ISSN 0321-4095, Voprosy khimii i khimicheskoi tekhnologii, 2025, No. 2, pp. 123-133

UDC 669.620.197:006.354

T.O. Derhach [a], D.A. Sukhomlyn [b], D.B. Hlushkova [a], A.Ye. Baliev [c]

SCIENTIFIC AND EXPERIMENTAL JUSTIFICATION FOR THE INDUSTRIAL APPLICATION OF ACCELERATED ELECTROCHEMICAL METHODS FOR TESTING RESISTANCE TO INTERGRANULAR CORROSION

[a] Kharkiv National Automobile and Highway University, Kharkiv, Ukraine
[b] Dnipro University of Technology, Dnipro, Ukraine
[c] «CENTRAVIS PRODUCTION UKRAINE» PJSC, Nikopol, Ukraine

The purpose of this work is to provide a scientific and experimental justification for the widespread industrial application of accelerated electrochemical methods for testing the resistance of austenitic stainless steel products to intergranular corrosion as an alternative to prolonged (up to 240 hours) boiling tests in acid solutions. A large-scale comparative study was conducted using standardized methods for assessing the intergranular corrosion resistance: (a) in weakly oxidizing environments – an accelerated electrochemical method of potentiostatic etching in 1 N $HClO_4$+0.25 N NaCl, compared with a prolonged test involving the boiling of samples in 35% H_2SO_4 with the addition of $CuSO_4$ and metallic copper (Practice E, ASTM A-262); and (b) in highly oxidizing environments – an accelerated electrochemical method of anodic etching of metallographic sections in 10% $H_2C_2O_4 \cdot 2H_2O$, compared with a prolonged test involving the boiling of samples in 65% HNO_3 (Practices A and C, ASTM A-262, respectively). The study was conducted on experimental 304L-type stainless steel samples with a carbon content of 0.018–0.05%, sensitized under different conditions, as well as on industrially manufactured Cr–Ni and Cr–Ni–Mo stainless steel products. A strong correlation was found between the results obtained using the proposed accelerated methods and the traditional prolonged tests. Additionally, quantitative criteria for satisfactory intergranular corrosion resistance were established when testing by the potentiostatic etching and Practice A methods. The study demonstrated the high corrosion resistance of special $\Sigma3$ twin grain boundaries when using method A, as described in the coincident site lattice theory. The obtained results support the recommendation of using the accelerated potentiostatic etching and Practice A methods as viable alternatives to prolonged testing procedures in industrial production of austenitic stainless steel products.

Keywords: austenitic stainless steels, intergranular corrosion, electrochemical methods, grain boundary structure, special boundaries, coincident site lattices.

DOI: 10.32434/0321-4095-2025-159-2-123-133

Introduction

Metal products made of austenitic stainless steels are widely used for applications requiring steel's unique properties and corrosion resistance, for instance, in chemical and petrochemical industries, oil refining, energy, aerospace, machine-building, nuclear power, automotive, architecture and other industries [1–4]. The most popular among the austenitic stainless steel are Cr–Ni and Cr–Ni–Mo steel grades 08Cr18Ni10Ti (321), 12Cr18Ni12Ti, 03Cr18Ni11 (304L, 304LN) and 03Cr17Ni14Mo_3 (316L and 316LN) due to their unique combination of high corrosion resistance, mechanical and technological properties, workability and weldability [3]. These steels are used in closed cycles of circulation of corrosive liquids at chemical, oil refining enterprises, mineral fertilizer production plants [4,5]; at nuclear and thermal power plants, they are used in the shells of heat-emitting elements, heat exchange equipment, racks for storing spent nuclear fuel, etc. [4]. A further development of production and consumption of products made of austenitic Cr–Ni and Cr–Ni–Mo steels is stimulated by the recent sharp drop in the price of one of their important quality components, nickel, which has almost tripled over the past 2 years: from 48,000 up to 16,000 dollars per ton.

Certainly, due to the tendency of corrosion-resistant steels to passivation, they can be exposed to the most dangerous local types of corrosion, the most common of which is intergranular corrosion (IGC) [2,3,5–7]. IGC develops at large-angle grain boundaries of steels and can lead to through corrosion damage and loss of strength of valuable equipment and to negative economic, humanitarian and environmental consequences. Therefore, mandatory acceptance and acceptance tests of metal products made of austenitic Cr–Ni and Cr–Ni–Mo steels are tests for resistance to the IGC in accordance with the requirements of domestic, foreign and international standards. According to their requirements, tests of metal products on the IGC are carried out by boiling the samples in solutions of acids of different oxluvation-reduction capabilities. Before the tests, the samples are subjected to a special provocative heating (sensitization), which contributes to the release of chromium and molybdenum carbides at the grain boundaries of steels and the appearance of their susceptibility to the IGC [2,3]. Depending on the operating conditions of the metal product, in weakly oxidizing or strongly oxidizing environments, it must be tested according to the methods E, and C according to ASTM A-262, respectively. The E method consists in boiling flat samples with dimensions of 1–3×6–20×50–80 mm (thickness, width, and length, respectively) for 8 hours in a solution of 35% sulfuric acid and copper sulfate with the addition of metallic copper. In such a solution, the corrosion potential $E_{cor}\approx+0.1$ V relative to the standard saturated silver chloride reference electrode Ag/AgCl is established on the test samples. It corresponds to weakly oxidizing environments and the transition region of electrochemical potentials on the anodic polarization curve of austenitic Cr–Ni and Cr–Ni–Mo steels. Resistance to the IGC is assessed by the presence or absence of characteristic intercrystalline cracks on the surfaces (tops of bends) of samples bent at an angle of 90^0 or Z-shaped, visible under magnification ×8–12. The C method is intended for testing products that are used in particularly aggressive, highly oxidizing environments. It involves boiling the same samples as in the E method for 5 cycles of 48 hours each (240 hours in total) in a 65% HNO_3 ($E_{cor}\approx+1.0...1.1$ V (Ag/AgCl reference electrode)), which corresponding to the beginning of the transpassive region of potentials, with initial and intermediate weighing of samples after each cycle.

