ABOUT CHANGES IN THE CHEMICAL COMPOSITION OF THE ELECTROLYTE IN THE PROCESS OF ELECTROLYTIC-PLASMA TREATMENT OF MATERIALS

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Abstract

There are the results of chemical analysis of the spent electrolyte (an aqueous solution of ammonium sulfate) after the process of electrolytic-plasma polishing stainless steel 12X18H10T (AISI 321) and steel 03H16N15M3 (AISI 316L), and chemical analysis of the solid residue produced after the electrolytic-plasma polishing. The results of these tests can more accurately describe the process model for electrolytic-plasma polishing.

Keywords: *finishing, Anode heating, polishing, electrolytic-plasma polishing, surface roughness, chemical analysis*

1. INTRODUCTION

One of the most common methods of surface treatment is polishing. Polishing gives the product a beautiful decorative shine, and is also used in the preparation of the surface coating.

Known methods for surface treatment of metals can be divided into three groups: mechanical, chemical and electrochemical. Electrolytic-plasma treatment (EPT) especially allocate among electrochemical methods of surface treatment.

At the beginning of the last century the foundations were laid for electrolytic-plasma treatment in studies heating and glow processes occurring on or near the surface of the electrode of small area [1]. Currently, the technology of processing of details by this method is not fully understood and is under research and development.

The phenomenon of cathode and anode heat conductive materials in aqueous electrolyte solutions, processes of local boiling of electrolytes in the vicinity of the electrode with a low surface, the formation of a continuous and stable vapor-gas shell, its electrical conductivity, thermophysical and electrochemical aspects of the anode heating options were reviewed in [1].

The phenomenon of the heating of metal details of the cathode to remove from the surfaces of various types of pollution and lubricants for further hardening of the surface of details and causing all sorts of metallic coatings (Zn, Ni, Zn-Ni, Ni-Cu etc.) were studied in [2-4].

Studies conducted in recent years in the field of electrolytic-plasma processing of metals and alloys were summarized in [5, 6]. There are the basic features of the technology for electrolytic-plasma polishing (EPP) and present new scientific and practical results on the treatment of various materials by this method.

Despite the large number of studies in this area, the researchers did not have a clear understanding of the mechanism of removal from the micro-roughness of the metal surface of the workpiece in the process of the EPP, and there is no accurate representation of what is a "working tool", whereby smoothing effect of metal surface manifested .

In this article there are the results of the chemical analysis of the spent electrolyte (aqueous solution of ammonium sulfate $(NH_4)_2SO_4$) and a solid precipitate formed on the bottom of the bath, after the process of the EPP 12X18H10T stainless steel (AISI 321) and steel 03H16N15M3 (AISI 316L). The model origin, development of steam shell with time, formation of a solid precipitate and changing the chemical composition of the electrolyte are analyzed based on research and experience [1-7],

2. THEORETICAL INFORMATION

2.1 Description of the process for electrolytic-plasma polishing

The essence of the method EPP is that by immersion in an aqueous electrolyte solution machined metal detail is applied the positive pole of high voltage power source, and the negative pole is applied to the metal bath, wherein the electrolyte is located. When the sample is immersed in an electrolyte, there is a thin vapor-gas cushion around the product, and the electric field intensity increases dramatically to the point where chemical, covalent, metallic, or other ties are destroyed, there are alternating redox processes that translate the elements found in the surface layer in the compound, which can be easily separated from the surface [6].

The dependence of the current density of the applied voltage is shown in Fig. 1 [1, 7].

