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SYNTHESIS AND PROPERTIES OF MIXED IRON AND BISMUTH VANADATES

The solvothermal method for the synthesis of mixed iron and bismuth vanadates was proposed. Physicochemical properties of the obtained samples: oil absorption, pH of the aqueous extract, particle size, density, – were determined. Electrochemical studies of the inhibitory properties of vanadates relative to the steel substrate were conducted. It is established that the received mixed iron and bismuth vanadates may be used in the paint industry as a replacement for lead-bearing and chromate pigments.

Introduction. Currently orthovanadates are most widely used in various industries. They are used as a mordant in dyeing fabrics, for fixing aniline on silk, as catalysts (e.g., iron vanadate is a catalyst component of oxidation of alcohols to aldehydes), they are in the composition of glasses and glazes [1]. Due to its low solubility in water and alkaline solutions bismuth orthovanadate refers to nontoxic yellow pigments [2]. This pigment is more expensive product than lead compounds, bat bismuth orthovanadate has a significantly higher coloring strength and much purer shade [2].To reduce costs and obtain a wider range of colors of pigments it is expedient to realize in the composition of bismuth orthovanadate complete or partial replacement of bismuth or vanadium to cheaper components.

The aim of the present work was to study the possibility of using solvothermal method [3] for the synthesis of mixed bismuth and iron orthovanadates, suitable to be used as paint pigments, as well as to study the inhibitory properties of the obtained samples.

Main part. The morphology and elemental composition of the synthesized products were studied by EDX method using scanning electron microscope JSM-5610 LV, with a system of chemical microprobe analysis EDX JED-2201, up to 0.5% accuracy.

X-ray analysis of the phase composition (XRD) of the synthesized products was performed on a diffractometer D8 Advance Bruker AXS (Germany) using Cu K_α -radiation. The resulting radiographs were processed using EVA program, included in the software diffractometer DiffractPlus. Phase composition was determined using X-ray data base of international Powder Diffraction file.

True density was adjusted by pycnometric method according to GOST 21119.5. Oil absorption of pigments and pH of 10% aqueous slurry were measured by standard methods (Standard GOST 21119.8 and 21119.3, respectively).

Polarization measurements were performed in a standard three-electrode elektrochemical cell YASE-2 with a platinum auxiliary electrode. The potentials were measured relatively to the saturated silver chloride reference electrode EVL-1M3 using potentiostat PAT-T 50-1. All potentials given in the paper, are translated into the scale of the standard hydrogen electrode. As the working electrode steel of 08 kp grade was used (GOST 8832). The visible surface of the electrode was 1.0 cm^2. When removing the potentiostatic polarization cathode curves the electrode was kept in a cell for 5 minutes until a stationary potential was set, and then at the displacement of potential to negative values with increments of 25 mV in 1–2 min a value of current was fixed.

After that the cell was switched off and the electrode was kept until a stationary potential was set. Likewise anodic curve was built. Measurements were carried out under constant stirring of the pigment slurry. Synthesis of mixed iron and bismuth vanadates was performed by solvothermal method using as a precursor aqueous solution of sodium metavanadate, iron sulfate (III) and bismuth nitrate.

For the synthesis reagents of $NaVO_3$, $Fe_2(SO_4)_3$ and $Bi(NO_3)_3 \cdot 5H_2O$ of mark "C. P." were used. Bismuth nitrate and iron sulfate were previously dissolved in 1 n. nitric acid solution, and then the solution of bismuth nitrate was poured into a solution of iron sulfate at a molar ratio of components n(Bi): n(Fe) equal to 1: 0 (sample 1), 3: 1 (sample 2), 1: 1 (sample 3), 1: 3 (sample 4), 0: 1 (sample 5). Sodium metavanadate was previously dissolved in alkali at a molar ratio of 1: 3, thus forming a sodium orthovanadate [4]. For the synthesis of bismuth and iron orthovanadates under constant stirring solutions of bismuth and iron salts were added to a solution of sodium orthovanadate. In this case orthovanadate production processes take place according to the reactions:

$$Bi(NO_3)_3 + Na_3VO_4 \rightarrow BiVO_4 + 3NaNO_3;$$

$$Fe_2(SO_4)_3 + 2Na_3VO_4 \rightarrow 2FeVO_4 + 3Na_2SO_4.$$

The dissolved state of the starting materials provided uniform distribution of material throughout the volume of the solution, its high degree of dispersion and a high rate of diffusion of reactants, and therefore allowed the reaction to proceed at high speed even at room temperature.

