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CERTAIN METALLIC MATERIALS FOR CHEMICAL MACHINE BUILDING

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by G. L. Schwarts

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CERTAIN METALLIC MATERIALS FOR CHEMICAL MACHINE BUILDING

[This is a translation of an article by G. L. Shvarts in Khimicheskoye Mashinostroyeniye (Chemical Machinery Construction), No 5, 1958, pages 39-42.]

In connection with the search for new materials resistant to the action of highly corrosive media, a series of complex studies has been undertaken during the last five years by the following institutions and organizations: NIIKhIMash in collaboration with Steel Institute: TsNIIChM, NIUIF, Gipronikel, Institute of Physical Chemistry AN USSR, and others. Technological characteristics and corrosion resistance of the new steels Kh-18-N-28-M-3 D 3, Kh 23 N 23 M 3 D 3, Kh 23 N 28 M 3 D 3 T, Kh 23 N 27 M 2 T, of the alloy Ni-Si-Cu; Aluminum AV2, titanium VTl, and of some other materials have been studied

The first three steels are resistant to warm solutions of sulfuric acid of all concentrations. The steel Kh 23 N 27 M 2 T is used for work in weak solutions of sulfuric acid under the conditions of the production of extraction phosphoric acid, and in other media.

The NIIKhIMASH developed the methods of welding, bending and pressing for these steels and studied their resistance to corrosion.

Welding of steels can be performed by two methods: by using an Argon-arc melting electrode made of wire of steel 0 Kh 23 N 28 M s D s T; and by hand-arc welding, using electrodes made of the same wire, coated with the mixture 15M.

Special procedures were developed for the control of the corrosion resistance of these new steels and these were incorporated into the new specifications (GOST - 6032-58) for testing stainless steels for intercrystalline corrosion.

The steel Kh 18 N 28 M 3 D 3 was found unsuitable for the construction of chemical equipment, because laboratory tests and industrial experience have shown it to be liable to intercrystalline corrosion after welding and sometimes in its initial state, even the carbon content of 0.03 - 0.05 percent. The same results were obtained in the Inst of Physical Chemistry AN USSR for the steel Kh 23 N 23 M 3 D 3.

The third steel Kh 23 N 28 M 3 D 3 T with the titanium content exceeding that of carbon at least five times, and with the carbon content below 0.07 percent, shows no tendency to intercrystalline corrosion on welding, for bending, and after other operations that

involved heating to critical temperatures for 10 - 20 minutes. The same results were obtained for the steel Kh 23 N 28 M 3 D 3 T with 0.06 percent carbon. The results of testing this steel and the steel Kh 23 N 27 M 2 T for general corrosion, are presented in the table (duration of test over 500 h.)

It is evident from the table that steel Kh 23 N 27 M 2 T is corrosion resistant in solutions containing up to 20 percent sulfuric acid at 80° C. This steel was shown by the laboratory and industrial tests to be suitable for equipment working in solutions of phosphoric acid and in the production of extracting phosphoric acid. This steel is immune to corrosion-cracking in concentrated solutions of sodium hydroxyde, and is recommended for work in this medium along with nickel N-1.

The table shows that the steel Kh 23 N 28 M 3 D 3 T and parts built from it by welding are immune to general corrosion in sulfuric acid of any concentration under temperature up to 80°C, as well as in a series of industrial media containing sulfuric acid. The same steel, containing less than 0.06 percent of carbon, and marked 0 Kh 23 N 28 M 3 D 3 T (EI 943), and its welded samples, showed no tendency for intercrystalline corrosion in all technological media and in standard solutions (according to specifications GOST -- 6032-58). However this steel was found liable to corrosion cracking in 20 - 50 percent sulfuric acid solutions, under the simultaneous effect of the medium and the stresses, resulting from welding, cutting or expanding residual.

Welded tubing made of steel 0 Kh 23 N 23 M 3 D 3 T, exposed to the action of 20 - 50 percent sulfuric acid, showed corrosion cracking of the transcrystalline character (Figs. 1 and 2). This was not observed for concentrations lower than 20 percent and those higher than 50 percent, of sulfuric acid. Annealing at 950°C, with subsequent air cooling, eliminates the residual stresses following technological operations and prevents corrosion cracking. It must be stated that the presence in solutions of sulfuric acid of such reducing agents as hydrogen sulfide lessens the corrosion resistance of steel 0 Kh 23 N 28 M 3 D 3 T. On the basis of both laboratory and industrial tests, this steel is recommended for building pumps for coke-chemical plants, reaction vessels for leaching cobalt-nickel concentrates, evaporators for non-ferrous metallurgy, etc.