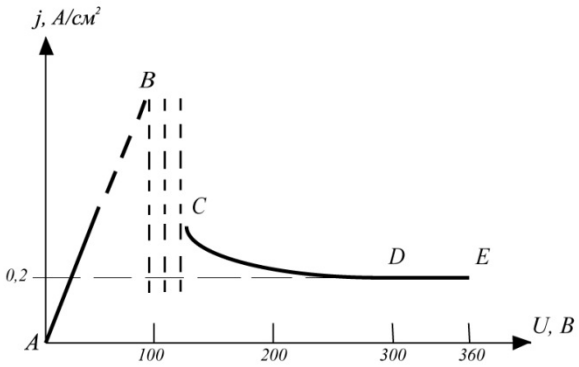

Fig. 1 – Voltage-ampere characteristic of EPP at the anode

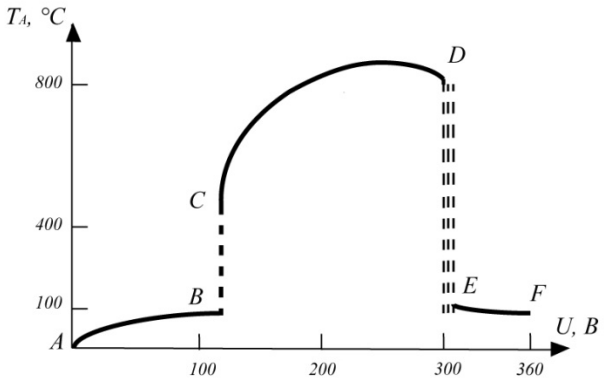

Fig. 2 – Voltage-temperature characteristic of the heating of the anode in the process of EPP

At low voltages, the flow of current in the solution volume is described by Ohm's law and the processes at the electrodes - Faraday's law (section *AB*) without any optical or acoustic effects. The increase in voltage leads to heating of the electrolyte in the anode zone mainly, because it focused almost all resistance. In the area *BC* there is interrupt mode current. The passage of current becomes pulsed character of the fact that a steam layer surrounding the anode, periodically condenses and again formed. The electrical breakdown of steam is the reason for the destruction of the shell, causing an explosive expansion and subsequent condensation of it. Spark discharges creates intermittent the glow, the emergence and disappearance of shell are accompanied by noise and crash. At point *C* steam-gas shell becomes stable; it passes through a direct current with low pulsations. The temperature of the anode increases sharply. The region *CD* is a high temperature heating regime. The current voltage characteristic is the nature of the incident because the shell thickness increases with increasing voltage, and its electrical resistance increases. In the area *DE* there is a stabilization current density and the process of EPP, and the current densities are in the range from 0.2 to 0.5 A/cm^2.

The current-temperature characteristic has a maximum at voltages of 260-280 V (Fig. 2). At lower voltages, the anode temperature rise due to the increase of power released in the steam -gas shell. At point *D* the anode temperature is sharply reduced, the current remains practically unchanged. In the area *DE* in the shell electrical discharges occur with a sprinkling of the electrolyte, which cools the anode [1, 7]. Based on practical research it revealed that in the area *EF* there is a decrease in temperature, alignment of its value, which tends to the temperature of the electrolyte, consequently strong heating of samples processed in the process of EPP does not occur.

2.2 Chemical and physical model of steam shell

In [2, 7], the authors tried to explain the processes taking place in the vapor-gas shell in the EPP. For this purpose, they have developed a model of steam shell, which in turn will identify the necessary parameters shell, with the help of which it will be possible to manage the process.

As it is well known, there are two types of boiling: bubble and shell. In order to process EPP a decrease roughness by removal microprojections with surface of the workpiece, the anode must be supported by the type of film boiling electrolyte [7]. In the area *CD* (Fig. 1) the thickness of the vapor shell increases under high voltage that promotes the growth of its electrical resistance, causing strong heating of the anode [1]. Isolation in the anode zone of sufficient energy to boiling in a volume of the electrolyte, gives rise to a release surface of the anode gas bubbles, which in turn initiates the electrolyte boiling and bubble boiling develops into shell. The surface of the solution at the boundary of a shell filled with steam ions and molecules of dissolved substances, a number of water molecules included in the hydration shells of these ions. During boiling hydrated molecules involved in exchange with the vapor phase molecules that contributes to the transfer of individual ions in solution casing (Fig. 3, a) [2].

