Study of electrochemical properties of austenitic chromium-nickel steel 12Kh18N10T in concentrated sulfuric acid

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Considerable attention has always been paid to the issues of protection against chemical corrosion of technological equipment operating in aggressive environments, and even now this issue does not lose its relevance. Recovery of absorption heat is an integral part of the process of minimizing energy costs, and that is why special requirements are imposed on the quality and service life of heat exchange units. Within the framework of the work done, the electrochemical behavior of austenitic nickel-containing steel grade 12Kh18N10T (equivalent of AISI 304), used for the manufacture of process equipment for sulfuric acid production processes by the double contact - double absorption method, was studied. For the studied sample of austenitic nickel-containing steel, anodic potentiodynamic polarization curves were obtained, on which two weakly manifested passivation regions were noted. It has been established that the predominant contribution to metal losses is made by chemical corrosion, while during the operation of steel structures, iron is leached from the surface layer with formation of a protective nanofilm. Thickness of the resulting protective film is 35 nm or more, with the exposure time of steel in hot sulfuric acid for 200 hours. Increasing of the exposure time does not significantly affect the thickness or composition of the protective coating. Using X-ray phase analysis, it was established that the protective film is based on nickel and chromium compounds. The corrosion rate of equipment in the presence of a protective film does not exceed 0.1 mm/year, there are no pitting and intergranular corrosion. The data obtained will allow not only predicting and planning repair and maintenance work, but also organizing a corrosion prevention system without introducing additional reagents into the system.

Keywords: chemical corrosion, sulfuric acid production, austenitic nickel steel, protective film, hot absorption, passivation, polarization curves.
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Introduction

Growth of cities and increase of their population stipulates necessity in accelerated industrial development. Increase of production facilities, reconstruction and modernization of operating works as well as building the new ones according to the green chemistry concept, provide demand on the new raw and construction materials.

At present time, the metals and alloys which are using for fabrication of metal constructions for buildings and technological equipment are evident leaders among reliable and simple materials. Despite their advantages, metal constructions have one essential disadvantage: they are sensitive to corrosion, which can vary substantially (acidic, electrochemical, biological etc.) depending on the environment of technological process [1].

Many domestic [1-4] and foreign [5-11] authors considered the problems of corrosion protection. Corrosion processes can occur during storage and transportation of water with different applications [12, 13], oil transportation processes [14], technological processes in high-temperature conditions (heat exchangers, boilers etc.) [15, 16], as well as in production of chemically active substances (e.g. extractive phosphorous or contact sulfuric acids) [17] and in hydrometallurgical production [18]. Annual metal losses caused by corrosion can achieve 12 % of total metal production, and this calculation does not take into account indirect losses which are connected with recoveries after accidents, downtimes of production facilities etc. [12, 13, 19].

There are many researches [1-11] devoted to corrosion protection, but essentially less attention was paid to the problems of minimization of corrosion activity during material manufacture or studying corrosion safety aspects of chemical and physical properties of materials.

Sulfuric acid production is one of the most developed industrial directions, which is characterized by really enormous volumes of manufactured products. In this case sulfuric acid and its salts are considered as material with high corrosion activity; respectively, requirements to metal constructions increase significantly. The problems of energy and power saving, as well as reliability and industrial safety, are also rather actual for this production.

The process of sulfuric acid production includes absorption or condensation of sulfuric anhydride by sulfuric acid; as a result, enormous amount of heat is released as a result of exothermal reaction, and this heat is removed from the reaction area using the system of heat exchangers [20, 21]. It was just heat exchanging equipment that assumes corrosion “strike”, and more strict technical requirements are imposed just to material of heat exchangers.

Relatively expensive and unavailable titanium alloys or coatings [18, 22, 23], which are alloyed by rare earth metals (including coatings on their base), steel alloys [24, 25] as well as nickel-base steels and alloys [26, 27] are suggested to be used as the main directions for increase of operation time of heat engineering equipment.

