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# \_\_\_\_ NANOSCALE AND NANOSTRUCTURED MATERIALS AND COATINGS

# Corrosion–Electrochemical Properties of $\alpha$ -Fe + Fe<sub>3</sub>C + TiC Nanocomposites in Acidic Sulfate Solutions

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**Abstract**—Corrosion-electrochemical properties of model  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC three-phase nanocrystalline composites in acidic sulfate solutions are studied. Anodic processes on  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites are determined chiefly by the oxidation of ferrite and cementite components. The passivation of nanocomposites takes place due to the formation of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> · *n*H<sub>2</sub>O surface hydroxides with a high water content n = 0.7-2.2and low protective properties. The high activity of  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites with respect to hydrogen evolution is determined by the cementite component and increases with an increase in the dispersion of Fe<sub>3</sub>C inclusions. Under the effect of cathodic hydrogen, titanium carbide decomposes to produce free carbon.

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## **INTRODUCTION**

Metal-based composite materials, such as solid allovs and carburized steel, which involve strengthening a carbide phase that is homogeneously distributed in a viscous metallic matrix are widely used in industry [1, 2]. Despite the promising characteristics of carburized steels in modern technology, there are only a few works devoted to the corrosion-electrochemical properties of the materials [3].

In the case of nanostructured materials, one has additional possibilities to improve their useful characteristics due to the high dispersion (less than 100 nm) of phase inclusions and crystallites [4, 5]. From this point of view, it is expedient to produce and study nanostructured analogues of solid alloys and carburized steels.

A peculiarity of carbides of transient metals is the lowered overpotential of the cathodic hydrogen evolution. The most promising electrochemical catalysts are Fe<sub>3</sub>C, Fe<sub>5</sub>SiC, TiC, and WC carbides [6-8]. As was shown in [9, 10], nanoscale carbide (Fe<sub>3</sub>C) inclusions in conducting ( $\alpha$ -Fe) matrix obtained by mechanical smelting also provide very high catalytic activity, especially when carbide inclusions form grid structures. The activity of  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC nanocrystalline composites with respect to cathodic hydrogen evolution has not yet been estimated.

Carbide inclusions with a low overpotential of hydrogen evolution in sulfuric acid solutions can promote the passivation of the iron matrix [11]; however, in order to estimate the possible increase in the corrosion resistance, one should investigate the passivation characteristics of such composite systems.

The object of this work was to study the effect of the structure and phase state of  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC nanocrystalline composites produced by mechanochemical synthesis followed by dynamic pressing on the electrochemical properties in acidic sulfate solutions.

# **EXPERIMENTAL**

The conditions of mechanochemical synthesis and notations of specimens are listed in Table 1. A Fritsch P-7 planetary ball mill with an acceleration of 25g was used. Powders of original compounds in an amount of 10 g were fed in the mill. In the case of organic environments, the mill bowls were completely filled with the liquid. The bowls (with a volume of  $45 \text{ cm}^3$ ) and grinding balls (20 pcs., 10 mm) were made of \*ShKh15 steel (1% C and 1.5% Cr), which is especially hard and has a minimum content of alloying elements, in order to minimize the contamination of powders with foreign admixtures.

The obtained powders were compacted by magnetic pulse pressing [12]. The pressing was carried out by high-pressure pulses with an amplitude of 2 GPa and a duration of 300 µs at the continuous evacuation to  $10^{-3}$  Pa. Before pressing, the powders were exposed at 500°C in a vacuum for 1 h. The compacted species were disc-shaped with a diameter of 15 mm and a thickness of 2 mm.

X-ray diffraction studies were carried out with a DRON-3M diffractometer with filtered  $CuK_{\alpha}$  radiation. Qualitative and quantitative X-ray phase analysis and the determination of the crystal lattice parameters

Specimen	Or	iginal powder c	composition, at	MS anvironmont	MS duration b	
	Fe	Ti	С	TiC		mo unation, n
Fe70Ti15C15	70	15	15		Ar	16
Fe(70)TiC(30)	70			30	Ar	16
Fe70Ti15/tol20	70	15			toluene	20
Fe70Ti15/tol32	70	15			toluene	32
Fe70Ti15/VTES	70	15			3% VTES in toluene	32

Table 1. Composition of original powders, grinding environment, and duration of mechanochemical synthesis (MS)

Note: VTES is vinyltriethoxysilane.

were performed using relevant program packages [13, 14].