Occurrence conductivity in the anode shell is explained vapor emission anions in solution and their concentration shell around the gas bubbles (OH^-, SO_4^-, O^{2-}). The gas-vapor shell also contains electrons, ions of the electrolyte and the anode (H^+, Fe^{2+}, Fe^{3+}, Ni^{2+}, Cr^{3+}) [7]. When significant tensions the surface of the bubble becomes noticeable negative charge, whereby the contents of a bubble is ionized, and the bubble is formed inside the high-temperature plasma, which melts the top layer of the surface of the anode. Due to the high temperature, a gas bubble expands instantaneously (Fig. 3, b). Expanding, bubble of gas creates a high shock wave energy is partially dissipated in the electrolyte, and the rest of the energy is reflected from the boundaries of the "pair-electrolyte" and a lot of pressure compresses the gas bubble, causing it to collapse (Fig. 3, c). The collapse bubble occurs after the time of screening of the shock wave from the boundary of the "vapor-electrolyte" (Fig. 3, d). During the collapse bubble in the void fall ions and anions present in the steam shell, transported to the surface of the anode by the electric field and the effect of shock waves, which managed to be reflected from the interface between the electrolyte and the vapor phase (Fig. 3, e). The emission of ions from the anode surface should occur on the tops microperturbations. Interaction of anions from the anode surface leads to the formation of the oxide shell (Fig. 3, f). After the collapse bubble with gas and the bombing of the anode by anions in the cavity formed by the droplets fall into the electrolyte, and there come into contact with the surface of the anode, which makes its partial role in the formation of an oxide shell. Cycle times of "working" bubble and, consequently, its lifetime is a few thousandths of a second (10^{-6}–10^{-5}s) [1–7].

According to research conducted in the study of electrochemical processes [8], polishing process occurs when the rate of formation of the oxide shell is comparable to the rate melting of its high temperature plasma. The smallest detail of the surface roughness is achieved with a minimum thickness of the oxide shell, which should be sufficient to prevent the etching effect of the spray of electrolyte inside the steam shell. For this it is necessary that the rate of electrochemical processes of formation of the plasma membrane and its removal was high.