For each test cycle, a new portion of HNO_3 solution is required in the amount of 20 ml per 1 cm^2 of the sample surface. The rate of corrosion of the samples for each test cycle is evaluated by their specific mass loss (gravimetric method). The test results are considered satisfactory and the product suitable if the corrosion rate of the samples does not exceed 0.5 mm/year ($\nu_{cor}\leq0.5$ mm/year). Therefore, tests on the IGC are the longest and most expensive of the acceptance tests of products made of stainless steels. They significantly increase the total time of manufacturing products, delay their delivery and negatively affect the economic efficiency of production. Therefore, the introduction and widespread use in the industry of express methods of testing resistance to the IGC is urgent.

The analysis of accelerated test methods on the IGC showed that currently there is standard on electrochemical methods for determining the resistance of austenitic steels against intergranular corrosion in weakly oxidizing environments. It includes four methods:

a) potentiostatic etching (PE), which consists in keeping test samples in a solution of perchloric acid and sodium chloride (1 N $HClO_4$+0.25 N NaCl) for 15 minutes at E=+0.1 V (Ag/AgCl reference electrode). The assessment of susceptibility to the IGC is similar to the method Practice E, ASTM A-262;

b) a drop method, based on the assessment of the corrosion potential of steel under a drop of a solution of nitric acid and ferric chloride (HNO_3+$FeCl_3$);

c) a method of measuring the corrosion potential of steel in a solution of nitric acid, hydrochloric acid and ferric chloride (HNO_3+HCl+$FeCl_3$);

d) a method of potentiodynamic reactivation, which consists in polarizing the sample in a solution of sulfuric acid and potassium thiocyanate in a given range of potentials successively in the anodic and cathodic directions and comparing the amount of electricity spent in the process of reactivation and passivation.

However, all these methods have not been sufficiently tested so far, so they need widespread verification; their disadvantages are that they (except the PE method) involve the simultaneous testing of only one sample and are not recommended for the control of welded joints.

ASTM A-262 contains an accelerated electrochemical method of etching in oxalic acid (EOA) Practice A, which is proposed for the IGC testing of austenitic corrosion-resistant steels intended for operation in strongly oxidizing environments. It consists in anodic etching of samples (metallographic sections) in a 10% solution of dehydrate oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) at a current density of 1 A/cm^2 (1$\cdot$10^4 A/m^2) for 1.5 min, followed by analysis of the resulting microstructures [3,8]. The Practice A is recommended as a preliminary test before the long-term method Practice C and in some cases can be used as an independent method. However, the EOA (A method) has not yet gained widespread use in the industry due to the insufficient amount of statistical tests and information about their results, as well as the lack of specific recommendations regarding the criteria for the suitability or unsuitability of the metal.

The purpose of the work is to provide a scientific and experimental justification for the availability of widespread industrial application of accelerated electrochemical methods for testing the resistance to intergranular corrosion (IGC) of metal products made of austenitic stainless steels instead of long (up to 240 hours) methods involving the boiling of samples in acid solutions.

Materials and methods

Materials

In this work, the following materials were used:

— samples of forgings/billets made of the most common low-carbon chromium-nickel austenitic stainless steel 03Cr18Ni11 (304L) of heats with a different carbon content (0.018, 0.030 and 0.050%), after sensitization (temperature and soaking time in the range of 400—700^{0}C; 0.25—100 h), for obtaining metal with different degrees of susceptibility to IGC (Table);

— samples of industrial production products subject to and not subject to the IGC (pipe blanks, forgings, rolled sheets, hot-, cold- and heat treated tubes and pipes) made of steels 08Cr18Ni10Ti (321), 12Cr18Ni12Ti, 03Cr18Ni11 (304 L, 304 LN), 03Cr17Ni14Mo3 (316 L and 316 LN) with a carbon content of 0.015—0.030% and a nitrogen content of 0.04—0.18%, after sensitization at 650^{0}C, 1 h.

Methods

For mass tests at the IGC, the test methods

Corrosion resistance comparative data of testing samples of laboratory heats made of steel grade 304 L, tested according to Practice C and A, ASTM A-262

Carbon content, wt.%	Sensitization mode		V_{cor}, mm/year	Type of microstructure (% etched GB)
	t, ^{0}C	time, h		
0.018	400	10; 20; 50; 100	0.2–0.4	«step structure»
	500	20	0.3–0.4	«step structure»
	500	30	0.45–0.5	«dual structure» (≤20)
	500	50	0.45–0.5	«dual structure» (≤25)
	500	100	0.6–0.7	«dual structure» (≥30)
	550	50	0.7–0.9	«ditch structure»
	600, 650	2; 5; 10	0.3–0.45	«step structure»
	600, 650	15	0.6–0.8	«dual structure» (≥35)
	700	2; 5; 10	0.3–0.4	«step structure»
0.03	550	5; 10	0.4; 0.45	«step structure»
	550	20	1.2–1.9	«ditch structure»
	600	1	0.3–0.4	«step structure»
	600	2	0.45–0.5	«dual structure» (≤20)
	600	3	0.85–0.9	«dual structure» (≥35)
	600	5	1.3–1.4	«ditch structure»
	650	0.5	0.45–0.5	«dual structure» (≥25)
	650	1	1.1–1.3	«ditch structure»
	700	1; 2	0.3; 0.47	«dual structure» (≤25)
	700	5; 10	0.9–1.3	«ditch structure»
0.05	550	5; 10	0.3; 0.45	«step structure»
	550	15; 20	1.35; 1.65	«dual structure» (≥50)
	600	1; 3; 5	1.5–6.2	«ditch structure»
	650	0.25; 0.5	3.2–3.6	«ditch structure»
	700	1; 3; 5	8.6–13.5	«ditch structure»

according to ASTM A-262, E and C, were used as long-term ones.