Electron microscopic studies were carried out with a JSM 6490 raster microscope with embedded energydispersive and wavelength-dispersive X-ray analyzers. Atomic force microscopic measurements were carried out with a P47-SPM-MDT scanning probe microscope in air in the semicontact mode. NT-MDT silicon cantilevers were used. In order to clarify the phase-structure peculiarities, the surface of compacted specimens was etched with a 3% nitric acid solution in alcohol. Upon such treatment, only ferrite is etched out, while carbides are retained and well seen in three-dimensional images of the surface topography.

X-ray photoelectron spectroscopic studies were carried out with an ES-2401 spectrometer with a Mg anode. The spectrometer was calibrated with respect to Au4 $f_{7/2}$  line at 84.0 eV. The bond energy ( $E_b$ ) of C1s electrons in an alkyl group was assumed to be 285.0 eV. The surface was etched with a 1-keV Ar<sup>+</sup> ion flow at a current of 15  $\mu$ A. Under these conditions of ionic etching, a surface layer with a thickness about 10 Å is removed in 1 min.

Polarization measurements were carried out under potentiodynamic conditions with an IPC-Pro potentiostat in a standard YaSE-2 electrochemical cell at room temperature and natural aeration. The silverchloride electrode was taken as the reference electrode, while platinum electrode was taken as the auxiliary electrode. All potentials are given with respect to the standard hydrogen electrode, and currents are recalculated to the visible surface of specimens. Specimens were insulated in Epoxy resin. The surface treatment before electrochemical tests involved sandpapering and additional polishing with Al<sub>2</sub>O<sub>3</sub> powder wetted with distilled water. Acidic sulfate solutions ( $C(SO_4^{2-}) = 0.5 \text{ M}$ , pH = 0.4, 1.9, and 2.9) were prepared from chemically pure H<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> and distilled water. Armon iron (wt % × 10<sup>-3</sup> C 5 ×

distilled water. Armco iron (wt %:  $8 \times 10^{-3}$  C,  $5 \times 10^{-3}$  S,  $3 \times 10^{-3}$ P,  $3 \times 10^{-2}$ O, and  $6 \times 10^{-3}$  Mn), cementite produced by mechanochemical synthesis and magnetic pulse pressing [7], and ready titanium carbide compacted by magnetic pulse pressing were

taken as the reference specimens. Specimens were exposed to acidic sulfate solutions for  $\sim 15$  min and polarized under potentiodynamic conditions separately in cathodic and anodic directions at a rate of 1 mV/s.

## **RESULTS AND DISCUSSION**

#### 1. Structure–Phase Analysis of $\alpha$ -Fe + Fe<sub>3</sub>C + TiC Nanocrystalline Composites

The formation mechanisms of the structure-phase state of  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites were studied in detail in [15–17]. As an example, Fig. 1 shows electron microscopic images of Fe(70)TiC(30) and Fe70Ti15/tol20 powders upon mechanochemical synthesis. Powders produced by grinding a dry mixture of iron and ready titanium carbide contain not only a fine-particle fraction (~1 µm), but also relative large particles (~10 µm). Upon the mechanochemical synthesis in a liquid organic environment, more homogeneous powders composed of lamellar particle agglomerates with a size of 10–50 µm are formed. In all the cases, the Fe/Ti ratio in the powders upon the mechanochemical synthesis corresponds to that of the original mixture.

X-ray patterns of the composites upon pressing are shown in Fig. 2. Phase compositions, grain sizes, and lattice parameters are listed in Table 2. Specimens included three-phase systems involving  $\alpha$ -Fe, cementite, and titanium carbide; the number of carbide phases depends on the experimental conditions.

The minimum amount of cementite is present in Fe(70)TiC(30) and Fe70Ti15/to120 specimen. When the Fe70Ti15C15 specimen is prepared from the element powder mixture, titanium carbide and cementite (up to 36 wt %) are formed concurrently. When grinding in toluene, the amount of cementite increases with an increase in the duration of grinding. Vinyltriethoxysilane (VTES) additive substantially accelerates the formation of cementite.

The content of titanium carbide in most composites is close to 20 wt %. In the case of Fe70Ti15/VTES produced in the presence of silicon-organic additive, TiC content is lower, about 14 wt %, because a part of

SYUGAEV et al.



Fig. 1. SEM images of particles of mechanically activated powders and compacted specimens of (a, c) Fe(70)TiC(30) and (b, d) Fe70Ti15/to120 composites.

titanium is bound in silicides and oxides. Fe(70)TiC(30) and Fe70Ti15C15 specimens have the same TiC phase content, but the amount of cementite in Fe70Ti15C15 is higher than in Fe(70)TiC(30) by a factor of 2.5. If we take into account that the specimens were produced from mixtures with the same atomic part of carbon, the deficiency of carbon in the titanium carbide phase compared to the stoichiometric composition is larger in Fe70Ti15C15 than in Fe(70)TiC(30) by a factor of 2.5.