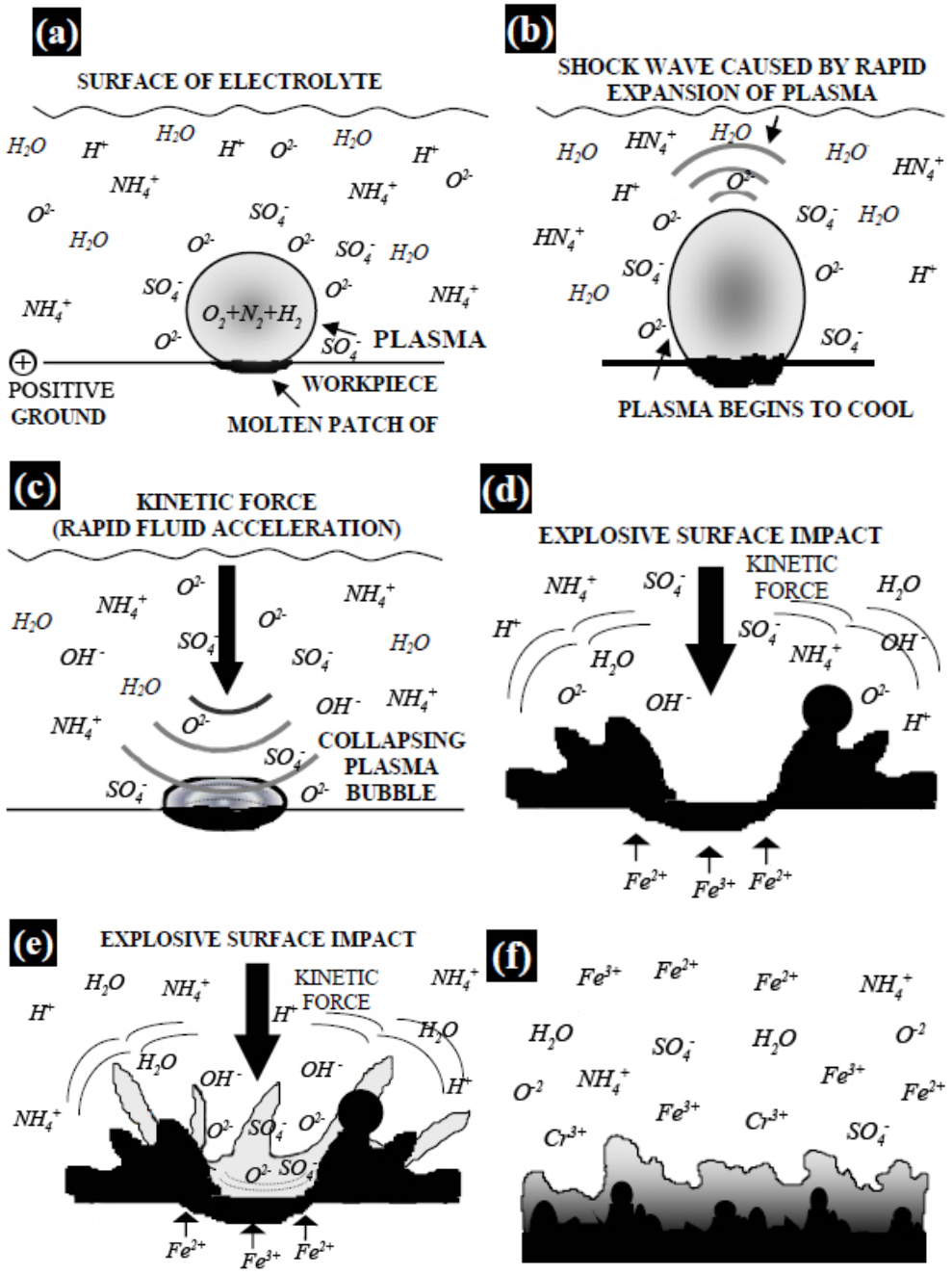

Fig. 3 The scheme mechanism EPP: a – gas bubble on the surface of the anode; b – a shock wave due to the cooling of a gas bubble; c – compression gas bubble bounced back from the border "vapor-electrolyte" shock wave; d – gas bubble collapse; e – filling voids ions and anions present in the vapor shell; f – forming an oxide shell on the anode surface.

Practical experience has shown that the melting of the surface layer of the sample takes place only in the process of warming up of the electrolyte, when there is a significant heating of the surface of the anode. Such a phenomenon is not observed in the process of electrolytic-plasma polishing. According to the microscopic study of the surface of the treated samples [10], removal of the surface layer of the material with the removal of α- and α'- phase occurs with the surface of the samples, the resulting amount of γ-phases is increased in the volume of the material.

At the microscopic intensity of the electric current is high, and therefore create a higher current density and electrical resistance on them less than on the grooves (Fig. 4). When current flows through the

electrolyte at the anode surface is formed of a liquid layer of anodic dissolution products having an increased viscosity and high electric resistance. The thickness of a viscous liquid shell varies in different parts of a rough surface; it is more in the recesses (h_1), than on the protrusions (h_2).

Due to the uneven surface of the insulation of the anode occurs uneven distribution of electric current therein. A higher density sets on the protrusions, than in the recesses. Therefore protrusions dissolve more intensively, which ultimately leads to the equalization of the rough surface.

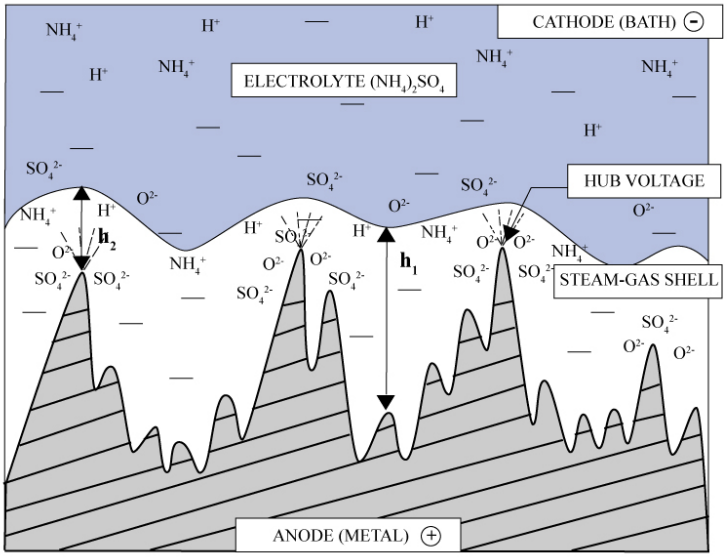

Fig. 4 The mechanism of electrolytic-plasma polishing

2.3 Physical and chemical processes occurring during the formation of a solid precipitate

Present on the metal surface defects: free lattice sites which should be occupied by iron atoms; nodes that belong to the oxygen atoms engaged in the iron atoms, facilitate the diffusion mobility of iron atoms, which can be moved to the surface to create new oxides and accelerate the oxidation process [1, 7].