As accelerated, the following methods were used:

1) a number of electrochemical methods, which according to their effect on the grain boundaries of austenitic corrosion-resistant steels should correspond to the long-term test method Practice E, ASTM A-262;

2) an EOA method involving an anodic etching of grindings in 10% $H_2C_2O_4{\cdot}2H_2O$, (Practice A, ASTM A-262) [8], which should correspond to the long-term method Practice C, ASTM A-262.

Corrosion mechanisms at grain boundaries were determined by the following procedures: chemical analysis of solutions after tests for the content of ions of the main alloying elements of steels, as well as construction of anodic potentiodynamic curves in 1 N $HClO_4$+0.25 N NaCl [9]. The general and grain-boundary structure of steels and special low-energy grain boundaries (GB) S3 according to the theory of coincident site lattice (CSL) [3,10] were investigated by the methods of light metallography on an «Axiovert» metallographic microscope at magnifications of 200–500 and raster electron microscopy on a SEM 106 M microscope. After EOA, each slide sample was examined in at least five fields of view. The share of grain boundaries occupied by etching was estimated by the method of intersecting lines.

Results and discussion

Comparative tests of samples of the studied steels for resistance against IGC by accelerated electrochemical methods and the long-term method Practice E showed the following. In addition to the above-mentioned shortcomings, accelerated methods in some cases did not ensure reproducibility of results and had a discrepancy with the results of long-term tests, especially with a small degree of steel susceptibility to the IGC.

It was established that the most promising among these accelerated electrochemical methods is the PE method. It is easy to perform, allows testing 10 or more samples at the same time, the composition of the test solution used in it is scientifically justified by the selective action of Cl^- ions in the NaCl solution on the chromium and molybdenum-depleted border areas of the grains and the passivating effect of $HClO_4$ on the body of the grain [9]. The evaluation of the results in it is similar to the method E.

The results of mass comparative tests of samples of metal products of industrial production using the PE and Practice E methods showed the following. On the tops of the Z-like bends of samples prone to the IGC, tested by both methods, similar intergranular cracks were observed (Fig. 1a,c,e), and on transverse metallographic sections cut from straight sections of curved samples, etching of steel grain boundaries (Fig. 1b,d,f). The greater the tendency of the steel to the IGC, the coarser were the cracks and the greater the tempering of the boundaries. There were no cracks on the surfaces of samples not exposed to IGC tested by both methods, and there were no etching of grain boundaries on the grinds (Fig. 1g,h).

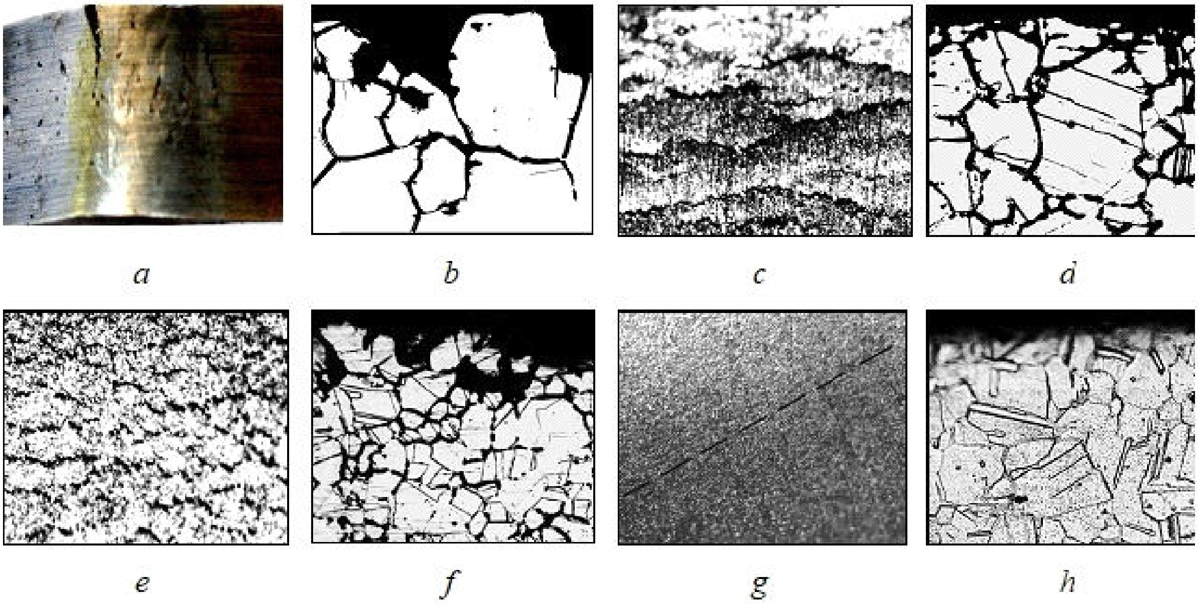


Fig 1. Tested surface (Z-bent) (a, c, e, and g, ×20) and microstructure after PE testing (b, d, f, and h; ×500) prone to the IGC (a–f) and passed (g and h) made of 06Cr18Ni11 (304) after prolonged sensitization (a and b); 12Cr18Ni12Ti (321) (c and d); and 03Cr18Ni11 (304L) with various carbon content (e–h)

Method of potentiostatic etching

When testing the samples by the PE method and by plotting the anodic potentiodynamic curves for a solution of 1 N $HClO_4$+0.25 N NaCl, the following data were obtained. On the anodic potentiodynamic curves of samples exposed to the IGC recorded by the PE method, activation areas were observed, which revealed the current peaks of steel dissolution (Fig. 2, curves 3–5), due to the rapid dissolution of chromium- and molybdenum-depleted border areas of the solid solution [2,3,7]. There were no activation areas on the anodic potentiodynamic curves of samples not exposed to the IGC, and curves had the appearance characteristic of corrosion-resistant steel prone to passivation (Fig. 2, curves 1 and 2).

