shows the results of elemental analysis of the surface of these samples. The presence of iron in the samples indicates that the electric arc interacts not only with the material of the electrode, but also with the case of the plasma torch made of stainless steel. Especially probable is the entrainment of the material of the plasma torch housing at the time of its launch, when the electric arc of one of its bindings moves along the inner surface of the arc channel. The presence of carbon in the sample is explained by the presence of carbon dioxide in the air used to generate the plasma.

From the analysis of the samples, it can be concluded that with an increase in the power of the AC plasma torch, the content of iron and copper in the products of erosion of the copper electrode increases, and the remaining elements, respectively, decreases.
Table 5 - Content of elements in the products of erosion of copper electrodes of AC plasma torches of various powers

| Element   | Content, mol. % |
|-----------|-----------------|
|           | Sample 1 (200 kW) | Sample 2 (450 kW) |
| Oxygen    | 50.29            | 47.04            |
| Copper    | 24.97            | 32.80            |
| Nitrogen  | 13.34            | 10.47            |
| Carbon    | 10.69            | 8.11             |
| Iron      | 0.71             | 1.58             |

X-ray diffraction patterns of the samples are shown in Fig. 2. X-ray diffraction patterns a and b have a similar character, the difference is in the intensities of the peaks. Comparison of the diffraction patterns with a file of powder diffractograms PDF 2 shows the presence of several crystalline phases in the investigated samples: orthorhombic copper (II) orthogranite, monoclinic copper (II) oxide and cubic copper oxide (I), the percentage of which is given in Table 6.

Figure 2. X-ray diffraction patterns of erosion products of copper electrodes of AC plasma torches of different capacities: a - sample 1, b - sample 2

Table 6 - Phase fraction in samples

| Phase                        | Content, mass. % |
|------------------------------|------------------|
|                              | Sample 1 \( R_{wp}=5.38\% \) | Sample 2 \( R_{wp}=6.67\% \) |
| Copper (II) trihydroxonitrate| 50.23            | 76.33            |
| Copper oxide (II)            | 6.86             | 18.34            |
| Copper oxide (I)             | 42.91            | 5.33             |

These assumptions are confirmed by the results of IR spectral analysis. Fig. 3 shows IR spectra of samples of erosion products of copper electrodes of AC plasma torch working in air and various capacities. They represent a similar complex picture with whole series of absorption spectra. The infrared spectra of sample 1 (Fig. 3a) obtained by operating an AC plasma torch with a power of 200 kW and sample 2 (figure 3b) of 450 kW are compared. Both spectra are characterized by the presence of bands of OH-groups: 3546 (vs), 3433 (us) cm\(^{-1}\) and NO\(_3\) groups: 1384 (vas), 1344 (us), 1047 (us), 840 (δs), 787 (δas) cm\(^{-1}\) [6]. Also on the IR spectra of the samples are peaks with wave numbers 1631 (δs), 1562 (δs) cm\(^{-1}\), related to the deformation vibrations of the H-O-H bond in adsorbed water. Obviously, these groups are part of the compound Cu\(_2\)(OH)\(_2\)NO\(_3\) [7].
Figure 3. IR absorption spectra of the samples under study: a - sample 1; b - sample 2

Also on these spectra there are peaks with wave numbers 1423 (vas), 1047 (us), 877 (δs), 679 (δas) cm⁻¹, which can be attributed to the vibrations of atoms in the CO₃⁻ group. However, during the X-ray phase analysis of the test samples, the presence of carbonates is not revealed, therefore, it can be assumed that the carbonates are in the amorphous phase.

Peaks with wave numbers 787 (us), 585 (us), 511 (vas), 456 (δ), 433 (δ) cm⁻¹ can be attributed to vibrations of Cu-O-Cu bond atoms in the copper (I) oxide molecule [8]. Peaks with wave numbers of 585, 456 cm⁻¹ to the stretching vibrations of Cu-O bond atoms in the molecule of copper (II) oxide [8, 9]. A peak with a wave number of 585 cm⁻¹ can be related to the stretching vibrations of the Fe-O bond in the Fe₃O₄ molecule [9, 10].

Fig. 4 shows the thermograms of the samples under study. Analyzing the change in mass (Fig. 4a curve 1) and the change in enthalpy (Fig. 4a curve 2), when heating sample 1, we see that at the beginning of heating, moisture begins to evaporate from the sample under investigation, which, possibly, the sample was enriched when exposed to humid air. About 208 °C there is a peak on curve 2, which corresponds to the endothermic effect, i.e. decomposition occurs, presumably copper (II) hydroxycarbonate (reaction 2) (Δm₁ = 0.282 mg) [11]. A temperature of 220 °C was followed by the release of structural water from copper (II) trihydroxinitrate and its further decomposition to form copper (II) oxide (reaction 3) [12, 13] (Δm₂ = 1.514 mg). In the temperature range 300 - 1025 °C, curve 2 has the form of a plateau, which indicates the stability of chemical compounds in this temperature range and the absence of chemical transformations. Near 1000 °C, curve 1 shows an increase in mass, indicating the conversion of copper (I) oxide to copper (II) oxide. The peak on curve 2, observed at 1050 °C, presumably corresponds to the decomposition of copper (II) oxide on copper (I) oxide and oxygen (reaction 4) (Δm₃ = 0.545 mg).

\[
\begin{align*}
(CuOH)₂CO₃ &\rightarrow 2CuO + CO₂ + H₂O \quad (1) \\
4Cu(OH)₂NO₃ &\rightarrow 8CuO + 6H₂O + 4NO₂ + O₂ \quad (2) \\
4CuO &\rightarrow 2Cu₂O + O₂ \quad (3)
\end{align*}
\]

At a temperature of 1089 °C, an endothermic effect is observed, accompanied by an increase in the mass of sample 1 (Δm₄ = 0.09 mg). This fact could not be explained by chemical transformations.