Table 1

The elemental composition of the samples obtained by solvothermal manner and after heat treatment

Sample	Element wt. %			Molar ratio of Bi : V : Fe
	Bi	V	Fe	
1 (before firing)	67.39	18.56	–	0.87 : 1 : 0
1 (after firing)	74.59	21.23	–	0.86 : 1 : 0
2 (before firing)	43.28	19.78	15.23	0.53 : 1 : 0.70
2 (after firing)	42.13	23.75	20.81	0.43 : 1 : 0.80
3 (before firing)	62.02	19.15	7.82	0.79 : 1 : 0.37
3 (after firing)	66.22	22.05	9.04	0.73 : 1 : 0.37
4 (before firing)	23.45	26.97	31.38	0.21 : 1 : 1.06
4 (after firing)	23.64	28.75	33.98	0.20 : 1 : 1.08
5 (before firing)	–	28.77	48.41	0 : 1 : 1.53
5 (after firing)	–	29.93	55.01	0 : 1 : 1.67

By adding small amounts of bismuth and iron solution to a solution of sodium orthovanadate colloidal solution from light brown to dark brown depending on the molar ratio of Bi to Fe was produced. Originally formed germ crystals are small, as the particles of the dispersed phase are suspended for a long time. When adding new portions of the precipitant a large number of tiny germ particles continues to isolate. Isolation of a substance from the supersaturated solution occurs preferably on the surfaces of these germ crystals. It results in relatively coarse and crystalline precipitate.

To transfer dekavanadate ions into a less condensed form of VO_4^{3-} pH value of obtained solutions was increased to 3.5 with 30% sodium hydroxide solution. As a result the transformation of a crystalline precipitate into the soft amorphous mass was observed. The introduction of 1n of sodium hydroxide solution into the resulting suspension and the increase of pH value to 6 leads to the formation of additional amorphous phase, which is adsorbed in the form of a loose layer on previously formed dense amorphous precipitate.

To reduce the degree of polydispersity of the precipitate obtained suspension was boiled for 3 hours. It was established that with the increase of the iron content the colour of the samples ranged from the yellow $BiVO_4$ to dark brown $FeVO_4$.

EDX method revealed, that the molar ratio of Bi: V (Table 1) in the composition of a synthesized product (sample 1) is 0.9. It indicates the presence of minor amounts of V_2O_5 admixtures of bismuth meta- and polyvanadates. When the concentration of ferric sulfate in the solution increases the accumulation of admixture iron compounds in the main product occurs (samples 2–5).

To transfer the X-ray amorphous phase into the crystalline the samples obtained by solvothermal manner were subsequently further calcined for 10 minutes at 550 °C. According to the X-ray phase analysis (Fig. 1), within the error of XRF, sample 1 is crystalline as it is evidenced by the appearance on the X-radiographs of the main phase reflexes of the synthesized bismuth orthovanadate [01-075-2481] of Chinobisvanite modification with the tetragonal system [5].

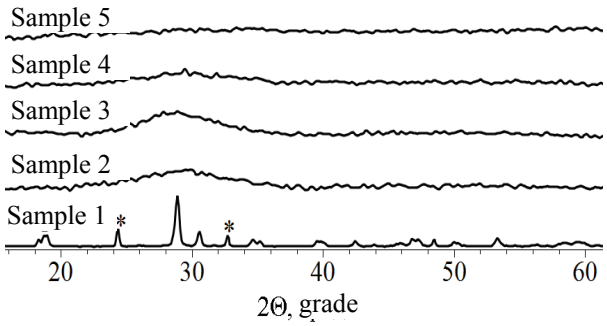

Fig. 1. X-radiographs of the initial samples

Sample 1 has an admixture phase of Bi orthovanadate of Dreyerite modification, whose amount is negligible. Samples 2–5 are X-ray amorphous. Subsequent heat treatment was accompanied by the occurrence of crystallization processes in powders (Fig. 2), which is evidenced by the appearance of reflexes (samples 2–4), of the main phase of the synthesized bismuth orthovanadate [01-075-2481] of Chinobisvanite modification with tetragonal system.