If we consider the composition of the oxide layer formed in the process of polishing, it varies considerably in thickness. The outer layer is usually higher oxides enriched, whereas the surface is advantageously lower oxides [7]. Thus, iron oxide is composed, when viewed from the outer to the inner layer of oxides Fe_2O_3, Fe_3O_4, while the surface of the metal is of nitrous oxide FeO [9].

The oxidation of iron can go in the next reaction:

$$3Fe + 4\,H_2O \rightarrow Fe_3O_4 + 8H^+ + 8\,e^- \quad (1)$$

The dissolution of iron from the anode surface may occur with the formation of both Fe^{2+}, and Fe^{3+}.

$Fe \rightarrow Fe^{2+} + 2\,e^-$;

$Fe^{2+} + O_2 \rightarrow Fe^{3+} + 2\,O^{2-} + e^-$;

The dissolution mechanism to form Fe^{2+} is preferred as the intermediate stage, since minimal value of the electrochemical potential meets to this process. However, iron Fe^{2+} ions in solution were not detected. Therefore it is necessary to take into account one-time occurrence of several electrochemical reactions. The general form of the steel anode dissolution reaction can be written as

$$Fe + 3\,H_2O \rightarrow Fe(OH)_3 + 3\,H^+ + 3\,e^-, \quad (2)$$

Here $Fe(OH)_3$ – idealized account of multiple forms $Fe_2O_3(H_2O)_x$ and $FeOOH(H_2O)_x$. The formation of hydrogen ions in the reactions (1) and (2) can serve as the basis of the detected acidifying electrolyte [1].

Similar oxidation reactions can be written for Ni^{2+}, Cr^{3+}.

Thus, the oxidation of chromium can go in the next reaction:

$2\ Cr^0 + 3\ H_2O \rightarrow Cr_2O_3 + 6\ H^+ + 6\ e^-$

Dissolution of chromium from the surface of the anode can occur to form both Cr^{2+}, Cr^{3+} and Cr^{6+}. Cr^{3+} is the most stable at high temperatures, i.e. chromium oxide (III) – Cr_2O_3 is precipitated.

Oxidation of nickel is:

$Ni^0 \rightarrow Ni^{2+} + 2\ e^-$

Nickel in the process of EPP often oxidized to Ni^{2+}. Nickel oxide (III) Ni_2O_3 is a strong oxidant and hence can't exist in the acidic environment of the electrolyte.

3. PRACTICAL RESULTS

Electrolytic-plasma surface treatment method affects the surface of the treated material, modifying it, and gives other properties. After processing, the material changes its microstructure in the surface layer, the roughness parameters and microhardness.

In this study the samples were subjected to the treatment, made of stainless steel 12X18N10T (AISI 321) (GOST 7350-77) and steel 03H16N15M3 (AISI 316L), which structure is shown in Table 1 (GOST 5632-72).

Table 1 The chemical composition of the steel 12X18N10T and 03H16N15M3 (GOST 5632-72).

Element	**Mass fraction of elements, %**	
	12X18N10T	**03X16N15M3**
Fe	67	64
Cr	17,0-19,0	15,0-17,0
Ni	8,0-9,5	14,0-16,0
Mn	No more 2,0	No more 0,8
Si	No more 0,8	No more 0,6
Cu	No more 0,3	
Ti	5·C-0,8	
S	0,02	No more 0,015
F	0,035	No more 0,020
Mo		2,5-3,0
Nb		0,25-0,50

In the process of EPP, according to the model above, there is removal of the upper layer sample; therefore, metal ions pass into the solution. Since Fe, Cr, Ni are the main components of steel 12X18N10T and 03H16N15M3, these elements and their connections must be in the waste solution and the solid precipitate, with the total amount proportional to the amount of these elements in steel. A study of the elemental composition of solid precipitate and spent solution has allowed checking the accuracy of the estimated physical and chemical processes occurring in EPP.

Measuring the values of roughness was carried out using a profilometer TR200 before and after processing samples by the method EPG. The surface roughness after EPO decreases with Ra = 0,2-0,3 nm up to Ra = 0,05-0,06 nm.

3.1 Investigation of the chemical composition of the exhaust ammonium sulfate solution

An analysis of the elemental composition of a sample, the spent ammonium sulphate solution after EPP, conducted in the test center of the SSI Powder Metallurgy Institute.