In the case of sample 2 (Fig. 4b), a similar situation is observed, but the temperatures of the thermal effects are shifted by 4-7 °C, which is permissible. At the same time, Δm₁ = 0.45 mg, Δm₂ = 4.669 mg, Δm₃ = 1.327 mg.

In the literature [14] it is pointed out that in the air, magnetite Fe₃O₄ already oxidizes to γ-Fe₂O₃ at low temperatures and with slight heating, α-Fe₂O₃ is formed with further heating above 300 °C. Perhaps because of so small a content of magnetite in the sample, the thermogram does not notice the course of these processes.
Figure 4. Thermograms of the erosion products of copper electrodes of plasma torches operating in air and at various powers: a - sample 1, b - sample 2: 1 - change in mass upon heating, 2 - change in enthalpy upon heating

Thus, the use of a set of physicochemical methods of investigation makes it possible to determine the main composition of the products of erosion of a copper electrode taking into account the amorphous phase of copper (II) hydroxycarbonate.

The obtained data indicate that during operation of copper electrodes in an AC plasma torch operating in air, the products of interaction between the material of the electrodes and air are formed on them. In the course of the study, physicochemical methods of analysis found that the products of erosion of the copper electrode of an AC plasma torch operating in air consist of copper (II) oxide trihydroxonitrate, copper (II) oxide, copper (I) oxide, copper (II) hydroxycarbonate, as well as a small amount of magnetite. The percentage of these substances in the products of erosion is determined by the thickness of the plasma torch. At relatively low powers (120-200 kW), the major portion is copper (II) trihydroxonitrate and copper (I) oxide. Increasing the power of the plasma torch of alternating current, the content of trihydroxonitrate in the products of erosion of the copper electrode substantially increases, the content of copper (II) oxide and magnetite also increases. Based on the composition of the products of erosion, one can put forward a hypothesis about their formation. In the binding zone of the electric arc, copper is heated, accompanied by melting, evaporation, spraying, etc. The ionized air stream interacts with copper particles: copper is oxidized to copper (I) oxide (reaction 4), oxidation of the formed copper (I) oxide to copper (II) oxide (reaction 5) also occurs, copper reacts with oxygen, carbon dioxide and water (reaction 6), nitrogen reacts with oxygen (reaction 7), copper (I) oxide reacts with nitric acid, hydroxyl and steam (reaction 8).

\[
\begin{align*}
4\text{Cu} + \text{O}_2 & \rightarrow 2\text{Cu}_2\text{O} \quad (4) \\
2\text{Cu}_2\text{O} + \text{O}_2 & \rightarrow 4\text{CuO} \\
2\text{Cu} + \text{O}_2 + \text{CO}_2 + \text{H}_2\text{O} & \rightarrow (\text{CuOH})_2\text{CO}_3 \quad (6) \\
\text{N}_2 + 2\text{O}_2 & \rightarrow 2\text{NO}_2 \quad (7) \\
\text{Cu}_2\text{O} + 2\text{OH}^- + \text{HNO}_3 & \rightarrow \text{Cu}_2(\text{OH})_2\text{NO}_3 \quad (8)
\end{align*}
\]

At the moment of plasma torch launching, the electric arc interacts with the plasmatron body, while the material is carried away, proceeding from the elemental composition of the erosion products-iron. Iron interacts with the plasma flow of air, forming an iron scale (reaction 9).

\[3\text{Fe} + 2\text{O}_2 \rightarrow \text{Fe}_3\text{O}_4 \quad (9)\]

4. Conclusion

When copper electrodes operate in an AC plasma torch operating on various mixtures, the interaction products of the electrode material with the plasma-forming medium are formed on them. The erosion of the electrode material can affect the operating mode of the plasma torch and the physico-chemical processes taking place in it, and erosion products can contaminate the products of plasma synthesis, and also participate in the chemical process as a raw material or a catalyst.

In the course of the study, physico-chemical analysis methods found that the products of erosion of the copper electrode of an AC plasma torch operating in air are copper (II) trihydroxonitrite, copper (II) oxide, copper (I) oxide, copper (II) hydroxycarbonate, and also a small amount of magnetite. The...
percentage of these substances in the products of erosion is determined by the thickness of the plasma torch. Increasing the power of the plasma torch, the content of trihydroxonitrate, copper (II) oxide and magnetite in the products of erosion of the copper electrode substantially increases.

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