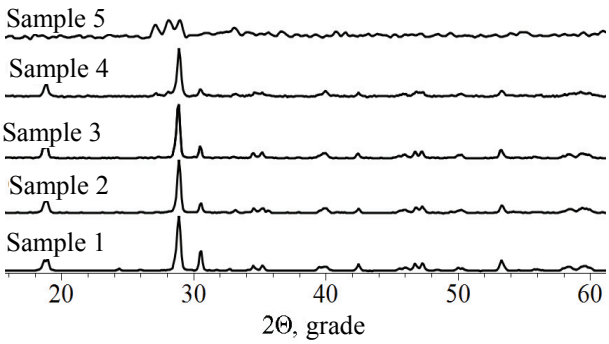

Fig. 2. X-radiographs of samples after heat treatment

After firing this admixture of bismuth orthovanadate of Dreyerite modification in sample 1 disappears and the content of the main phase increases. Sample 5 after firing remains X-ray amorphous, blurry reflexes correspond either iron orthovanadate or $Fe_2V_4O_{13}$ monoclinic system. According to scanning electron microscopy data elemental composition of the samples obtained before and after heat treatment differs slightly (Table 1).

Analysis of electron microscopy studies showed (Fig. 3) that the particles of synthesized $BiVO_4$ (sample 1) have sizes from 0.1 to 7.0 microns and a predominant (56.91%); particle size is from 0.1 to 2.0 microns. Samples 2–5 before firing constituted irregular shaped aggregates with dimensions: sample 2 – up to 200 microns; Sample 3 – up to 50 microns; sample 4 – up to 150 microns; Sample 5 – up to 200 microns.

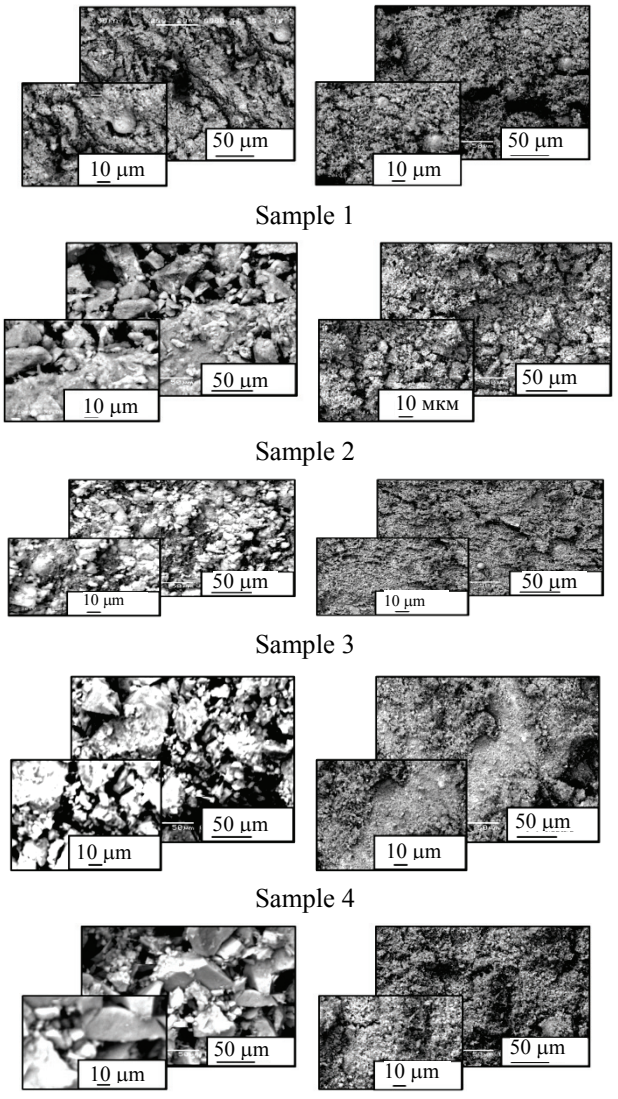

Fig. 3. Electron microscopy image of samples obtained by solvothermal way: initial (*a*) and after the heat treatment (*b*)