A study of the elemental composition spent solution of ammonium sulfate after EPP conducted on certified atomic emission spectrometry with inductively coupled plasma «ACTIVA M» (France) (calibration certificate of 20.09.2014 №29348-50). The error of the method is the relative 3–5 percent.

Qualitative and quantitative composition has been defined as a result of the study of the elemental composition, the ammonium sulfate spent solution after EPP. The results are shown in Table 2.

Table 2 Content of elements in the spent solution after ammonium sulfate EPP

Element	**Concentration, mg / l**
Ni	209
Cr	70
Ca	40
Si	31
Mn	26
Fe	13
K	9
Cu	4
Co	3
Zn	Менее 1

Analysis of data obtained from the study of the elemental composition spent solution after ammonium sulfate EPP shows that ions of Ni, Cr, Fe and Mn contains in large quantities in the solution, which enter the solution from the surface layer of the processed material. Because the solution has acidic environment (pH=2,2), it is based on the dissociation constants of the ions Fe^{2+}, Fe^{3+}, Cr^{3+}(pH≈3-4), almost all of the ions Fe^{2+}, Fe^{3+} and Cr^{3+} ions is partially associated with oxide and precipitate. The dissociation constant for Ni^{2+} is significantly higher (pH≈ 7–8) ions therefore remain largely in solution in the form of ions and may hydroxycomplexes. With further increase of the pH, Ni ions also bind with the oxide and precipitate. Thereby it is possibly cleaning solution from contaminants (in the form of metal ions) and clean utilization the ammonium sulfate spent solution.

3.2 The study of the chemical composition of the sediment

An analysis of the elemental and phase composition of the solid precipitate forming after EPP, conducted in the test center of the SSI Powder Metallurgy Institute. The study was conducted on the elemental composition certified XRF spectrometer ED 2000 (calibration certificate BY 01 № 451-50K BelSIM of 26.12.2012), and phase composition - X-ray diffractometer DRON-3 CuKα-radiation.

X-ray fluorescence method for the determination of elements, spectrometer ED 2000 is based on it, is based on the intensity of the characteristic lines of the fluorescence element of its mass fraction in the sample. Excited by the primary X-ray radiation characteristic elements in the sample is decomposed into the spectrum followed by measurement of the analytical signal and determining the mass fraction elements using calibration curves.

Explanation of spectra is performed using the so-called "profiles" of elements – peaks of each element measured on pure samples. These profiles are superimposed on the spectrum analyzed and used to calculate the integrated areas of the peaks corresponding.

The analysis of X-ray fluorescence spectrometer for ED 2000 found that the test sample has the following chemical elements: Fe, Cr, S, Ni, Ti, Cu, Mo, Si, Mn (Table 3).

Table 3 Chemical composition of the sample of the solid residue formed after EPP

	Element	**Mass fraction, %**	**Relative error,%**
Elements of passing into solution and a precipitate of steel	Fe	66,18	0,12
	Cr	11,38	0,19
	Ni	0,9	0,02
	S	18,1	0,24
	Si	0,93	0,07
	Cu	0,26	0,01
	Ti	0,58	0,02
	Mn	0,08	0,03
	Mo	1,04	0,01
Elements that are impurities in the water, the ammonium sulfate etc.	V	0,09	0,01
	P	0,23	0,05
	Ca	0,13	0,01
	Zn	0,09	0,01
	As	0,014	$1,66 \cdot 10^{-3}$
	Nb	0,014	$2,51 \cdot 10^{-3}$

Analyzing the data in Table 3, it should be noted that some of the elements (Fe, Cr, S, Ni, Ti, Cu, Mo, Si, Mn) pass into solution, and, consequently, in the precipitate by removal of the upper layer of steel during EPP. According to [10], removal of the surface layer of the material is from 10 to 30 microns, and the depth of softening layer is of the order of 100 microns. It should also be noted that the analysis identified a number of impurities (V, P, Ca, Zn, As, Nb), i.e. element goes into solution and precipitate out of the water, the salt of ammonium sulfate and other means. The error of the method for determining the relative was 8-10 percent.

