ACCELERATED POTENTIOKINETIC METHODS OF DETERMINING THE TENDENCY OF STAINLESS STEELS TOWARD INTERCRYSTALLITE CORROSION

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This article is devoted to the development of rapid and practically convenient methods of determining the tendency of Kh18N10T and ÉI-943 steels toward intercrystallite corrosion. This tendency is estimated by reference to the shape of the potentiokinetic curves on the reverse transition from the passive state. A criterion for the tendency toward such corrosion is the presence of an anode-current loop. In the absence of any tendency toward intercrystallite corrosion the current falls monotonically.

Intercrystallite corrosion is one of the most dangerous forms of corrosion (local variety). The most probable reason for the development of intercrystallite corrosion in stainless steels is the precipitation of secondary phases (chromium carbides, the σ-phase, and others with a high chromium content) along the grain boundaries, and the associated impoverishment of the boundary zones with respect to chromium [1-3]. The tendency of Kh18N10T steel toward intercrystallite corrosion is best determined by boiling the samples for 15-24 h in a sulfuric acid solution of copper sulfate (with the addition of copper chippings) until transverse cracks appear in samples bent at an angle of 90°; in the case of the more highly-alloyed steel ÉI-943, the boiling time is 144 h (All-Union State Standard 6032-58, method AM and method B). The development of faster and more reliable methods is highly desirable for industrial laboratories carrying out such tests on a systematic basis. The method of determining the tendency of Kh18N10T steel toward intercrystallite corrosion by potentiostatic etching and the metallographic examination of polished samples [4] is cumbersome and never free from the subjective aspect to estimation.

TABLE 1. Chemical Composition and Tendency Toward Intercrystallite Corrosion of Kh18N10T and ÉI-943 Steels (Aged at 650°C for 1 h and at 700°C for 20 min respectively), as Determined by Method AM, Described in All-Union State Standard 6032-58

Type of steel	Nos. of melts	Melt form	Chemical composition, %									Ti/C ratio	Results of intercrystallite-corrosion tests on tempered steels*
			C	Si	Mn	S	P	Cr	Ni	Ti	Mo		
Kh18N10T	130†	Laboratory	0,12	0,72	2,53	0,012	0,012	18,20	10,70	0,23	—	2	Coarse cracks
"	131†	"	0,07	0,56	1,66	0,014	0,012	18,01	10,58	0,25	—	3,6	" "
"	R-34739	Industrial	0,08	0,58	1,32	0,009	0,030	17,82	10,55	0,48	—	6,0	No cracks
"	R-40143	"	0,07	0,59	1,37	0,009	0,033	17,73	10,25	0,35	—	5,0	
"	R-38102	"	0,10	0,60	1,11	0,009	0,029	17,30	10,50	0,40	—	4,0	
"	R-37774	"	0,06	0,66	1,19	0,012	0,027	17,48	10,28	0,48	—	8	
"	R-40937	"	0,10	0,54	1,29	0,011	0,028	17,60	10,80	0,40	—	4,0	Cracks
"	R-50767	"	0,08	0,71	1,38	0,012	0,023	17,80	10,66	0,30	—	3,7	
"	R-49791	"	0,07	0,43	1,28	0,011	0,023	17,87	10,45	0,25	—	3,6	
ÉI-943	151†	Laboratory	0,065	0,69	0,60	0,009	0,015	23,90	27,6	0,34	2,86	5	Coarse cracks
"	152	"	0,036	0,69	0,59	0,009	0,018	25,73	27,83	0,68	3,82	10	No cracks

*The presence of cracks denotes a tendency toward intercrystallite corrosion and vice versa.
†In the quenched state these steels are not corrosion-prone.

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TABLE 2. Activation Potential (E_{act}) and Current (i_{act}) of Steel 130 in 20% H_2SO_4, as Expressed Functions of the Rate of Recording the Anodic Curve (Reverse run) at 21-23°C

Heat treatment	Tend to intercry. corr. (AM meth.)	Rate of recording the curve, V/h	E_{act}, V	i_{act}, mA/cm²	Heat treatment	Tend to intercry. corr. (AM meth.)	Rate of recording the curve, V/h	E_{act}, V	i_{act}, mA/cm²
Tempering	+	30	+0,1	0,9	Quenching	−	3	+0,12	0,77
Quenching	−	30	+0,1	0,075	Tempering	+	0,6	+0,22	0,83
Tempering	+	3	+0,16	1,8	Quenching	−	0,6	+0,15	0,43

Note. Before recording the reverse curve from a potential of +0.75 V, the samples were held in the solution without current for 5 min, activated cahodically at a potential of −0.3 for 5 min, and then passivated at +0.75 V for 5 min. 2. The "+" sign means that the steel is inclined towards intercrystalline corrosion, the "−" sign that it is not.