Articles made of this steel have been already used on an industrial scale. Pumps 2KhF6 and 2FKhC6 made of steel Kh 23 N 28 M 3 D 3 T have been planned for metallurgical plants. Experimental models of these pumps were tested in the disposal plant of the Moscow coke-gas works, and at the Shchelkovo Chemical plant on the acids coming from the first tower scrubber, under the conditions of the action of 50 - 60 percent sulfuric acid at 50 - 60°C.

An installation has been developed for the automatic control

of the process of production of super-phosphate. The controlling point of the flow of the 40 percent sulfuric acid includes a pneumatic valve made of steel Kh 23 N 28 M 3 D 3 T. At present, machine works have begun to produce capacitive apparatus and heat-exchangers made of steel O Kh 23 N 28 M 3 D 3 T.

For many industries the concentration of waste sulfuric acid is of great importance. Vacuum evaporation is the fastest and most economical way. The NIIKhIMMASH, developed the best chemical composition of an alloy that would be resistant under the conditions of the vacuum evaporation of sulfuric acid, and determined its technological characteristics (change, melting, welding). The composition of the alloy: 11.2 - 12 percent S; 4 - 4.5 percent Cu, the rest - Ni, and admixtures of not more than: 0.1 percent Mn, 0.1 percent Al, 0.5 percent Fe, 0.1 percent C, and 0.01 percent S. Additional alloying with aluminum and manganese lower its corrosion resistance in boiling sulfuric acid. This alloy exhibits a higher corrosion resistance when the contact with oxygen is limited, than when it is abundant (Fig. 3).

This alloy is welded by the hand-arc procedure using electrode rods of the same alloy covered by KKhD010. The work is being done in special furnaces, with preheating to 700 - 720°C and subsequent cooling of the welded pieces together with the furnace.*

Protracted tests of experimental heating elements of welded castings made of Ni-Si-Cu alloy performed in 1958, have shown that this alloy can be used to advantage in the production of the industrial evaporators working under the pressure of heating elements.

The NIIKhIMMASH has studied the corrosion cracking of welded autoclave vessels used for obtaining highly concentrated nitric acid by the method of direct synthesis. It has been found** that vessels of aluminum AV 2, made by hand-arc welding, would not last more than nine months due to the destruction of the seam metal by inter-crystalline corrosion. With wall-thickness of 25 mm the local corrosion in weld seams exceeds 30 mm per year. On the basis of the studies conducted it is recommended that the welding of the reaction autoclave vessels be performed either by automatic argon-arc method followed by hammering of the seam, or by automatic welding using electrode AV000, alloyed with titanium.. In cases where automatic welding is impossible, hand-arc welding with AV000 electrode should be used, provided the operation is performed in multiple passes.

In certain technical media, as for instance in the one for the treatment of raw concentrates of tungsten, the known corrosion resistant alloys cannot be used. Besides tungsten and molybdenum

*This research has been done by I. N. Yukalov, Yu. I. Kazenov, G. L. Shvarts, A. V. Nosov, G. A. Shumratova, Yu. G. Sidorkina, with the participation of the staffs of the laboratories of casting, welding and corrosion.

**These studies have been conducted by A. N. Krutikov and F. B. Slomyanskaya.

these media contain sulfides (Na_2S , H_2SO_4 , fluorides (CaF_2 and HF), and hydrochloric acid. Results of the tests of various metals and alloys performed by the NIIKhIMMASH in the working equipment of a concentration plant of one of the metallurgical combines, are presented in Fig. 4.

Judging by the loss of weight, all materials tested in the first medium were sufficiently resistant (corrosion velocity amounting to 0.1 - 0.15 gm/meter sq. hours). However, the steel Kh 23 N 28 M 3 D 3 T, as well as its welded samples, suffered spot-corrosion, and the alloys EI435 and EI461 - local corrosion.