After heat treatment sample 2 is an aggregate of up to 20 microns; 3 and 4 are fine powders with particle size of up to 2 microns; 5 – is fine powder with a particle size of up to 5 microns.

As a result, the predominant particle size of the samples 1–5 is up to 10 microns. Generally, the use of pigments in the paint industry with such small particle size can significantly improve the performance indicators of the finished product such as intensity, gloss, hiding power [6]. Express evaluation of the inhibitory properties of the synthesized pigments was performed by removing the anodic potentiostatic curves [7] on the steel of 08kp in 3% NaCl solution at 20°C (Fig. 4).

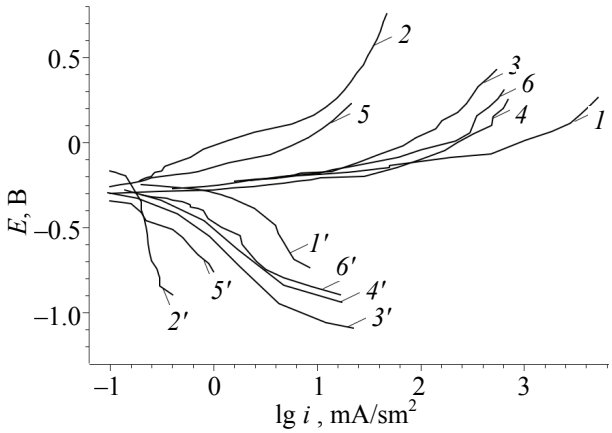

Fig. 4. Anode (*1*, *2*, *3*, *4*, *5*, *6*) and cathode (*1′*, *2′*, *3′*, *4′*, *5′*, *6′*) polarization curves in NaCl (3%), without inhibitor (curves *6* and *6′*) and a suspension of samples (*1–5*) obtained after firing (curves *1–5* and *1′–5′*)

The concentration of pigment in the suspension constituted 0.5 g/100 ml of solution. As can be seen from the presented data (Fig. 4, Table 2) the introduction of bismuth orthovanadate into a solution of NaCl does not significantly reduce steel corrosion currents. By increasing the degree of substitution of bismuth for iron in the composition of prepared samples the increase of their inhibitory properties is observed.

Table 2

Corrosion current density i_{cor} for NaCl solution (3%), without inhibitor and in the suspension of samples

Number of sample	pH of the suspension	I_{cor} mA/cm^2
3% NaCl	6.75	0.339
1	6.39	0.316
2	6.49	0.112
3	7.11	0.076
4	6.47	0.057
5	6.36	0.020

Corrosion currents decrease monotonically and in the pigment suspensions obtained by complete replacement of bismuth for iron reach the values of 0.020 mA/cm^2, which is 17 times lower than in the NaCl solution.

The study of the physical and chemical properties of the synthesized pigments showed that the pH value of their aqueous suspensions is 6.4–7.1 (Table 2), which ensures stability of the steel substrate in contact with the pigment.

Oil absorption of the obtained samples is comparable with oil absorption of highly basic zinc chromates (30 g / 100 g of pigment), which defines a relatively low cost of painting material based on them. The true density of the synthesized samples established by pycnometric method is 6.0–7.5 g / cm^3, which is comparable to the orange lead chromate $PbCrO_4 \cdot PbO$ [8].

Conclusion. Accomplished studies allowed to suggest a technique of solvothermal synthesis of bismuth and iron orthovanadates by using aqueous solutions as a precursor. As a result powders from yellow to dark brown in color with a size-morphological characteristics, physical, chemical and inhibitory properties that meet the requirements of the pigments used in the paint industry were obtained.

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