Mass comparative tests of steel samples of industrial production for resistance to the IGC were conducted by Practice E and PE method with the determination of the value of the anodic current of steel dissolution ($\lg I_a$) in 1 N $HClO_4$+0.25 N NaCl at E=+0.1 V (Ag/AgCl reference electrode (Fig. 3). If during the test according to the Practice E, the susceptibility of steel to the IGC was not detected when using the PE method, the value of $\lg I_a$ of the samples on the potentiostatic curves did not exceed $1\cdot10^{-4}$ A/cm^2 (Fig. 3, curves 1–4), that is, the following condition was fulfilled: $\lg I_a \leq 1\cdot10^{-4}$ A/cm^2. Accordingly, if during the test by Practice E method, the steel was prone to the IGC, then the $\lg I_a$ value of the samples exceeded $1\cdot10^{-4}$A/cm^2 ($\lg I_a > 1\cdot10^{-4}$ A/cm^2) and increased with an increase in the degree of susceptibility to the IGC (Fig. 3, curves 5–8).

Based on these results, in addition to the presence or absence of intergranular cracks at the top of the bend of the sample, the limit $\lg I_a \leq 1\cdot10^{-4}$A/cm^2 was adopted as an additional quantitative criterion for the satisfactory resistance of metal products to the IGC when tested by the PE method. Curves 1 and 2 in Fig. 3 correspond to this condition. Curves 5–8, for which $\lg I_a > 1\cdot10^{-4}$A/cm^2, characterize the samples tendency to the IGC.

The results obtained show the feasibility of introducing and widespread use of the accelerated PE method for acceptance testing at IGC of products made from austenitic stainless Cr–Ni and Cr–Ni–Mo steels intended for weakly oxidizing environments (nuclear power plants, chemical and mechanical enterprises, engineering, etc.) The designed methodology ensures the reduction of testing time by more than 30 times.

Method EOA (Practice A)

So far, the accelerated methodology to the IGC susceptibility by means of anodic etching of testing samples in 10% $H_2C_2O_4\cdot2H_2O$ at $1\cdot10^4$ A/м^2, 1.5 min (Practice A, ASTM A 262) is recommended as rapid preliminary methodology for stainless steel materials which is intended for final testing according to prolonged and expensive 240 hours corrosion test Practice C, ASTM A 262.

As a result of mass comparative tests by long-term and accelerated methods of experimental heats of steel type 304 L (Table), as well as metal products of industrial production made of austenitic grades 304L, 304LN, 316L and 316LN with different degrees of susceptibility to the IGC, the following five main types of microstructures have been detected

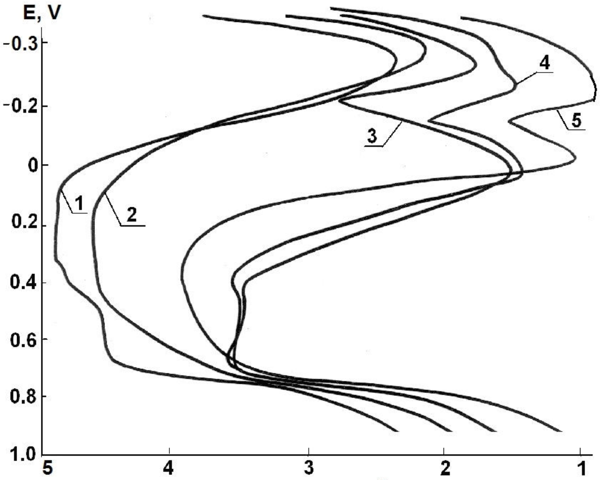


Fig 2. Anodic potentiodynamic curves recorded in 1 N $HClO_4$+0.25 N NaCl solution for samples made of grade 321: failed (1 and 2) and with different tendency to the IGC (3, 4, and 5)

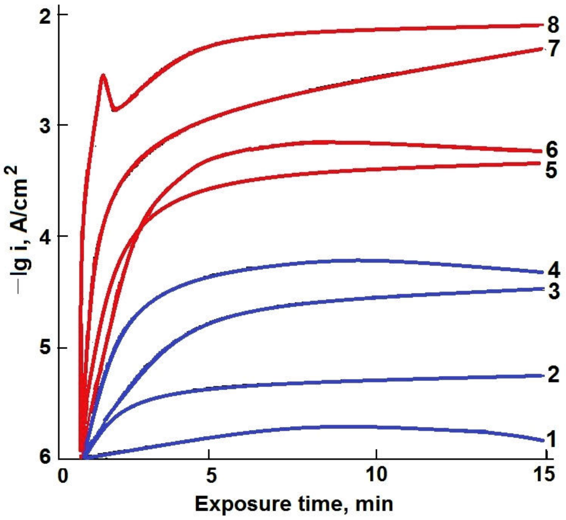


Fig. 3. Potentiostatic curves in 1 N $HClO_4$+0.25 N NaCl (E=+0.1 V) for samples of 316LN (1); 304LN (2); 304L (3, 5, and 6); and 321 (4, 7, and 8)

(Figs. 5–7, 9, Table):

1) «Ditch» structure (Fig. 4,a–c).

Such a structure was observed on samples of sensitized experimental steel grade 304 L with an increased carbon content (Fig. 4,a,b), as well as near the internal carburized surface of cold -rolled pipes made of steel grade 304L (Fig. 4,c).

Typical of «ditch» structure is that the grain boundaries of the general type (or trivial) are etched until they form continuous ditches, caused by the releasing of high chromium and chromium molybdenum carbides of the $Cr_{23}C_6$ and $(Cr,Mo)_{23}C_6$ type; at the same time, at least one or several grains are completely surrounded by ditches.