Investigations show that potentiostatically-recorded anodic curves of steels exhibiting a tendency toward intercrystallite corrosion differ from those of steels not exhibiting this tendency in respect to the potentials and currents associated with the transition from the active to the passive state [5-8]. On the basis of this relationship, a potentiokinetic method of determining the tendency of Kh18N10T steels toward intercrystallite corrosion in 5% boiling sulfuric acid by reference to the steel activation potential was proposed in [9]. One slight disadavantage of this method lies in the high temperature of the solution.

The aim of the present investigation (carried out by the Institute of Physical Chemistry, Academy of Sciences of the USSR, in conjunction with the Elektrostal' Factory and the All-Union Scientific-Research Institute of Ferrous Metallurgy) was to develop a rapid and practically convenient potentiokinetic method of determining the tendency of Kh18N10T and ÉI-943 steels toward intercrystallite corrosion. Using a p-5827 potentiostat [10], we studied steel samples taken from laboratory and industrial melts; the chemical compositions and tendencies of these steels toward intercrystallite corrosion are indicated in Table 1. In laboratory melts 130, 131, and 151 the ratio of titanium to carbon was low, and these steels were inclined toward intercrystallite corrosion after an incubation period of tempering. The samples for study took the form of plates with a working surface of ~3 cm²; at the end of each sample was a cylindrical protuberance with a notch for fixing in the holder, the latter being insulated from the solution by means of a glass tube.

The samples of industrial melts 25 × 80 × 3 mm in size usually employed in the AM method were tested without any special holder; the samples were half-immersed in the test solution, the immersed surface area being ~10 cm².

There was some evidence to the effect that the existence of a water-line might distort the form of the anodic polarization curve for Kh18N10T steel (this occurred, for example, in a solution of 5% H_2SO_4 containing KCNS, the curve being plotted in the forward sense at a rate of 1 V/h [11]); we therefore made a special check on the influence of the waterline under our own conditions. We found that when the anodic

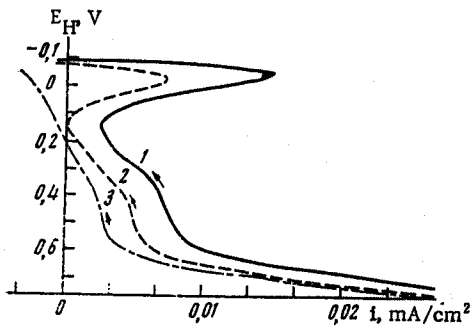

Fig. 1

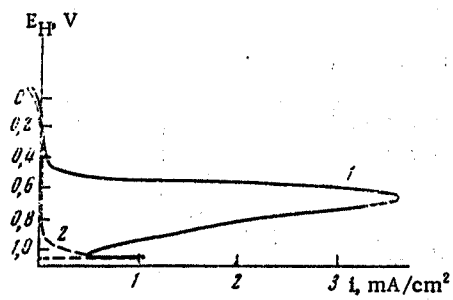

Fig. 2

Fig. 1. Anodic curves (reverse run) for steels 130 and 131 in 10% H_2SO_4 at room temperature for a recording rate of 12 V/h: 1) 130 tempered; 2) 131 tempered; 3) 130 quenched.

Fig. 2. Anodic curves (reverse run) for steel 151 in 0.5 N NaCl at room temperature for a recording rate of 30 V/h. Before plotting the curve the samples were held in the solution at a potential of −1.0 V for 1 min; the reverse run started from a potential of + 1.05 V: 1) 151 tempered; 2) 151 quenched.

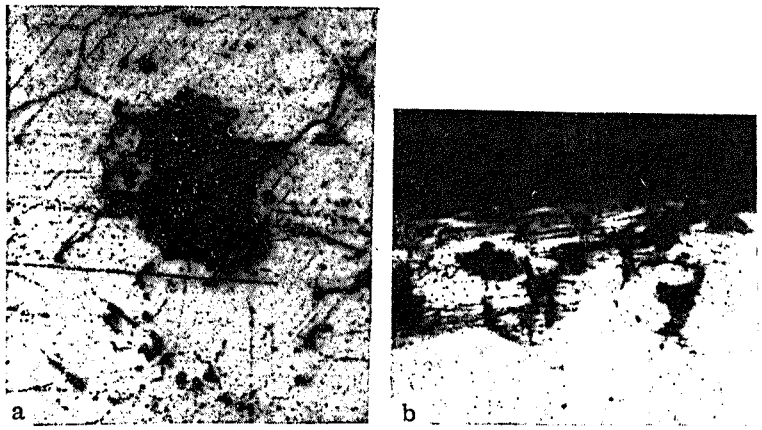

Fig. 3. a) Appearance of the surface of a polished sample of tempered steel 151 inclined toward intercrystallite corrosion after 30 min holding in 0.5 N NaCl at + 0.75 V at room temperature (cathodic activation before the experiment at −1.0 V for 1 min); b) the same for a cross section. × 340.