The iron lattice parameter (a) of the most of specimens falls in a range of 0.2872-0.2874 nm, being larger than that of individual iron. This is determined

by the presence of up to 2 at % titanium in the form of solid solution in iron.

Figures 1c and 1d show electron microscopic surface images of the cross sections of composites upon pressing. Composites produced in organic environments are chemically homogeneous and have a low porosity. The images of specimens produced by grinding dry mixtures involve dark spots (Fig. 1c) that, according to the data of X-ray microanalysis, are TiC inclusions.

Figure 3 shows AFM images of composites upon the selective etching of ferrite. In all the cases, carbides (light spots) are uniformly distributed over the com-

**Table 2.** Phase composition of composites N (wt %,  $\pm 3\%$ ), coherent scattering areas  $\langle L \rangle$  (nm,  $\pm 1$  nm), and lattice parameters *a*, *b*, and *c* (nm)

Specimen -	α-Fe			TiC			Fe <sub>3</sub> C		
	N	$\langle L \rangle$	$a \pm 0.0001$	N	$\langle L \rangle$	$a \pm 0.005^{*}$	N	$\langle L \rangle$	<i>a, b, c</i> (±0.01*)
Fe(70)TiC(30)	67	13	0.2873	19	10	0.430	14	8	0.51, 0.68, 0.45
Fe70Ti15C15	44	11	0.2874	20	4	0.430	36	3	0.51, 0.69, 0.45
Fe70Ti15/tol20	64	14	0.2872	23	5	0.430	13	3	0.51, 0.69, 0.45
Fe70Ti15/tol32	30	14	0.2874	. 19	5	0.430	51	5	0.51, 0.68, 0.45
Fe70Ti15/VTES	22	12	0.2871	14		0.430	64	13	0.51, 0.69, 0.46

Note: We failed to reach the better resolution because of the line broadening and overlapping.

posite surface and have a typical size of 20-100 nm. On Fe(70)TiC(30) specimen, in addition to uniformly distributed small carbide particles, there are much larger particles with sizes of 1-10 µm. In Fe70Ti15/to132 and Fe70Ti15/VTES, a homogeneous grid structure of nanoscale carbide inclusions is formed (Figs. 3d, 3e).

#### 2. ELECTROCHEMICAL PROPERTIES OF NANOCRYSTALLINE $\alpha$ -FE + Fe<sub>3</sub>C + TiC COMPOSITES

#### 2.1. Anodic Processes on Individual Phases and $\alpha$ -Fe + Fe<sub>3</sub>C + TiC Composites

Figure 4 shows polarization curves of  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites (Fig. 4a) and individual phases involved in the composites (Fig. 4b). Parameters of the polarization curves are given in Table 3. The ferrite phase has the lowest dissolution overpotential, and it that dissolves at corrosion potentials of  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites (about 250 mV). Cementite actively dissolves at E > 0 mV, which leads to the surface accumulation of free carbon [7, 10]. In the case of composites, the anodic peak of cementite is not seen because of the intense dissolution of the ferrite phase in the limiting anodic current range.

The TiC phase has the lowest oxidation rate, which is determined by the formation of the protective surface layer composed of TiO<sub>2</sub> oxide and TiC<sub>x</sub>O<sub>y</sub> oxycarbide [18]. The intense oxidation of titanium carbide produces TiO<sup>2+</sup>, CO, or CO<sub>2</sub>, which corresponds to the anodic peak at  $E \sim 1200 \text{ mV} \{8, 19-22\}$ . The peak current density of the individual TiC oxidation is I mA/cm<sup>2</sup>, which is lower than anodic currents of the composites in this range of potentials. However, the high dispersion of the TiC inclusions may facilitate



Fig. 2. X-ray patterns of composites: (a) Fe(70)TiC(30); (b) Fe70Ti15C15; (c) Fe70Ti15/tol20; (d) Fe70Ti15/tol32; and (e) Fe70Ti15/VTES.

their oxidation and result in higher anodic current at  $E \sim 1200$  mV.