Special low-energy boundaries of the $\Sigma 3^n$ type in coincident site lattice are sometimes observed inside grain boundaries of the general type (shown by arrows in Fig. 4,a). On coherent (straight-line) sections of GB $\Sigma 3$, which are characterized by a reduced specific surface energy of 19 erg/cm^2 (19·10^4 J/m^2) comparing to the energy of the general type (trivial) boundaries 209 erg/cm^2 (209·10^4 J/m^2) [6,10–12], carbides were absent after tempering; accordingly, there was no over etching of such boundaries. Samples with a «ditch» structure were not resistant to the IGC when tested by usig the long-term method Practice C; their corrosion rate (ν_{cor}) significantly exceeded the maximum allowable of 0.5 mm/year (Table) and had been increased with each of subsequent test cycle.

2) «Step» structure (Fig. 5,a–c).

This structure is typical of austenitic Cr–Ni and Cr–Ni–Mo steels with an ultra-low carbon content (less than 0.020%) [3,8,10] and is characterized by a large number of special low-energy twin boundaries $\Sigma 3$ (CSL). In Fig. 5,a,b, SB $\Sigma 3$ CSL are shown by arrows, and Fig. 5,c shows an electron microscopic image of SB (carbon replica method). There are no etching ditches on the grain boundaries; and the boundaries appear in the form of steps, or thin lines due to the different etch ability of two crystallographically oriented neighboring grains with different crystallographic orientations. Samples with this structure were always characterized by a reduced rate of corrosion when tested by method C (ν_{cor}<0.5 mm/year; actually from 0.3 to 0.4 mm/year) (Table).

3) «Dual» structure (Fig. 6,a–c).

These structures combine the first two types of structures (some ditches at grain boundaries in addition to steps, but no one grain completely surrounded).

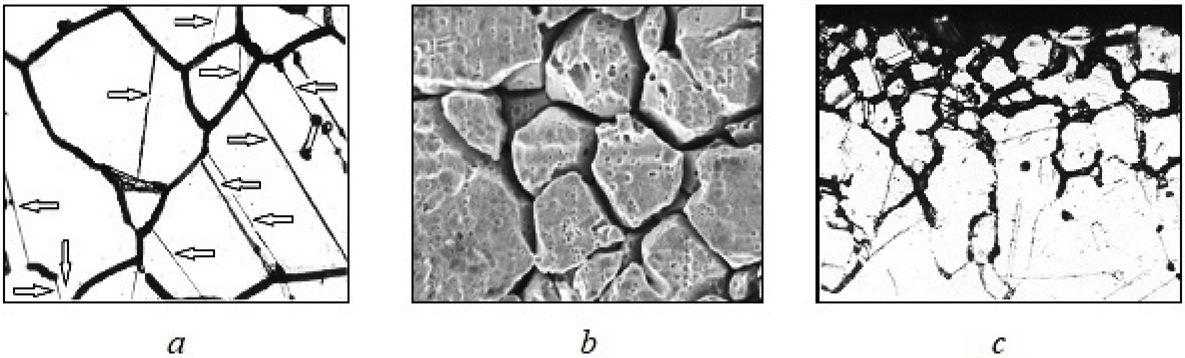


Fig. 4. «Ditch» structure after testing by Practice A of sensitized samples made of steel 304 L, magnification ×500: a and b – experimental heats with 0.05% C; (b – REM image); c – near the inner surface of cold-rolled tubes of industrial roduction

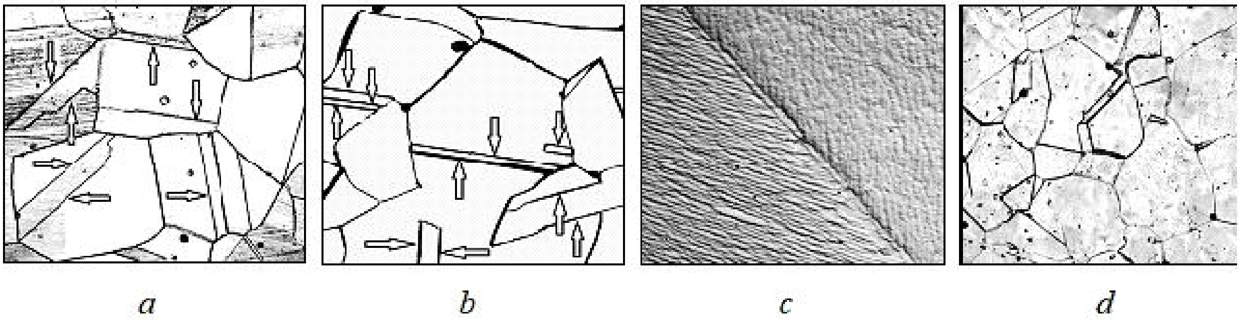


Fig. 5. «Step» structure after testing steel samples by Practice A: a–c – 304L with 0.018% C (a and b – magnification ×500); c – magnification ×6000, extraction replica); d – tubes of industrial production made of steel 316 LN, magnification ×300

Grain boundaries with a «step» structure mostly belong to special low-energy ones; they are shown by arrows in ig. 6,a and b. Earlier studies showed that coherent SB Σ3 CSL do not corrode even when testing samples using the Practice C method.

According to the ASTM, such a structure is considered uncertain in relation to the resistance of metal products to the IGC and requires a long test by Practice C method.

However, the results of mass comparative tests and studies showed that if during the examination after EOA the surface of the testing samples in five fields of view, the etched boundaries occupied less than 25% of the total surface of the boundaries (Fig. 6,a), then when tested by the Practice C, ν_{cor} was less than 0.5 mm/year, which corresponds to products resistant to the IGC. If the etched borders occupied greater than 25% (Fig. 6,b,c), then ν_{cor} at least in one test cycle was greater than 0.5 mm/year, which characterizes the product as not resistant to the IGC. The larger the surface of the grain boundaries occupied by etching ditches after EOA, the greater was the corrosion rate of the samples when tested by the Practice C (Table).