curves (in the reverse direction) were plotted rapidly in 10% H_2SO_4, the existence of the waterline had no marked influence on the electrochemical characteristics, nor did it alter our conclusions regarding the tendency of Kh18N10T steel towards intercrystallite corrosion. In order to avoid unnecessary complication of the method we therefore proceeded on the basis of using an air atmosphere with an uninsulated waterline on the sample.

Before the experiment the samples were cleaned with emery paper No. 240, which corresponded to the seventh class of surface finish, then washed in distilled water and dried.

Kh18N10T Steel. After recording the potentiokinetic curves of Kh18N10T steel in 20% H_2SO_4 at room temperature, we determined the potentials of total passivation and the passivation currents (E_{tp} and i_p) for the formed run and the corresponding activation potentials and currents (E_{act} and i_{act}) for the reverse run. We found that the difference between these values for corrosion-prone and corrosion-resistant steels respectively appeared more clearly on the reverse-curves and also depended on the rate of recording (Table 2).

We see from Table 2 that for a high rate of recording there are no differences in E_{act} between corrosion-resistant and corrosion-prone samples, but a large difference in i_{act}; on the other hand, for a low recording rate the difference in E_{act} increases and that in i_{act} diminishes. It thus follows that, if we desire to use the potential E_{act} as a criterion for the tendency toward intercrystallite corrosion, lower recording rates (3 and 0.6 V/h) are preferable; if we desire to use differences in current density i_{act} as criterion, it is better to vary the potential more rapidly. For practical applications under industrial conditions rapid methods are more appropriate; we therefore studied the possibility of establishing behavioral differences between corrosion-resistant and corrosion-prone steels by reference to the value of i_{act}.

By appropriately choosing the conditions of preliminary anodic etching in the potential range −0.05 to + 0.05 V, we largely suppressed the anodic activation of quenched (corrosion-resistant) steel when recording the reverse anodic curve, whereas for the tempered (corrosion-prone) steel activation remained unimpaired. Tests in 10% H_2SO_4 at room temperature included the following operations: cathodic activation at −0.35 V for 1 min, anodic etching at 0.0 for 2 min, recording of the reverse anodic curve from + 0.75 V at a rate of 12 V/h to a potential of −0.1 V. The experimental time was ~ 8 min. Laboratory and industrial steels inclined toward intercrystallite corrosion tested in this way were activated on the reverse run of the anodic curve at potentials between + 0.2 and −0.1 V, whereas steels not so inclined were not activated (Fig. 1, Table 3).

On the basis of these results the presence of an anodic current loop in the potential range between + 0.2 and −0.1 V with a maximum at 0 ± 50 mV may be taken as good criterion for the tendency toward intercrystallite corrosion. The maximum current density of the anodic loop (i_{act}) will characterize the

TABLE 3. Results of Accelerated Tests to Determine the Tendency of Kh18N10T Steel Toward Intercrystallite Corrosion in 10% H_2SO_4 by Reference to the Potentiokinetic Anodic Curves (Reverse Run) at 21-23° for a Recording Rate of 12 V/h

No. of melt	Form of melt	Heat treatment	i_{act}, mA/cm²	Tend to intercry. corr. (AM meth.)	Maximum depth of intercrystallite corrosion (AM method), μ
130	Laboratory	Tempering	13	+	100
131	"	"	7,6	+	30
130	"	Quenching	No activation	—	0
37774	Industrial	Tempering	"	—	0
38102	"	"	"	—	0
40143	"	"	"	—	0
34739	"	"	"	—	0
50767	"	"	9	+	40
49791	"	"	7	+	30
49937	"	"	3	+	23

Note: The "+" sign means that the steel is inclined toward intercrystallite corrosion, the "-" sign that it is not.

degree of tendency of the steels toward intercrystallite corrosion. Comparison showed that there was a clear correlation between the depth of intercrystallite corrosion on Kh18N10T steels tempered at 650° for 1 h after tests by the AM method and the current density of their activation i_{act}.

Tests on the tendency of 85 Kh18N10T industrial steel melts toward intercrystallite corrosion were carried out in the Elektrostal' Factory by the foregoing potentiokinetic method. The All-Union State Standard tests (AM method) showed that 68 melts were corrosion-resistant and 17 corrosion-prone. According to the potentiokinetic method 65 melts were resistant and 20 prone. These results demonstrate the satisfactory agreement between the two methods.