Study of electrochemical properties of austenitic chromium-nickel steel of 12Kh18N10T grade (the most widely spread and relatively cheap) in the contact with concentrated sulfuric acid is the main aim of this research.

Materials and methods of research

The examined samples of austenitic chromium-nickel alloys were molten in the Institute of high-quality steels of the Central scientific and research institute of ferrous metallurgy (TsNIIchermet).

Elementary composition of solid samples was determined using scanning electronic microscope JEOL1610LV with energy dispersion spectrometer SSD X-MaxIncaEnergy (JEOL, Japan; Oxford Instruments, UK).

Corrosion velocity was determined via metal mass variation in time (gravimetric method based on Δ of mass loss).

Chemical composition of 12Kh18N10T steel sample is presented in the **Table 1**.

Anodic potentiodynamic curves were registered in the potentiostat PI-50-11. Electrochemical cell was placed in the ultra thermostat U-51 with silicon oil; the temperature in the thermostat was hold using contact thermometer with accuracy ± 0,1 °C.

Examined electrodes were presented by cylinder cores which are pressed in hot state in fluoroplastic F-4. Saturated chlorine-silver electrode (KhSE) was used as a comparative electrode. Corrosion potential was established during 30 min.

Anodic potentiodynamic polarization curves at the temperatures 140, 160, 200 °C and potential scanning velocities 0.5 mV/s were registered after establishment of corrosion potential.

Auger electron spectroscopy was carried out for investigation; it used PHI-6100 unit (with Al electrode, energy of primary electronic beam 15 kV, radiation $AlK\alpha_{1,2}h\nu = 1486$ eV) for determination of elements distribution through thickness of the alloy surface layer after its exposing in sulfuric acid at different conditions. For this purpose, pickling of the sample surface was conducted by ion beam Ar^+ with energy $E_{kin} = 6$ keV (pressure Ag = $20x10^{-3}$ Pa). Pickling velocity makes 400 nm/h (6.7 nm/min).

Exposing of the 12Kh18N10T steel sample was carried out at the temperature 120 °C, sulfuric acid concentration 99.2 %, exposing time 200 hours.

Results and discussion

Anodic potentiodynamic polarization curves of 12Kh18N10T steel are presented on the **Fig. 1**.

The data presented on the Fig. 1 can provide the following conclusions.

- Austenitic high-alloy steel is weakly passivated in sulfuric acid with concentration 99.2 % (mass.). Two weakly appeared passivation areas are observed: the first near +0.9 – 1.3 V for the curves *1* and *3* and +0.8 – 1.3 V for the curve *2*; the second near +1.5 – 1.7 V for the curves *2* and *3* and +1.65 – 1.7 V for the curve *1*.

- Sensitivity of austenitic steel to passivation increases with temperature rise (curves *1* and *3*).

Concentration of sulfuric acid, its temperature and exposing time of samples in aggressive medium are the main factors of steel corrosion in sulfuric acid. This process occurs in the conditions when forming heat of sulfuric acid steam phase in conversion gas of sulfur trioxide and SO_3 absorption heat of sulfuric acid are extracted owing to heat transfer from absorbing acid. Reliable theories or mechanisms of corrosion resistance, which can explain this appearance, are absent in technical literature. At the same time discovering the mechanism of corrosion process opens the ways for development of more corrosion resistant materials. The examined steel sample was exposed at preset conditions, and then chemical composition of the surface layer is studied. Thickness of the surface layer made 35 nm. The data about composition of initial metal and the surface layer are presented in the **Table 2**.

Auger spectra of the surface layers for the initial material 12Kh18N10T were registered before exposing in sulfuric acid (sample No. 1) and after exposing (**Table 3**).