Thus, the electrochemical behavior of  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites is determined by the following peculiarity; the oxidation of the individual phases involved in the composite takes place at potentials that substantially differ from each other. For this reason,

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**Table 3.** Parameters of polarization curves on Armco iron, cementite, titanium carbide, and  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites in 0.05 M H<sub>2</sub>SO<sub>4</sub> + 0.45 M Na<sub>2</sub>SO<sub>4</sub>: *E* (mV, ±5 mV) and *i* (mA/cm<sup>2</sup>, ±5%)

Specimen	Parameters of polarization curves						
Specimen	E <sub>cor</sub>	<i>i</i> <sub>c</sub> (-400 mV)	$i_{a}(-200 \text{ mV})$	<i>i</i> <sub>p</sub> (1250 mV)			
Armco Fe	-325	0.6	35.2	0.05			
Fe <sub>3</sub> C	-195	26.2	~0	3.9			
TiC	-145	2.3	_	-			
Fe(70)TiC(30)	345	4.4	22.4	1.6			
Fe70Ti15C15	-240	13.4	5.0	1.3			
Fe70Ti15/tol20	-240	25.9	11.0	3.8			
Fe70Ti15/to132	-235	21.0	5.0	-			
Fe70Ti15/VTES	-230	24.1 ·	5.4	6.2			



Fig. 3. AFM surface images of compacted specimens upon etching in 3% nitric acid solution in alcohol: (a) Fe(70)TiC(30); (b) Fe70Ti15C15; (c) Fe70Ti15/to120; (d) Fe70Ti15/to132; and (e) Fe70Ti15/VTES.

the surface composition of composites should noticeably change with an increase in the anodic potential, and the subsequent anodic processes are determined by the surface layer of the corrosion products formed. In particular, the formation of a passive film takes place on a surface enriched with Fe<sub>3</sub>C and TiC (E = -250 to 0 mV) and free carbon (E > 0 mV).

# 2.2 Passivation of $\alpha$ -Fe + Fe<sub>3</sub>C + TiC Composites

Passive nanocrystalline  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites dissolve at a high rate. The current density at complete passivation ( $i_{cp}$ ) is determined by the amount of free carbon accumulated on the surface, which negatively affects the structure of the passive film, as was clearly shown in [10, 23] for  $\alpha$ -Fe + Fe<sub>3</sub>C systems. The

 $i_{cp}$  value on composites produced by mechanochemical synthesis in liquid organic environments is higher than that of the specimens produced from dry mixtures by a factor of three to ten, which is determined by the high dispersion of carbide inclusions. At the dissolution potentials of the ferrite matrix, the probability of carbide sludge deposition is higher in the case of specimens containing relatively large carbide inclusions. Therefore, the amount of carbides that accumulate on the surface of Fe70Ti15C15 and Fe(70)TiC(30) is smaller and the protective properties of the passive film are better.

Complete passivation potentials ( $E_b$ ) of  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites are higher than those of Armco iron and Fe<sub>3</sub>C by 300-600 mV. The substantial difference between the  $E_{cp}$  values reflects the different chemical nature of the passive films formed on  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites and on Armco iron or Fe<sub>3</sub>C.

On cementite, the passivation potential about 500 mV corresponds to the formation of a two-layer  $Fe_3O_4/\gamma$ - $Fe_2O_3$  passive film with a relatively low content of bound water. Then,  $\gamma$ - $Fe_2O_3 \cdot nH_2O$  hydroxides with *n* close to unity are formed in the film defects, and an additional anodic peak appears [7, 10]. A peculiarity of  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites is as follows: a primary passive film composed of water-free  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is not formed, and the initial passivation is due to the formation of strongly hydrated  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>  $\cdot nH_2O$ .

The peculiarity is determined by the presence of titanium carbide in the composites. It is accumulated on the surface during the prevailing dissolution of  $\alpha$ -Fe and Fe<sub>3</sub>C components. Ellipsometric tomography was used in [18] for studying the structure of surface titanium carbide layers in sulfuric acid at potentials preceding the intense dissolution range. It was found that a TiO<sub>2</sub> layer covers the TiC surface and, under the layer, carbon and titanium oxycarbide sublayers are formed. In the case of comentite and  $\alpha$ -Fe + Fe<sub>3</sub>C composites [7, 10], the primary water-free  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> passive film forms on a hydrophobic surface enriched in carbon. On  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites, TiC inclusions covered with a TiO<sub>2</sub> layer increase the hydrophilicity, and water-free  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> does not appear.

Insofar as hydroxides chemically dissolve in acids at the higher rates, the  $i_{cp}$  values on  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites are higher. The equilibrium potentials  $(E_{eq})$  of the transformation into Fe<sub>3</sub>O<sub>4</sub> are also higher on hydroxides, i.e.,  $E_{eq}$ (Fe<sub>3</sub>O<sub>4</sub>/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) <  $E_{eq}$ (Fe<sub>3</sub>O<sub>4</sub>/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> · nH<sub>2</sub>O) [24, 25], which results in the high  $E_{cp}$  values.