Further investigations showed that the sensitivity and reproducibility of the method here developed for determining the tendency of Kh18N10T steels toward intercrystallite corrosion by reference to the activation current (i_{act}) could be increased by adding 0.0025 g/liter of KCNS to 10% H_2SO_4 solution. The preparation of the samples and the plotting of the anodic curve remained the same. Samples of Kh18N10T industrial steel melts (11 corrosion-prone, 30 corrosion-resistant) indicated 100% agreement with the results of the All-Union State Standard tests.

0Kh23N28M3D3T (ÉI-943) Steel. This type of steel has a high corrosion resistance in sulfuric acid solutions at room temperature and is not activated on recording the forward and reverse curves in either the quenched or the tempered states. Activation of these steels only occurs in the presence of chlorine ions. The anodic curves recorded at rates of 12 and 30 V/h were therefore studied in solutions of 1% HCl containing traces of 0.5 N NaCl, and also in neutral solutions of 0.5 and 1.5 N NaCl, without preliminary anodic etching.

In plotting the reverse curves of a corrosion-prone steel (melt 151) in these solutions, well-defined activation appeared in the form of an anodic loop (Fig. 2). In corrosion-resistant samples (tempered 152 and quenched 151 and 152) this failed to appear. On holding a polished sample of tempered 151 steel inclined toward intercrystallite corrosion in 0,5 N NaCl at anode-loop potentials of + 0.75 V for 30 min, there was a rise in anode current, accompanied by intensive etching of the grain boundaries and the chipping of individual crystalallites (Fig. 3a). The cross section of Fig. 3b illustrates intercrystallite corrosion to ~ 70 μ deep.

The activation of this type of Mo-containing steel in the solution in question at potentials more positive than + 0.2 V may be due, not only to the chromium-impoverishment of the boundary zones, but also to the direct dissolution of the Mo-rich secondary $\varkappa$-phase precipitating along the grain boundaries in the course of tempering (aging). As regards Cr content the $\varkappa$-phase differs little from the σ-phase, but is capable of easier anodic activation by the overpassivation mechanism on account of its molybdenum content.

In order to choose the optimum conditions for recording the anodic curves, we made a series of experiments in 0.5 N NaCl and studied the influence of the potential corresponding to the beginning of the anodic curve and the potential of cathodic activation on the form of the recording. These experiments showed that in 0.5 N NaCl the activation current i_{act} appearing on the reverse run of the curves increased on displacing the potential of cathodic activation in the negative direction (to —1.0 V) and on displacing

the potential corresponding to the beginning of the anodic recording in the positive direction (to 1.05 V). On the basis of these tests we chose the following procedure as an accelerated method of determining the tendency of ÉI-943 steel toward intercrystallite corrosion: test solution 0.5 N NaCl, cathodic activation of —1.0 V for 1 min, then reverse plotting of the anodic potentiokinetic curve at a rate of 30 V/h from potential + 1.05 V to potential + 0.2 V. The time required for the experiment 3 min. The anodic curves for steel 151 (quenched and tempered) obtained in this way are presented in Fig. 2. The tendency toward intercrystallite corrosion is estimated under these conditions by reference to the appearance of an anodic loop in the potential range between + 1.05 and + 0.2 V. The absence of an anodic loop in this range, together with a steady fall in the current, indicates that the ÉI-943 steels are not inclinded toward intercrystallite corrosion. This method was tested on 35 industrial melts of ÉI-943, of which 33 were not inclined toward intercrystallite corrosion and two were so inclined according to the All-Union State Standard. Complete agreement with the State Standard was obtained on using the potentiokinetic method.

The Elektrostal' Factory is now testing all manufactured industrial melts of Kh18N10T and ÉI-943 steels for tendency toward intercrystallite corrosion by the standard and potentiokinetic methods working in parallel, in order to accumulate more extensive data and possibly to recommend the inclusion of accelerated potentiokinetic test methods for intercrystallite corrosion in the All-Union State Standard.

CONCLUSIONS

1. We have studied the influence of various factors (intial preparation of the surface, composition of the solution, rate of plotting the curves) on the difference between the anodic potentiokinetic curves of stainless steels respectively with and without a tendency toward intercrystallite corrosion.

2. We have found that plotting the anodic potentiokinetic curves in the reverse direction offers a rapid way of determining the tendency of austenitic stainless steels to intercrystallite corrosion.

3. We have evolved the best method for carrying out rapid (3-8 min) potentiokinetic determinations of the tendency of Kh18N10T and ÉI-943 steels toward intercrystallite corrosion; the results agree closely with the longer tests (24-144 h) used as standard procedures at the present time.

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