Table 1. **Chemical composition of the examined sample**

Molten steel grade	Content of the elements, % (mass.)							
	C	Si	Mn	Cr	Ni	Mo	Ti	Fe
12Kh18N10T	0.100	0.56	1.83	18.9	10.1	-	0.6	basic

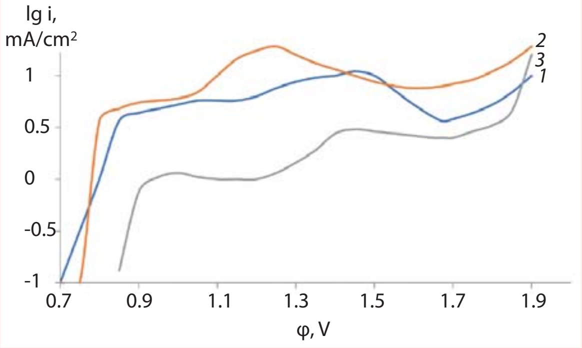

Fig. 1. Anodic potentiodynamic polarization curves: *1* – at the temperature *t* = 140 °C; *2* - at the temperature *t* = 160 °C; *3* – at the temperature *t* = 200 °C.

Table 2. **Chemical composition of the sample No. 2**

Chemical element	Basic metal, % (mass.)	Averaged composition of the surface layer, % (mass.)
Fe	70.37	69.46
Cr	19.11	19.44
Ni	10.00	10.10
Ti	0.46	0.60
S	0.08	0.04
Totally	100	100

Table 3. **Exposing conditions for the samples made of 12Kh18N10T steel in sulfuric acid**

No.	H_2S0_4 concentration, % (mass.)	Temperature *t*,°C	Exposing time τ, hours	Corrosion depth index П, mm/year
1	The sample of intial steel 12Kh18N10T before exposing in sulfuric acid			
2	98.3	120	200	0.2400
3	100.0	120	200	0.0014
4	99.3	200	400	0.1200

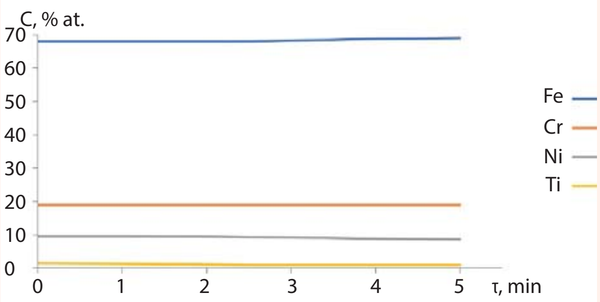

Fig. 2. Distribution of the elements in the surface layer of initial sample

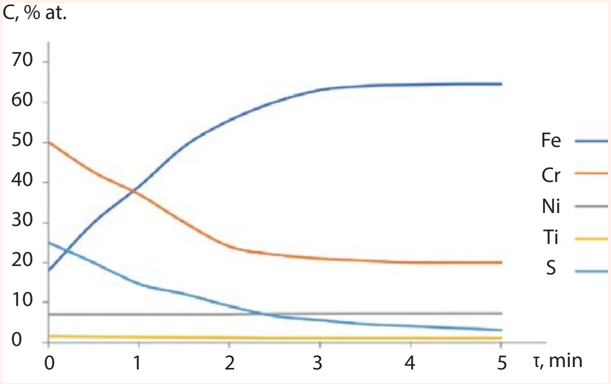

Fig. 3. Distribution of the elements in the surface layer of the sample No. 2

Processing of the obtained results of Auger spectra allowed to determine distribution of the elements through depth of the surface layer of material and its corrosion products (**Fig. 2-5**). Thickness of the surface layer makes 35 nm for exposing time τ =5 min.

Analysis of content of the elements in the examined materials allows to suggest that redistribution of the elements takes place as a results of corrosion process in the surface layer of steel 12Kh18N10T. This redistribution includes lowering of Fe content and elevation of content of alloying elements.

