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INFLUENCE OF GAS ENVIRONMENT ON THE COMPOSITION AND PROPERTIES OF HEAT TREATMENT PRODUCTS OF GALVANIC SLIMES

The process and composition of heat treatment of products of galvanic slimes which have different qualitative and quantitative composition of chromophore determining components are studied depending on the heat treatment conditions. It is established that the heat treatment of the galvanic slimes under different oxygen concentrations in the gas phase and chromophore determining compounds leads to the formation of a number of phases of variable composition in the form of oxygen solid solution in different modifications of iron oxide − magnetite Fe_3O_4, maghemite γ-Fe_2O_3 and hematite α-Fe_2O_3. It is shown that crystal structures of solids with well-defined arrangement of atoms retain stoichiometry only at a certain partial pressure of oxygen on the step of slime heat treatment. This pressure is a function of temperature. The formation of ferrite products determines the color of pigment-filler and content of water-soluble substances.

Introduction. One of the promising areas of processing precipitation of galvanic manufactures is to get on their basis decorative materials for the production of building materials. The global demand for mineral pigments and extender pigments is 5.5 – 6.0 million tons and every year this number is steadily increasing. Among all the pigments iron oxide pigments, in terms of consumption, occupy 18 – 20% of the market. The supply of pigments and extender pigments to the Republic of Belarus is currently provided mainly from Russia, Ukraine, Germany, China.

Approximately 19 tons of sludge, characterized by a high iron content, which is chromophore are produced annually by the machine-building, metalworking and other enterprises of our country. According to [1, 2], the color characteristics of the iron oxide pigment materials derived from the heat-treated slimes of galvanic manufactures are mainly determined by the content of iron oxides in the form of hematite α-Fe_2O_3, maghemite γ-Fe_2O_3 or magnetite Fe_3O_4. Moreover, the slimes contain compounds of chromium, nickel, copper, the content of which depends on the composition of the wastewater from galvanic manufactures and at the level of 2−25 wt. %, which affects the color tone of the iron oxide pigment materials. During the heat treatment of compounds γ-Fe_2O_3 − α-Fe_2O_3 − Fe_3O_4 are extremely sensitive to changes in temperature and oxygen partial pressure in the gas environment. It follows from the data[2] that the crystalline structures of forming iron-containing compounds with a strictly defined arrangement of the atoms retain stoichiometry only at a certain partial pressure of oxygen, which is a function of temperature. It was shown [3] that at the solid phase chemical interaction of iron oxides with other metal oxides, phases of variable composition compound that are prone to high disorder and characterized by a high concentration of non-equilibrium defects are formed. As a result of the presence of atomic, electronic defects, a part of the atoms and ions leave the regular positions in the lattice and move to a new position, potentially resulting in the formation of the new phase [3]. Not only the probability [4] of cationic substitutions is noted, but also the change of the atomic state ΣMe/O in crystalline structures. In this connection, depending on the composition of galvanic slimes and conditions of their heat treatment, the formation of a series of phases of variable composition in the form of solid solutions of oxygen in various modifications of iron oxide and spinels, that differ both in a chemical composition, structures and color tone. However, despite the large number of published data, information on the effect of the gaseous medium on the phase composition of heat treatment products of galvanic slimes is practically absent.

The aim of this work is the study of the process and products of heat treatment of galvanic slimes, differing in qualitative and quantitative composition of chromophore defining components, depending on the heat treatment conditions.

Experimental part. Galvanic sludge generated at the machine-building enterprises of the Republic of Belarus and characterized by containing the compound of iron, chromium, nickel, zinc, copper and calcium, were the objects of study. Their chemical composition in terms of the metal oxides is shown in Table 1. The investigated slimes dried at 100°C, were heat treated in a muffle furnace at 850°C for 2 hours in open and well closed crucibles under otherwise identical conditions, in particular the mass of the sample, the diameter and height of the crucible. The phase composition of the products obtained was determined by XRD analysis, the content of major ingredients - according to standard techniques.

The summarized data on the effect of heat treatment conditions on the phase composition of the sludge and the color of the resulting products are shown in Table 2. Products after drying and heat treatment of sludge at 850°C have an intense dark brown or black and brown colour. According to the results of X-ray analysis (Fig.), the products of heat treatment obtained both in open crucibles and closed ones, contain chromophore determining crystalline phases in the form of magnetite and hematite. Thus, iron-copper-containing slurry No. 1, heat treated at 850ºC in an open crucible comprises magnetite. According to [4], magnetite has the structural formula $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$, and the static distribution of the two-and trivalent cations in the octahedral lattice. Like other oxygen-containing phases of varying composition a certain stoichiometry at a partial pressure of oxygen is retained. The absence of calcium carbonate in heat treatment products which, according to X-ray diffraction is present in the starting sludge, indicating its decomposition with emission of CO_2 in the gas phase, which causes reduction of oxygen partial pressure over a solid phase. This forms CaO, which can react with Fe_2O_3 to form ferrite type $4CaO \cdot FeO \cdot Fe_2O_3$, which can't completely dissolve magnetite, however, magnetite can dissolve calcium ferrites. As it follows from the experimental data, despite the high content of zinc compounds in sample No. 2, when it is heat treated in an open crucible, only one crystal phase – magnetite is identified; and a closed type – three phases: magnetite, calcium carbonate and zinc oxide. The presence of the crystalline phase ZnO in the sample may be due, first, to its low solubility in iron oxides and the ability to maintain its structure, secondly, the possibility of the formation of the spinel phase $Zn_xFe_{3-x}O_4$ in the low oxygen, the values of interplanar distances of which differ little from the phase values ZnO.