The best corrosion resistance under the conditions of trisulfide of molybdenum drying has been shown by tantalum, titanium BTI, titanium alloy and the antichlor alloy. In the second medium, all the materials tested, except titanium alloy DT4, and tantalum have shown a lowered resistance. The steel Kh 23 N 28 M 3 D 3 T and the alloys EI 461 and EI 435 have suffered considerable spot-corrosion. The third medium tested indicated a lowered resistance for the alloy EI435, antichlor, EI461, and titanium OT4. Although the general corrosion velocity of the steel Kh 23 N 28 M 3 D 3 T was below 0.1 gm/s sq hour, the welded samples suffered a considerable local corrosion. The alloy of titanium OT4 also suffered local corrosion. High corrosion resistance were recorded for tantalum and titanium. VTI. Thus on the basis of tests conducted in industrial conditions, the technically pure titanium BTI is recommended as construction material for building single roll driers, used for drying the highly corrosive concentrates of tungstic acid and molybdenum trisulfide.

Medium	Concentration %	As delivered		preheated to 650°C for 2 h.		Welded samples	
		General corrosion less than mm/year	Tendency to Inter-crystalline and corrosion cracking	General corrosion less than mm/year	Tendency to Inter-crystalline and corrosion cracking	General corrosion less than mm/year	Tendency to Inter-crystalline and corrosion cracking
Steel Kh23N28M3D3T							
Extraction-phosphoric acid at 80°C	20% P ₂ O ₅ 1% SO ₃ 0,15% F	0,05	none	1,0	both tendencies observed	0,05	No intercrystalline corrosion. Cracking observed in seam and in thermal region
Phosphoric acid at 80°C	55	0,05	»	—	—	0,05	Same
Sulfuric acid at 80°C	10	0,01	»	—	—	0,008	»
Same	20	0,005	»	0,005	Inter-crystalline corrosion noted. Cracking absent.	0,09	No intercrystalline corrosion. Crack, observed
»	30	0,1	»	—	—	0,12	Same
»	40	0,1	»	—	—	0,07	»
»	50	0,1	»	—	—	0,03	»
»	65	1,0	»	—	—	0,63	No intercrystalline corrosion. Cracking observed in seam and in thermal region
»	98	0,1	»	—	—	0,106	»
Sulfuric and nitric acids at 80°C	76 H 0,004	0,05	»	0,1	—	0,05	»
Nitrosyl-Sulfuric acid at 80°C	—	0,5	»	0,5	Spot and local corrosion noted	0,05	Same
Steel Kh23N27M2T							
Extraction-phosphoric acid at 80°C	20% P ₂ O ₅ 1% SO ₃ 0,15% F	0,005	»	0,005	No corrosion cracking. Inter-crystalline corrosion noted.	0,005	»
Phosphoric acid at 80°C	55	0,005	»	0,005	Same	0,005	»
Sulfuric acid at 80°C	20	0,005	»	0,005	None	0,005	»
NaOH 20g/lit at 200°C and 350°C	—	0,05—0,5	»	—	—	—	»

Notes: 1. Corrosion velocity of steel Kh23N28M3D3T in sodium hydroxide (200g/lit) (at 200° and 350°C less than 0.5 mm./year. No tendency for intercrystalline corrosion.

2. Corrosion speed of same steel in media encountered in coke-chemical industries: less than 0.1 mm. per year; Composition of medium 1: 8-12 or 38% sulfuric ac. Medium 2: —alternating action of 38% and 89% sulfuric acid at 60°.

3. Corrosion velocity of same steel in hydrometallurgical media is less than 0.1 mm/year. Welded samples show tendency to corrosion cracking in medium 2. (Composition of medium 1) 125 g/lit nickel sulfate, 0.5 copper sulfate, 200 sulfuric acid at 60°C. medium 2: 25 g/lit nickel sulfate, 1-2 copper sulfate, 400 sulfuric ac. at 105°C; medium 3: concentrated anodic slime of the "South-Ural nickel" combine., in acid leaching at 135°C; medium 4: secondary nickel concentrate of "Severonikel" in acid leaching at 135°C.

4. Steel Kh23N27M2T and its welded samples have low resistance in sulfuric acid (44%) at 80° C; mixture of sulfuric (76%) and nitric (0.004%) at 80° C. and to nitrosyl-sulfuric acid.