So, Fe concentration in the surface layer of all samples decreased almost by 4 times and made less or near 20 % (mass.) in comparison with usual content 70 % (mass.). On the opposite, chromium concentration rose sharply almost by 3 times (60 % (mass.) in the surface layer comparing with 18 % (mass.) in the depth of alloy). Titanium content in the thin subsurface layer increased almost by an order. Nickel concentration varied slightly. High sulfur content (up to 28 % (at.)) was also observed in the surface layer, what can testify about forming of metal sulfates.

X-ray photoelectron spectroscopy of the samples displayed presence of large oxygen amount in the surface layer of samples (**Table 4**).

Essential oxygen content (exceeding the required content for sulfur binding in metal sulfates) can testify that part of this oxygen participates in forming of oxides and hydroxides of metals in the surface alloy and, probably, in passivation of metals due to forming of mono- and polymolecular layers of oxygen which is adsorbed on the active surface areas.

Corrosion velocity of the samples decreased consequently by 2 orders in the process of sulfuric acid concentration increase from 98.3 to 100 % (mass.).

We can suggest that chemical corrosion provides the main input in corrosion destruction of the alloy for the considered conditions. High corrosion resistance of the alloy can be explained by forming of corrosion products on the film surface, which are presented by chromium and titanium sulfates (occupying together more than 65 % of the contact surface with aggressive medium) as well as ferrum and nickel corrosion products. It is known that sulfates of the above-

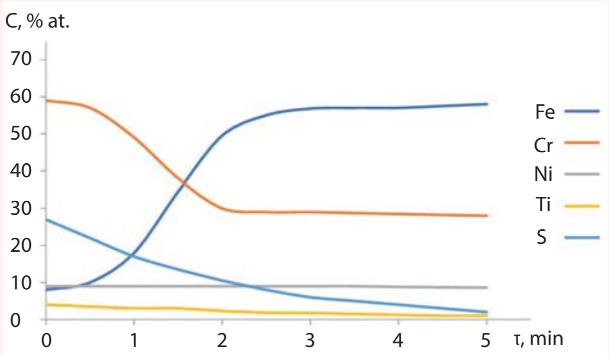

Fig. 4. Distribution of the elements in the surface layer of the sample No. 3

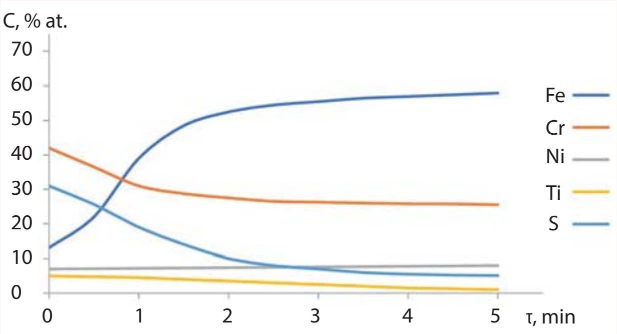

Fig. 5. Distribution of the elements in the surface layer of the sample No. 4

Table 4. **Chemical composition of the surface layer of the sample No. 2**

No.	Element	Concentration		
		% at.	% mass.	% mass., not accounting O
1	Fe	12.61	27.58	50.54
2	Cr	8.83	18.00	33.00
3	Ni	0.98	2.30	4.36
4	Ti	0.35	0.65	1.10
5	S	4.83	6,04	11.00
6	O	72.40	45.42	-
Total		100.00	100.00	100.00