The radiograph of iron-, nickel-, chromium-containing sample No. 3, heat-treated at 850ºC in an open crucible, corresponds to α- Fe_2O_3 on a set of interplanar spacings. The formation of hematite only in this case may be due to the high content of iron compounds and low content of calcium carbonate compounds (Table 2), in the process of decomposition of which a smaller amount of CO_2 is formed.

It is known [5] that the nickel and chromium ions have a stabilizing effect, characterized by the ability to maintain stable crystal lattice of the formed compounds of a spinel type.

According to [3], one can assume that at 850°C when the heat treatment proceeds in an open crucible, the oxygen partial pressure in the environment may exceed the equilibrium, the condition of the system is unstable and accompanied by the transition of oxygen from the gaseous phase into the solid phase lattice. The atoms of oxygen adsorbed on the surface of the crystals pull the missing electrons from the cations and are converted into oxygen ions, and finish constructing the cubic lattice of iron oxides. It was noted [4], that at a certain limit concentration of defects, the available crystal structures become non-stable and destroyed, which leads to a weakening of the binding energy of oxygen with metals and dissolution of Fe_2O_3 in Fe_3O_4.

Table 1

Chemical composition of galvanic slimes

No. of slime	Place where slime is formed	The main components in sludge wt. %					
		Fe_2O_3	NiO	CuO	ZnO	Cr_2O_3	CaO
1	RUE «Zenit» (Mogilev)	50.79	0.52	26.44	8.93	2.19	6.27
2	JSC «Belelectromontazh» (Minsk)	41.53	–	–	34.69	4.81	14.34
3	JSC «BZAL» (Baranovichi)	68.69	8.06	0.97	1.25	9.39	2.37

Note. The content of components in samples dried at 100°C.

Table 2

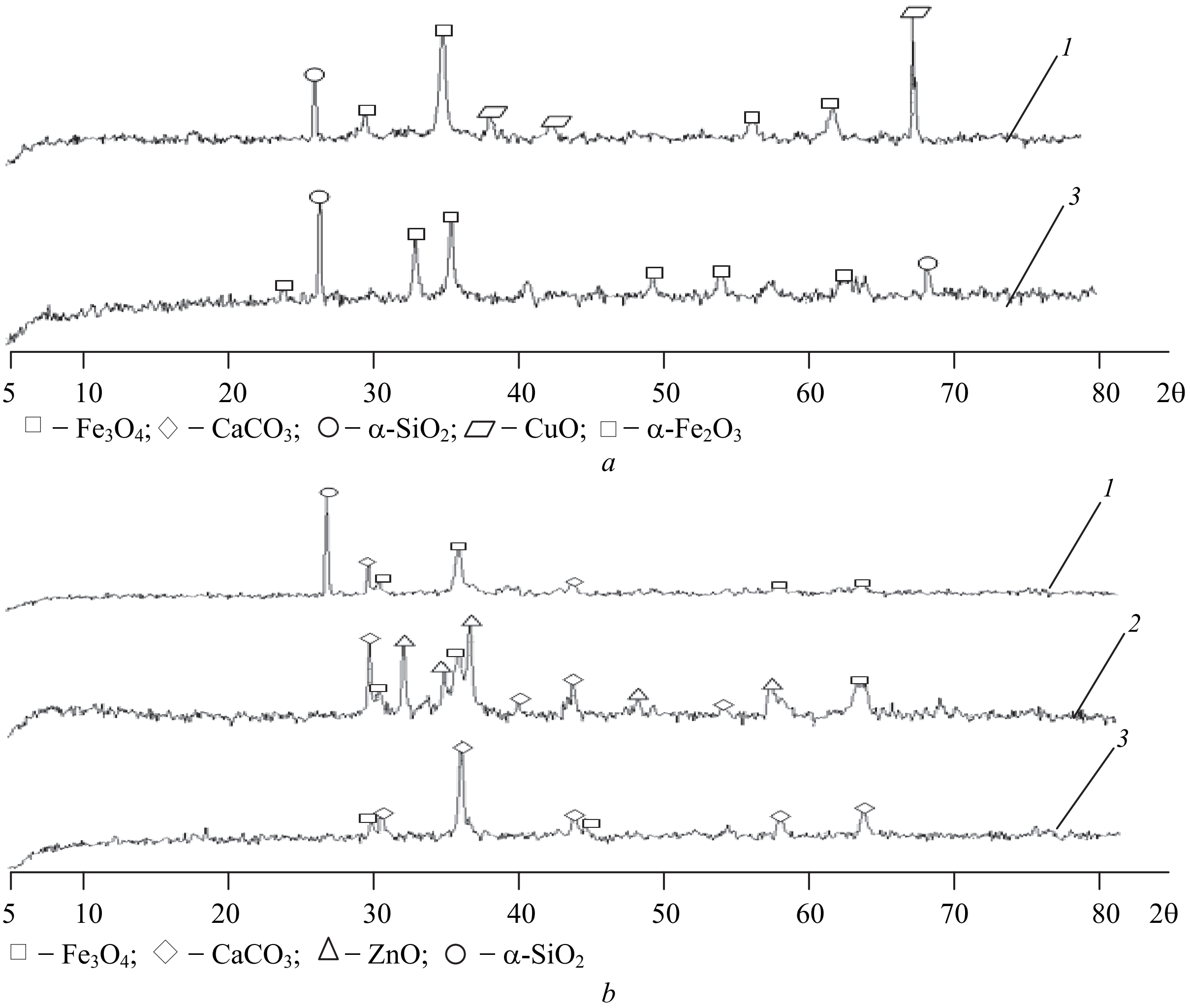
Influence of air environment during thermal treatment of slimes on the color of the products formed