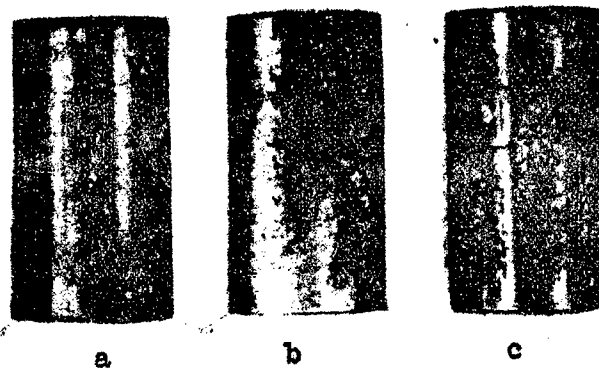


Fig. 1

Outward appearance of a tubing made of steel OKh23N28M3D3T after 500 hour test in sulfuric acid at 80°C. a - in 20 percent sulfuric acid; b - in 40 percent sulfuric acid; c - in 50 percent sulfuric acid



Fig. 2.

Micro-section of a sample of tubing made of steel OKh23N28M3D3T after testing in 40 percent sulfuric acid.

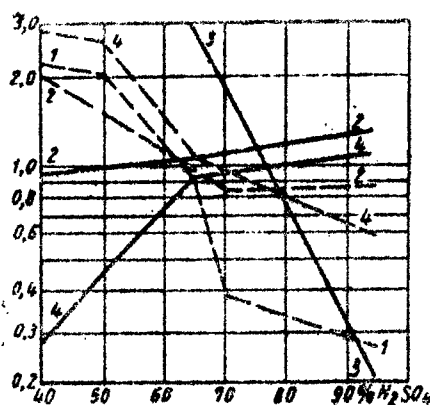


Fig. 3.

Corrosion resistance of various compositions of Ni-Si-Cu alloy in sulfuric acid.

1-containing 1.55 percent Al; 2-containing 1.1-1.23 percent Mn (heat 131); 3-same for welding of V (TsNIIChERMet); 4-no additions; limited contact with oxygen; excess of oxygen. Duration of tests: 500 hours.

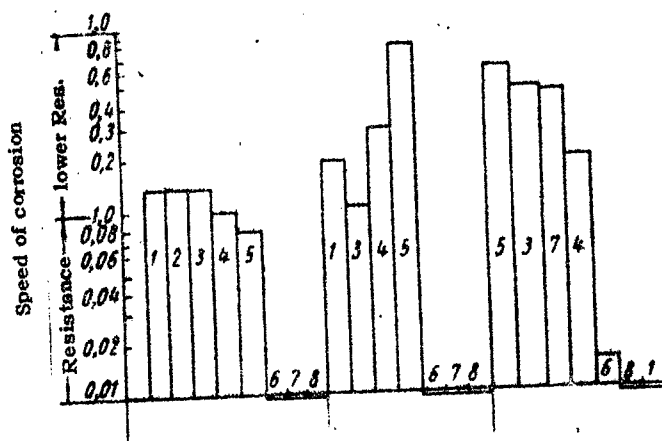


Fig. 4.

Relative corrosion resistance of metals and alloys in media encountered in hydro-metallurgical processes.

a. straight upon the drying shelf of the annealing furnace with temperature around 120-200° C during the drying of molybdenum trisulfide; (composition; et-rw%

a. straight upon the drying shelf of the annealing furnace with temperature around 120-200° C during the drying of molybdenum trisulfide; (composition: 35-42% Mo 1.5-2.9% tungstic acid, 55-70% water, small amounts of HCl, sodium sulfide, hydrogen sulfide and silica; duration of test 1200h.

b. in the drying drum with steam temperature 140° C over the tungstic concentrate (composed of 70% tungstic acid, 2-3% Mo, 2-10%g/lit & HCl, 5-15% calcium fluoride, 10-15% water, 5% of silica plus HF and others; duration of tests 648-742 hours)

c. in the receiver tank of the press-filter during the filtration of molybdenum trisulfuric pulp at 80-90° C; duration of test 1536 h.

1-steel Kh23N28M3D3T; 2- Ni-Si-Cu alloy (Hastelloy DL; 3-Fe-Si-Mo alloy (antichlor); 4-alloy EI461 (Hastelloy B (Ni-Mo)); 5- alloy Ni-Cr EI435; 6-Titanium VT1; 7-Titanium alloy OT-4; 8-Tantalum.

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