Figure 7 shows as an example of the temperature-time dependences of susceptibility to IGC (Rollasson curves), built on the basis of the results of comparative tests using the methods of C and A sensitized at 500–700^{0}C for 0.5–20 h. Test samples of 304L steel with 0.030% C (Fig. 7,a) and 0.018% C (Fig. 7,b) show complete convergence of mass test results by two methods.

In addition to the above types of standard structures, after EOA, the structures 4) «grain-boundary pitting I» and 5) «grain-boundary pitting II» can also be observed (Fig. 8,a,b).

In the examined metal products of industrial production, the «grain boundary pitting II» structure was caused by structural and selective corrosion of steel, associated with the dissolution of deformed non-metallic inclusions, in particular, manganese sulfides, and the high-chromium intermetallic σ-phase [13]. Figure 9 illustrates the deformed σ-phase (a) in the structure of hot-extruded pipes made of 03X18N11 (304L) with a degree of deformation of 95%; associated structural and selective corrosion on the ends of the samples (b and c) when tested in boiling 65% HNO_3 according to the method C (the corrosion rate of the

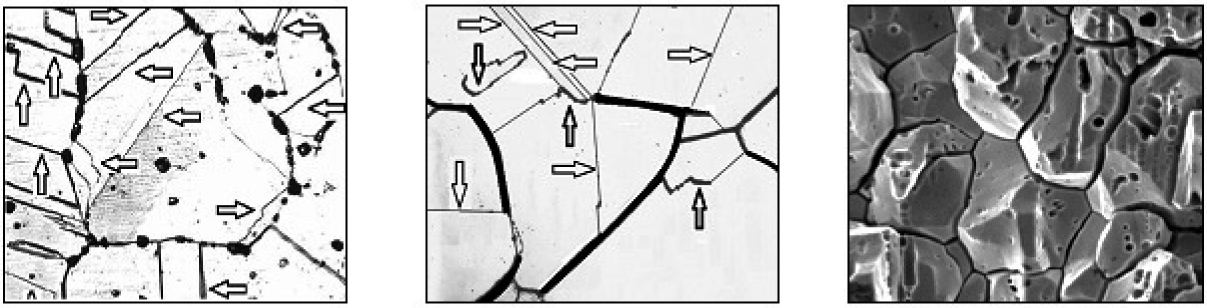
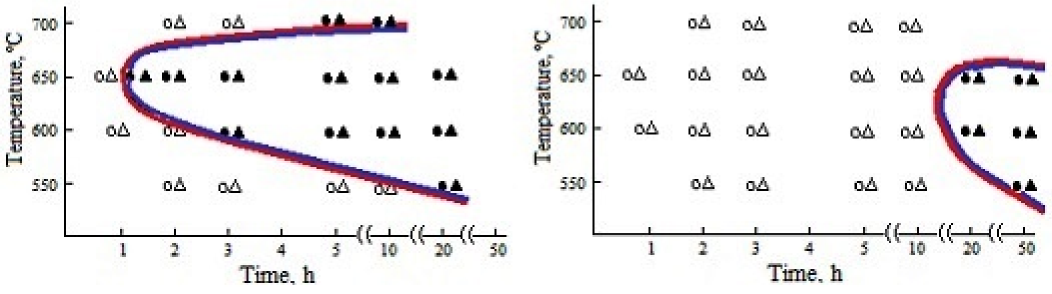

a *b* *c*

Fig. 6. «Dual» structure of steel samples 304L (a and b) and 316L (c, REM image) after testing by Practice A, magnification ×500; a, b and c – 15, 45, and 35% of the etched grains, respectively



a *b*

Fig. 7. Rollasson curves of test samples of 304L steel plotted according to the results of tests by methods C (red curve) and A (blue curve): a– 0.030% C; and b – 0.018% C. ●▲ – samples susceptible to the IGC; ○△– samples resistant to the IGC

samples reached more than 3 mm/year); and «grain-boundary pitting II» (d) when tested to method A.

One of the five above-mentioned structures is usually observed on a cross-section of sample austenitic corrosion-resistant steel etched during testing to Practice A (Fig. 2–8,9,c). Sometimes there can be a «mixed» structure, for example, simultaneously «ditch» and «grain-boundary pitting II» (Fig. 10,a); «intermediate» and «grain-boundary pitting II» (Fig. 10,b); «grain-boundary pitting I» (pittings with a light bottom are shown by arrows) and «grain-boundary pitting II» (Fig. 10,c).

The analysis of mass test results showed that «step», «intermediate» structures with ≤25% etched grain boundaries and «grain boundary pitting I» indicate the resistance of steel to intergranular corrosion. The «ditch» structure, as a rule, indicates the tendency of steel to the IGC. When obtaining structures «intermediate» with >25% etched grain boundaries and «grain boundary pitting II», additional testing of samples in boiling 65% HNO_3 according to the C method is recommended to prevent false rejection of suitable precious metal products.

Previously conducted research with the help of highly sensitive γ-spectrometry method proved that the root cause of the IGC of Cr–Ni steel 03Cr18Ni11 (304L) and, even more so, Cr–Ni–Mo steel 03Cr17Ni14Mo3 (316L) in boiling 65% HNO_3 is the predominant dissolution of carbides enriched in chromium and molybdenum at grain boundaries [3]. This is due to the lower corrosion resistance of chromium and, to an even greater extent, molybdenum at high anodic potentials due to the formation of soluble higher oxides of the specified