No. of sample	Slime	Conditions of thermal treatment					
		in open crucibles			In closed crucibles		
		Phase composition	The content of water-soluble substances, wt. %	Color	Phase composition	The content of water-soluble substances, wt. %	Color
1	Iron-, copper-containing	Fe_3O_4 (magnetite), SiO_2, CuO	1.19	Dark-brown	Fe_3O_4 (magnetite), $CaCO_3$, SiO_2	0.94	Dark-brown
2	Iron-, zinc-, calcium-containing	Fe_3O_4 (magnetite)	2.36	Dark-brown	Fe_3O_4 (magnetite), $CaCO_3$, ZnO	1.35	Dark-brown
3	Iron-, nickel-, chrome-containing	α-Fe_2O_3 (hematite), SiO_2	5.34	Red-brown	Fe_3O_4 (magnetite), $CaCO_3$	0.83	Black-brown

The presence of peaks with interplanar spacing characteristic of magnetite Fe_3O_4 (Fig.) is noted in heat treatment of products obtained in closed crucibles for all studied groups of slimes. Besides, the presence of calcium carbonate $CaCO_3$ is noted, which is not decomposed under the given heat treatment conditions. Apparently, in a closed volume with a deficiency of oxygen the equilibrium state of the system is also unstable and is accompanied, as noted by the authors [4], by the equalization of the chemical potentials of oxygen and removing it from the lattice of the iron oxide in the gaseous medium, with a simultaneous decrease of an oxidation state of an equivalent amount of Fe^{3+} до Fe^{2+}.

Different content of oxygen in the gaseous medium during thermal treatment of slimes affects not only the chemical and phase composition of the resulting products, but also on the content of water-soluble substances. Thus, the products obtained in an open crucible, have a high content of water-soluble substances. This is particularly noticeable for samples No. 2 and 3, in which the content of chromium in terms of Cr_2O_3 is 4.8 and 9.4 wt. %, respectively. This is apparently due to the oxidation of chromium (III) and chromate formation during the thermal treatment, what was shown previously [6]. In the gaseous environment with a lack of oxygen the formation of chromate is decelerated, which follows from the experimental data presented in Table 2.

According to the experimental data (Table 2), the thermal treatment at the same temperature, but different composition of the gas phase over a solid medium influences both the phase, the chemical composition of the resulting products, and their color tone. Thus, the formation of hematite phase during the heat treatment of iron-, nickel-, chromium-containing slime in an open crucible causes the red-brown color of the products of the heat treatment. The lack of oxygen in the reaction zone during the same heat treatment results in the formation of black-brown product that is likely to be associated with the content of the trivalent chromium compounds, the oxidation state of which is low under these conditions.



Radiographs of the samples obtained in different air environment:
a – in open crucibles; *b* – in closed crucibles:
1 – sample No. 1; *2* – sample No. 2; *2* – sample No. 3 (Table 2)

Conclusion. It was established that the chromophore determining crystalline phases in the products of heat treatment of sludge at 850°C are (depending on slimes composition) magnetite or hematite.

It has been shown that the increase in the oxygen concentration in the gaseous phase leads to an intensification of the process of oxidation of Cr (III) in Cr (VI), an increase of water-soluble substances through the formation of chromate and the resulting products of heat treatment of black-brown color.

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