According to [25], the hydration degree of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> · nH<sub>2</sub>O determines the mechanism of the active—passive transition of iron and its alloys. At small *n*, reaction

$$3Fe_{3}O_{4} + 4nH_{2}O \longrightarrow 4\gamma - Fe_{2}O_{3} \cdot nH_{2}O$$

$$+ Fe^{3+} + 3e.$$
(1)





is more probable. This is typical of iron in sulfate solutions ( $n \sim 0.04$ ). The same process seems to occur when the primary passive film forms on cementite.

SYUGAEV et al.



Fig. 5. Polarization curves of Fe70Ti15C15 composite in acidic sulfate solutions with  $C(SO_4^{2-}) = 0.5$  M depending on pH: (1) 2.9, (2) 1.9, and (3) 0.4.

At a substantial hydration degree (n > 0.23) and a high chemical dissolution rate of the passivating oxide, the reaction

$$2Fe_{3}O_{4} + (3n+1)H_{2}O$$

$$\longrightarrow 3\gamma - Fe_{2}O_{3} \cdot nH_{2}O + 2H^{+} + 2e.$$
(2)

becomes more probable. According to this mechanism, the secondary stabilization of the passive film on cementite proceeds. This is the most likely process at the active-passive transition in  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites.

Assuming that the complete passivation potential is close to the equilibrium potential of reaction (2), we can estimate the degree of hydration of the passivating  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> · nH<sub>2</sub>O layer on  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites. Then, the Gibbs energy of reaction (2) can be written as follows:

$$\Delta G^{0} = -zFE^{0} \sim -zF(E_{\rm cp} + 0.059 \rm{pH}), \qquad (3)$$

which enables us to calculate the  $\Delta G_f^0$  formation energy of the passivating  $\gamma$ -Fc<sub>2</sub>O<sub>3</sub> · *n*H<sub>2</sub>O hydroxide. The degree of hydration (*n*) can be estimated based on the empirical expression for the change in the molar thermodynamic formation energy of normalized  $Fe_{s}H_{R}O_{1.5}$  oxide [25]:

$$\Delta G^{0} = -4.19(45 + 40.8S + 9.44R) \text{ (kJ/mol)}.$$
 (4)

The following *n* values were obtained in this way for  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites: 0.9 on Fe70Ti15C15, 0.7 on Fe(70)TiC(30), 1.3 on Fe70Ti15/tol20, 2.2 on Fe70Ti15/tol32, and 1.1 on Fe70Ti15/VTES. The highest degrees of the passive layer hydration are typical of the specimens produced by mechanochemical synthesis in organic environments.

According to the thermodynamic data [24], the formation of mixed  $x\text{FeO} \cdot y\text{TiO}_2$  oxides should be highly probable at the boundaries of TiC inclusions or at the oxidation of ferrite alloyed with titanium (~2 at %) during the oxidation of  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites. Let us consider the possible mechanisms of the effect of  $x\text{FeO} \cdot y\text{TiO}_2$  mixed oxides on the passivation of composites.

First of all, mixed oxides formed could serve as a barrier and lower the dissolution current of the composites. The actual relatively high dissolution currents do not support the idea of the barrier effect of  $xFeO \cdot yTiO_2$ . Second, the mechanism of the electrochemical stabilization of the protective  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> oxide should be changed in the presence of mixed oxides according to the reaction ( $xFeO \cdot yTiO_2$  is normalized to 1 M FeO):

$$2 \operatorname{FeO} y/x \operatorname{TiO}_2 + (n+1) \operatorname{H}_2 \operatorname{O}$$

$$\longrightarrow \gamma \operatorname{Fe}_2 \operatorname{O}_3 \cdot n \operatorname{H}_2 \operatorname{O} + 2y/x \operatorname{TiO}_2 + 2\operatorname{H}^+ + 2\operatorname{e}.$$
(5)

Thermodynamic calculations show that, at any x and y values, the equilibrium potential of reaction (5) is more negative than that of reaction (2) by 200–300 mV. Hence, if the stabilization of the passive film were due to the formation of  $x\text{FeO} + y\text{TiO}_2$  mixed oxides, the complete passivation potentials of  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites should decrease compared to Armco iron and Fe<sub>3</sub>C. Actually, we observe the opposite trend. This means that the role of  $x\text{FeO} + y\text{TiO}_2$  mixed oxides in the passivation of  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites should decrease compared to Armco iron and Fe<sub>3</sub>C. Actually, we observe the opposite trend. This means that the role of  $x\text{FeO} + y\text{TiO}_2$  mixed oxides in the passivation of  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites in acidic sulfate solutions is small.