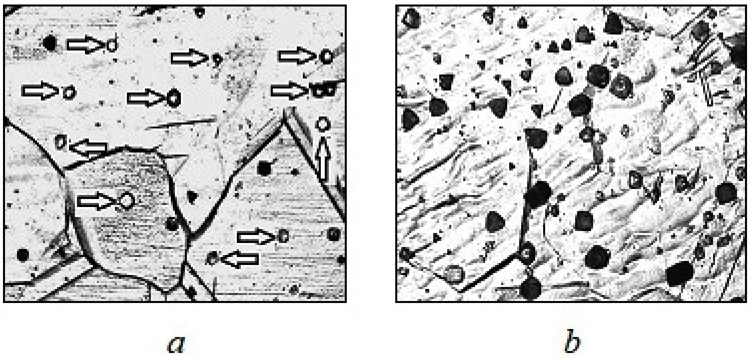

a b

Fig. 8. «Grain boundary pitting I» structures (a, magnification ×300) and «grain boundary pitting II» (b, magnification ×500)

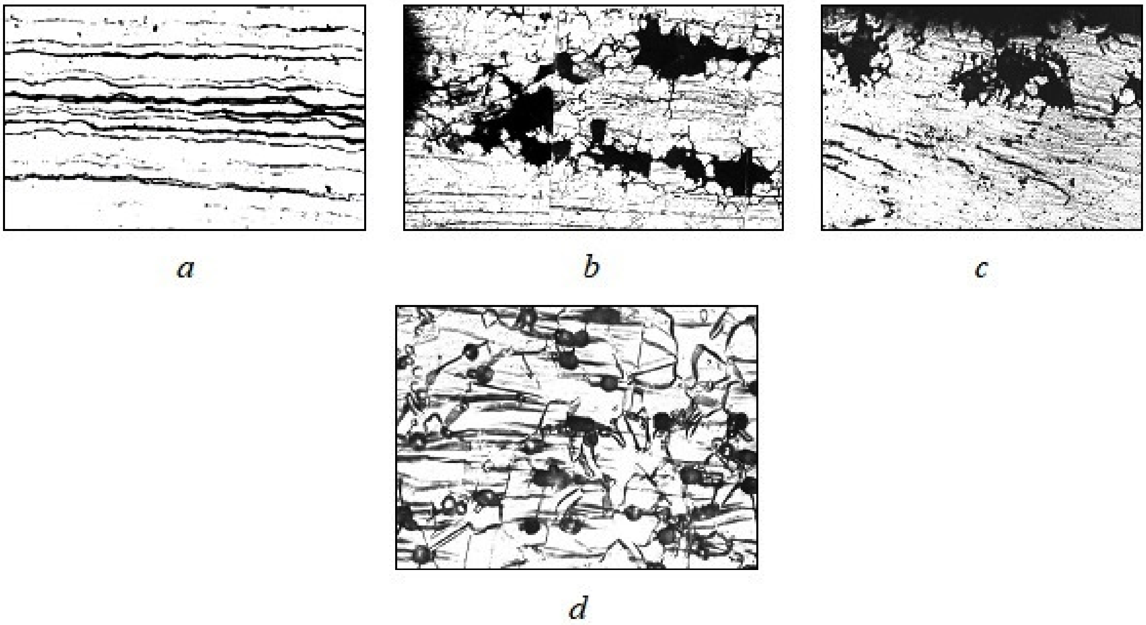

a b c d

Fig. 9. Deformed s-phase (a), structural and selective corrosion (b and c) after testing to Practice C and «grain boundary pitting II» (d) after the test Practice A of hot-extruded samples pipes made of steel 304L, magnification ×500: a and b – longitudinal cuts; c and d – transverse cuts

elements: $Cr_2O_7^{2-}$ and MoO^{3-} and loss of their passivating protective properties.

Chemical analysis of oxalic acid solutions after tests of samples prone to the IGC according to the EOA method showed an increased content of chromium and molybdenum ions in them and a reduced content of iron and nickel ions compared to the content of these elements in steels:

$\{[Cr]/[Fe]\}_{solution} > \{[Cr]/[Fe]\}_{steel}$,

and

$\{[Mo]/[Fe]\}_{solution} > \{[Mo]/[Fe]\}_{steel}$.

This testifies to the fact that during Practice A, as when testing in boiling 65% HNO_3 (Practice C), the predominant dissolution of chromium and molybdenum-enriched carbides occurs at the grain boundaries and proves the identity of the IGC mechanisms when tested by accelerated electrochemical method and long method.

When conducting mass tests using the method A of samples with a high degree of susceptibility to the IGC, it was also proven that a 1 liter of solution of 10% $H_2C_2O_4 \cdot 2H_2O$ can be used repeatedly for up to 500 samples of metallographic testing samples.

Taking into account the obtained results will make it possible to apply a simple and economical accelerated method A for finishing tests of metal products in the conditions of industrial production and significantly (up to 1000 times) to reduce the testing time.

Conclusions

1. The results of comprehensive research and statistical comparative tests of austenitic stainless steels on resistance to intergranular corrosion by standard long-term and accelerated electrochemical methods were obtained.

2. It was shown the complete convergence of the results and the identity of the corrosion mechanisms during tests by the long-term methods of Practice E and Practice C according to ASTM A-262 and the corresponding accelerated electrochemical methods PE and Practice A, ASTM A-262.

3. It was also shown that coherent SB Σ3 CSL are not subject to corrosion, both when tested by the accelerated Practice A method and long-term Practice C method.

4. For the first time, the quantitative criteria for satisfactory resistance to the IGC of austenitic Cr–Ni and Cr–Ni–Mo steels, tested in a weakly oxidizing environment by the PE method, were proposed: limitation of the steel dissolution current density ($lgI_a \leq 1 \cdot 10^{-4}$ A/см^2) at the anodic potentiostatic curve in a solution of 1 N $HClO_4$+0.25 N NaCl at E=+0.1 V (Ag/AgCl reference electrode).

5. For the first time, the quantitative criteria for suitability to the IGC of austenitic Cr–Ni and Cr–Ni–Mo steels with an «intermediate» structure when tested according to Practice A were designed: ≤25% of the surface of over etched grain boundaries on a metallographic section in the structure of steel.