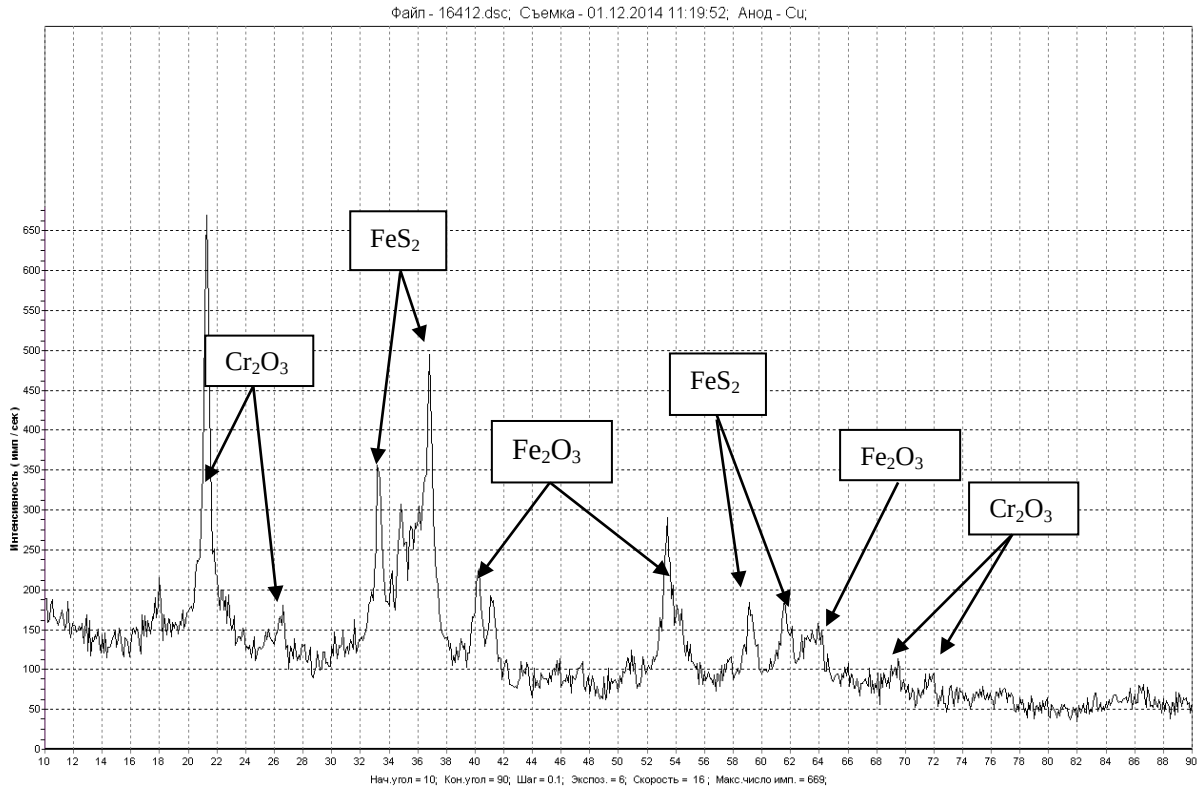

Fig. 5 radiograph test sample of dry sludge after EPP

Fig. 5 shows the roentgenogram test sample of dry residue after EPP, where the most intense peaks Cr_2O_3, FeS_2 и Fe_2O_3 are marked. Starting angle displacement detector is 10°, end angle – 90°; step for step movement detector mode – 0,1; rotational speed detector – 16 °/min; main instrumental measurement error pulse count rate of X-rays – no more 0,5%.

An analysis of the elemental and phase composition of the solid precipitate forming after EPP, which was spent on X-ray fluorescence spectrometer ED 2000 and X-ray diffractometer DRON-3 in CuKα-radiation, revealed that Fe and Cr in the related forms (oxide, sulfide) is basically fall in the precipitate, also Ni, Ti, Cu, Mo, Si, Mn are present in minor amounts, which are present in the precipitate as oxides, sulfides and other compounds.

4. CONCLUSION

In the paper there are data on the distribution of the main elements that go into solution during EPP between the filtrate and the precipitate. It was found that Fe is located primarily in the pellet, and Mn, Cr distributed between the precipitate and filtrate, which testifies to their more soluble due to the possible formation of anionic forms. This is typical for Cr, whose content in the filtrate is 20-30 times more than the precipitate. This phenomenon may be due to the formation of colloids. Ni is mainly in the form of a solution in an ionic form, it is also possible the formation of hydroxycomplexes.

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