Studying the effect of the pH of a sulfate solution on the anodic processes on Fe70Ti15C15 composite (Fig. 5), we found that it is small in the range of 0.4– 2.9. The complete passivation currents are nearly equal at pH 1.9 and 2.9. At pH 0.4, the  $i_{cp}$  increases by a factor of five, which is seemingly caused by a sharp increase in the chemical dissolution rate of the passivating  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> · nH<sub>2</sub>O hydroxide. Thus, anodic processes on  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites are chiefly the oxidation of ferrite and cementite components. Passivation of  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites is due to the formation of weakly protective  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> · nH<sub>2</sub>O hydroxides (n = 0.7-2.2).

PROTECTION OF METALS AND PHYSICAL CHEMISTRY OF SURFACES Vol. 47 No. 3 2011

326

#### 2.3. Cathodic Process on $\alpha$ -Fe + Fe<sub>3</sub>C + TiC Composites

According to the rate of hydrogen evolution at the same overpotential ( $\eta_H = -400 \text{ mV}$ ), individual phases can be ranked as follows: Fe (1) < TiC (4)  $\leq$  Fe<sub>3</sub>C(50). Hence, the catalytic activity of  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites in acidic electrolytes should be determined by the content and morphology of the most active cementite phase. The hydrogen evolution rate on the specimens produced by the mechanochemical synthesis in organic environments and characterized by the highest dispersion of cementite is practically the same as that of individual Fe<sub>3</sub>C (Fig. 4, Table 3). An Fe(70)TiC(30) specimen produced from ready titanium carbide has the lowest Fe<sub>3</sub>C content, and its catalytic activity with respect to the cathodic hydrogen evolution is low.

The slopes of the curves on cementite and  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites are  $b_e \sim 60$  mV at small cathodic polarization (~100 mV) and gradually increase to the limiting cathodic current value at pH 1.9 and 2.9 at the more negative potentials (Fig. 6). The limiting currents at pH 1.9 and 2.9 are close to the calculated limiting diffusion flow of H<sub>3</sub>O<sup>+</sup> ions to the surface. At pH ~0.4, the limiting current is not achieved, even at a substantial polarization (~800 mV); however, the current densities are again close to the calculated diffusion current densities (~2 A/cm<sup>2</sup>). The problem of the mechanism of the cathodic hydrogen evolution on  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites needs further investigation.

Thus, the high activity of  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites with respect to hydrogen evolution is determined by the cementite component and increases with an increase in the amount and dispersion of cementite inclusions. Because of the intense cathodic reaction, the resistance of  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites against acid effects is lower by an exponent than that of Armco iron.

#### 2.4. Effect of Preliminary Cathodic Polarization of Electrochemical Properties and Composition of Surface Layer on α-Fe + Fe<sub>3</sub>C+ TiC Composites

It is well known that titanium carbide actively interacts with hydrogen with the formation of diverse compounds, namely, a solid solution of hydrogen in carbide, TiC<sub>x</sub>H<sub>y</sub> titanium carbohydrides  $(x + y \le 1)$ , and TiH and TiH<sub>2</sub> titanium hydrides [8, 26]. The effect of hydrogen that evolved during long cathodic polarization (an hour at -800 mV) was analyzed on Fe70Ti15C15, Fe(70)TiC(30), and Fe70Ti15/tol20 specimens.

It was found that the preliminary cathodic polarization substantially affects the electrochemical behavior of Fe70Ti15C15 composite (Fig. 6) and does not affect Fe70Ti15/tol20 and Fe(70)TiC(30). This is determined by the stronger carbon deficit of the titanium carbide phase in Fe70Ti15C15 and agrees with



Fig. 6. Polarization curves of Fe70Ti15C15 composite in  $0.05 \text{ M H}_2\text{SO}_4 + 0.45 \text{ M Na}_2\text{SO}_4$ : (1) without preliminary cathodic polarization and (2) upon the cathodic polarization for 1 h at -800 mV.

the data of [26], where the intensity of interaction between individual  $\text{TiC}_x$  phases ( $x \le 1$ ) and hydrogen was found to increase with an increase in the carbon deficit.