Table 5. **Experimentally revealed values E_{bon}**

Elements	E_{bon}, eV, experimental	E^{tabl}_{bon}, eV, for the element	E^{tabl}_{bon}, eV, for compounds	
Fe	709.4 712.0	706.8	$FeSO_4$	709.1
			$Fe_3(SO_4)_2$	711.4
			Fe_2O_3	711.4
			Fe_3O_4	710.9
			FeO	709.8
			FeOOH	711.6
Cr	578.5 588.4	574.2 584.1	$Cr_2(SO)_3$	580.2
			CrO_3	579.3
			Cr_2O_3	576.8
			CrO_2	576.3
			CrOOH	577.0
Ni	856.7	853.1	$NiSO_4$	857.0
			NiO	854.6
			$Ni(OH)_2$	856.5
S	165.5 166.9 167.4 167.9 168.3	164.2	$FeSO_4$	168.5
			$Fe_2(SO_4)_3$	168.9
			$Cr_2(SO)_3$	167.9
			$NiSO_4$	169.4
O	531.6 532.8 533.0	543.1 in O_2 529.6 in oxidizing surface of Fe	$FeSO_4$	532.5
			$Fe_2(SO_4)_3$	531.8
			$NiSO_4$	532.4
			$Cr_2(SO)_3$	-
			Cr_2O_3	530.7
			Cr_2O_3	530.8
			NiO	530.0
			Fe_2O_3	530.3
			FeO	530.0
			Fe_3O_4	530.2
			FeOOH	532.0
			$Ni(OH)_2$	532.0
			CrOOH	531.4

mentioned metals are characterized by low solubility in high concentrated sulfuric acid, what allows in its turn to provide reliable material protection from further destruction using the film [28].

Thickness of the forming film of corrosion products on the examined samples is different: it is minimal for the sample No. 2 and makes appr. 35 nm. In this case ferrum and chromium concentrations are 67.5 and 21 % (mass.) respectively for pickling during 5 min by Ar^+ ions, what is close to the values of these components in metal mass (70 and 18 % (mass.) respectively). This fact can be considered as one more indirect proof of decisive role of corrosion products film for alloy protection in the conditions of aggressive medium. Increase of holding time does not increase film thickness.

To identify the corrosion products, the spectra of surface film and metal mass were registered for the sample No. 2. Identification of compounds was carried out by shift value ΔE_{bon} of bonding energy E_{bon} of the main element [29].

Table 5 displays the experimentally revealed values E_{bon} of the main elements which are presented in the surface layer of the sample No. 2, in comparison with the reference data [26] of E_{bon} for free elements and their possible compounds.

Based on the data presented in the Table 5, the following conclusions can be done:

- all elements in the surface layer are in non-free state and are bonded chemically, what appears in essential shifts of the measured bonding energy values for all elements in comparison with the value E_{bon} for free atoms;
- ferrum sulfates $FeSO_4+Fe_2(SO_4)_3$ as well as nickel and chromium sulfates are the most possible compounds in the surface layer of the sample exposing in sulfuric acid.

Conclusion

It was established within the framework of research of electrochemical properties of 12Kh18N10T steel, that chemical corrosion provides the main input in corrosion destruction of austenitic chromium-nickel steel.

Content of the main elements in the surface layer is redistributed; lowering of Fe content and increase of content of alloying elements are also noted. High oxygen content in the sub-surface layer can testify on presence of sulfates.

It was established that increase of concentration of alloying components in the sub-surface layer promotes significant decrease of corrosion velocity. This appearance is explained first of all by lowered solubility of metal sulfates in concentrated sulfuric acid. Thickness of forming protective film is ≥ 35 nm, while increase of holding time to more than 200 hours has no effect on this parameter.

Steel 12Kh18N10T can be recommended as a construction material for heat exchangers, which are used for recuperation of absorption heat and condensation in the process of sulfuric acid manufacture. This recommendation is valid for the definite technological parameters: sulfuric acid concentration 99.4-100 % (mass.), acid temperature 160-200 °C. Total corrosion velocity does not exceed 0.1 mm/year within the selected ranges of temperature and sulfuric acid concentration; pitting and intergranular corrosion are not observed [30]. Technological parameters, which were selected from the point of view of minimization of corrosion losses, provide simultaneously rather high motion force and process speed. The recommended ranges of varying the parameters are sufficiently wide to provide measurement of the real process parameters and their holding with use of corresponding technological remedies of automatic control and variation.

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