The surface layers of Fe70Ti15C15 and Fe70Ti15/to120 composites upon the cathodic polarization were studied using the X-ray photoelectron spectroscopy. The spectra of both specimens were similar (Table 4, Fig. 7). Titanium is absent in the surface layer; its traces appear only upon 10 min of ionic etching. It seems likely that titanium hydrides, which tend to chemically dissolve in an acidic sulfate solution to

Table 4. Composition of surface layers of Fe70Ti15C15 composites upon cathodic treatment in 0.05 M  $H_2SO_4 + 0.45$  M  $Na_2SO_4$  for 1 h at -800 mV

lonic etching	Element content, at %					
duration	С	0	Fe	Ti		
]	45	40	15	0		
11	40	35	25	traces		
21	45	30	25	traces		



Fig. 7. C1s and Fe3p spectra of Fe70Ti15C15 composite upon the cathodic polarization for 1 h at -800 mV in 0.05 M H<sub>2</sub>SO<sub>4</sub> + 0.45 M Na<sub>2</sub>SO<sub>4</sub> and ionic etching, min: (1) 1 and (2) 21.



Fig. 8. X-ray patterns of Fe70Ti15C15 composite: (1) without preliminary cathodic polarization and (2) upon the cathodic polarization for 1 h at -800 mV in 0.05 M H<sub>2</sub>SO<sub>4</sub> + 0.45 M Na<sub>2</sub>SO<sub>4</sub>.

produce  $[Ti(SO_4)_3]^{2-}$  ions and hydrogen, are formed at the cathodic polarization [8].

An oxide layer on the specimens has a thickness of no more than 20 nm, which is indicated by the decrease in the spectral line intensity of oxides  $(E_{\rm h} \sim$ 56.0 eV) and an increase in the Fe<sup>0</sup> and Fe<sub>3</sub>C line intensity (at  $E_{\rm b} \sim$  53.5 eV) in Fe<sub>3</sub>p spectra [27], as well as the appearance of Fe<sub>3</sub>C line ( $E_{\rm b} \sim$  283.3 eV) in C1s spectrum [28] upon the ionic etching.

In the X-ray patterns of Fe70Ti15C15 specimen (Fig. 8) upon the cathodic treatment, a contribution from cementite increases, while that of titanium carbide decreases and reflexes of graphite appear in the range of  $2\Theta = 26^{\circ}$  (Fig. 8, insert). Thus, the decompo-

sition of titanium carbide during the cathodic treatment produces chiefly free carbon rather than hydrocarbons as follows:

$$TiC + 2H_3O^+ + 2e \longrightarrow TiH_2 + C + 2H_2O.$$
 (6)

The accumulation of carbon on the surface leads to the decrease in the limiting cathodic current (Fig. 6) due to the screening effect, as well as to the increase in the anodic current due to the negative effect on the structure and protective properties of the passive film [7, 10]. Thus, during the cathodic polarization of  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites, free carbon and titanium hydrides, which undergo chemical dissolution in an acidic sulfate solution, are formed on the surface. The strongest interaction with hydrogen is typical of the specimens that are characterized by the carbon deficit of the titanium carbide phase.

#### CONCLUSIONS

Three-phase  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites are produced by mechanochemical synthesis followed by dynamic pressing as nanocrystalline analogues of carburized steels, and their corrosion-electrochemical properties in acidic sulfate solutions are studied.

Anodic processes are found to be determined chiefly by the oxidation of ferrite and cementite components. The passivation of the composites proceeds due to the surface formation of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> · *n*H<sub>2</sub>O hydroxides with a high water content (*n* = 0.7–2.2), as a result of which the passive films are weakly protective.

The high activity of  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites with respect to the cathodic hydrogen evolution is shown to be determined by the cementite component and increase with an increase in the amount and dispersion of Fe<sub>3</sub>C inclusions. The high rate of cathodic hydrogen evolution on the surface of Fe<sub>3</sub>C inclusions leads to a decrease in the resistance of composites in acids. Hydrogen that evolves on the surface of  $\alpha$ -Fe + Fe<sub>3</sub>C + TiC composites interacts with titanium carbide inclusions to produce free carbon and titanium hydrides. Titanium hydrides formed on the surface undergo chemical dissolution in acidic sulfate solutions.

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## REFERENCES

- 1. Kiparisov, S.S., Levinskii, Yu.V., and Petrov, A.P., *Karbid titana: poluchenie, svoistva, primenenie* (Titanium Carbide: Production, Properties, and Applications), Moscow: Metallurgiya, 1987.
- Gurevich, Yu.G., Narva, V.K., and Frage, N.V., Karbidostali (Carburized Steels), Moscow: Metallurgiya, 1988.
- 3. Shapovalov, E.T., Zashch. Met., 1993, vol. 29, p. 809.
- Nanocrystalline Materials: Their Synthesis-Structure-Property Relationships and Applications, Tjong, S.C., Ed., Elsevier, 2006.
- 5. Valiev, R.Z. and Aleksandrov, I.V., *Ob"emnye nanostrukturnye metallicheskie materialy* (Three-Dimensional Nanostructured Metallic Materials), Moscow: Akademkniga, 2007.
- 6. Tsirlina, G.A. and Petrii, O.A., *Itogi Nauki Tekhn., Ser. Elektrokhimiya.*, 1987, vol. 24, p. 154.
- Syugaev, A.V., Lomacva, S.F., Maratkanova, A.N., et al., *Fizikokhim. Poverkhn. Zashch. Mater.*, 2009, vol. 45, no. 1, p. 84. [*Prot. Met. Phys. Chem. Surf.* (Engl. Transl.), 2009, vol. 45, no. 1, p. 81].
- 8. Freid, M.Kh. and Lilin, S.A., *Elektrokhimiya*, 1979, vol. 15, no. 2, p. 163.
- 9. Lomaeva, S.F., Syugaev, A.V., and Elsukov, E.P., Khim. Fizika Mezoskopiya, 2008, vol. 10, no. 2, p. 186.
- Syugaev, A.V., Lomaeva, S.F., and Reshetnikov, S.M., *Fizikokhim. Poverkhn. Zashch. Mater.*, 2010, vol. 46, no. 1, p. 74. [*Prot. Met. Phys. Chem. Surf.* (Engl. Transl.), 2010, vol. 46, no. 1, p. 82].
- Tomashov, N.D. and Chernova, G.P., *Teoriya korrozii i korrozionnostoikie konstruktsionnye splavy* (Theory of Corrosion and Corrosion-Resistant Structure Alloys), Moscow: Metallurgiya, 1986.
- 12. Ivanov, V.V., Paranin, A.s., and Vikhrev, A.N., RF Patent No. 083328, *Byull. Izobret.*, 1996, no. 25, p. 4.

- 13. Powder Diffraction File, Alphabetical Index, Inorganic Phases, Swarthmore: International Center for Diffraction Data, 1985.
- 14. Shelekhov, E.V. and Sviridova, T.A., *Metalloved. Termich. Obrab. Metal.*, 2000, no. 8, p. 16.
- 15. Lomaeva, S.F., Povstugar, I.V., Volkov, V.A., et al., *Khimiya Interes. Ustoich. Razvitiya*, 2009, no. 6, p. 629.
- Lomaeva, S.F., Maratkanova, A.N., Volkov, V.A., et al., *Khim. Fizika Mezoskopiya*, 2010, no. 1, p. 120.
- 17. Lomaeva, S.F., Volkov, V.A., Maratkanova, A.N., et al., *Materialovedenie*, 2010. no. 6, p. 58.
- 18. Kotenev, V.A., Chukalovskaya, T.V. and Chebotareva, N.P., Zashch. Met., 1997, vol. 33, no. 2, p. 144.
- 19. Freid, M.Kh. and Lilin, S.A., *Elektrokhimiya*, 1979, vol. 15, no. 2, p. 198.
- 20. Tomashov, N.D., Chukalovskaya, T.V., Chebotareva, N.P., and Kudryavtsev, V.I., Zashch. Met., 1989, vol. 25, no. 6, p. 911.
- 21. Tomashov, N.D., Chukalovskaya, T.V., Medova, I.L., and Egorov, F.F., *Zashch. Met.*, 1985, vol. 21, no. 5, p. 682.
- Tomashov, N.D., Chukalovskaya, T.V., Krylov, I.K., et al., Zashch. Met., 1986, vol. 22, no. 5, p. 684.
- 23. Syugaev, A.V., Lomaeva, S.F., and Reshetnikov, S.M., *Zashch. Met.*, 2008, vol. 44, no. 1, p. 58.
- Tyurin, A.G., *Termodinamika khimicheskoi i elek-trokhimicheskoi ustoichivosti splavov. II. Nizkotemperatur-noe okislenie* (Thermodynamics of Chemical and Electrochemical Resistance of Alloys. II. Low-Temperature Oxidation), Chelyabinsk: Chel. Gos. Univ, 2004.
- 25. Sukhotin, A.M., *Fizicheskaya khimiya passiviruyushchikh plenok na zheleze* (The Physical Chemistry of Passivating Films on Iron), Leningrad: Khimiya, 1989.
- 26. Pancheshnaya, V.P., Knyazheva, V.M., Klimenko, Zh.V., and Antonova, M.M., *Zashch. Met.*, 1980, vol. 16, no. 6, p. 684.
- 27. McIntyre, N.S. and Zetaruk, D.G., *Anal. Chem.*, 1977, vol. 49, no. 11, p. 1521.
- Yomoto, H., Nagamine, Y., Nagahama, J., and Shimotomai, M., Vacuum, 2002, vol. 65, p. 527.