6. Implementation and wide usage of proposed accelerated electrochemical methods of PE and Practice A make possible to reduce by 30 and 1000 times the corrosion testing time to detect the IGC resistance of products made of austenitic stainless steels. This development will definitely improve the technological cycle and significantly increase the efficiency of production of stainless steel products highly demanded by the world market.

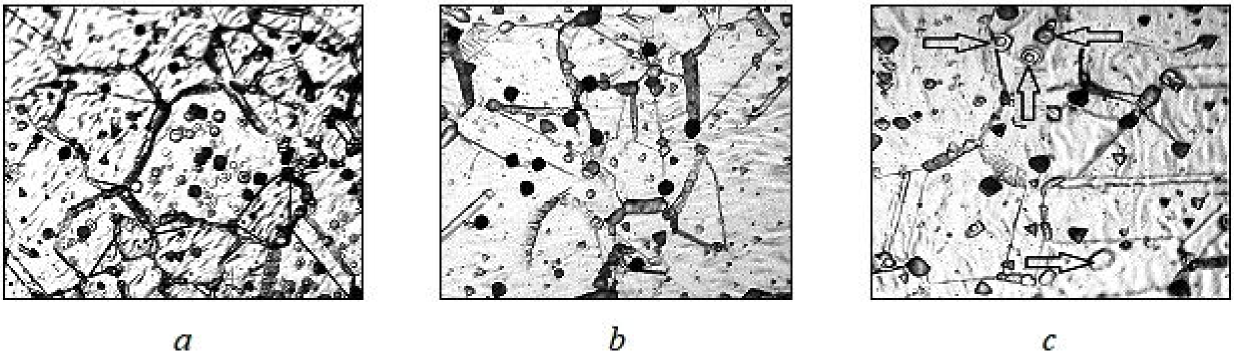


Fig. 10. «Dual» structure after the test Practice A of cold-rolled samples pipes made of steel 304:
a – «ditch» and «grain boundary pitting II»; b – «intermediate» and «grain-boundary pitting II», c – «grain-boundary pitting I» and «grain-boundary pitting II», magnification ×400

REFERENCES

1. *Lo K.H., Shek C.H., Lai J.K.L.* Recent developments in stainless steels // Mater. Sci. Eng. R Rep. – 2009. – Vol.65. – P.39-104.

2. *Vakhrusheva V.S., Dergach T.A., Sukhomlin G.D.* O sovremennykh trebovaniiakh k korrozionnoi stoikosti trub iz osobo nizkouhlerodistykh nerzhaveiushchykh stalei dla atomnoi enerhetiki // Probl. At. Sci. Technol. – 2008. – Vol.2. – No. 92. – P.73-77.

3. *Dergach T.O.* Teoretychni ta tekhnologichni osnovy keruvannya strukturoyu dlya pidvyshchennya koroziinoyi stiikosti trub z nyzkolegovanykh i vysokolegovanykh stalei. – Dyss. ... dokt. tekhn. nauk. – 2018. – 391 p.

4. *Maziasz P.J., Busby J.T.* Properties of austenitic steels for nuclear reactor applications // Compr. Nucl. Mater. – 2012. – Vol.12. – P.267-283.

5. *Joshi A., Stein D.F.* Chemistry of grain boundaries and its relation to intergranular corrosion of austenitic stainless steel // Corrosion. – 1972. – Vol.28. – No. 9. – P.321-330.

6. *New* sights on intergranular corrosion resistance mechanism of type 304 austenitic stainless steel by adjusting carbon contents / Mou L., Bian T., Zhang S., Liu B., Wu P., Zhang J., et al. // J. Mater. Res. Technol. – 2023. – Vol.26. – P.666-680.

7. *The influence* of surface-active elements on grains boundary structure and resistance against intergranular corrosion of austenitic Cr–Ni and Cr–Ni–Mo steels / Dergach T.O., Sukhomlin G.D., Deyneko L.M., Jiang Z.-H., Tian J. // Mater. Sci. – 2023. – Vol.59. – P.56-61.

8. *Pryskoreni* elektrokhimichni metody viprobuvannia austenitnykh koroziinostiikykh stalei na stiikist' proty mizhkrystalichnoi korozii / Dergach T.O., Suhomlin G.D., Baliev A.Ye., Suhomlyn D.A. // Visnyk Pridniprovskoi Derzhavnoi Akademii Budivnytstva ta Arhitektury. – 2020. – Vol.3. – No. 229-230. – P.46-56.

9. *Medvedeva L.A., Knyazheva V.M., Kolotyrkin Y.M.* To the question of choosing a standard corrosive medium for obtaining the anodic potentiodynamic curve of steels of type 18-10 // Prot. Met. – 1986. – Vol.21. – No. 3. – P.24-26.

10. *Bolshakov V.I., Sukhomlin G.D., Dergach T.O.* Metodichni osnovi doslidzhennya zernogranychnoi struktury v staliakh z γ, α i $\alpha+\gamma$ fazovym stanom // Visnyk Pridniprovskoi Derzhavnoi Akademii Budivnytstva ta Arhitektury. – 2017. – Vol.3. – P.10-21.

11. *Murr L.E.* Interfacial phenomena in metals and alloys. – United States: Addison-Wesley Publishing Company, 1975. – 387 p.

12. *Improving* the intergranular corrosion resistance of 304 stainless steel by grain boundary network control / Hu C., Xia S., Li H., Liu T., Zhou B., Chen W., et al. // Corros. Sci. – 2011. – Vol.53. – P.1880-1886.

13. *Hsieh C.C., Wu W.* Overview of intermetallic sigma (σ) phase precipitation in stainless steels // Int. Sch. Res. Notices. – 2012. – Vol.2012. – Art. No. 732471.

Received 09.12.2024

НАУКОВЕ ТА ЕКСПЕРИМЕНТАЛЬНЕ ОБҐРУНТУВАННЯ ЗАСТОСУВАННЯ В ПРОМИСЛОВОСТІ ПРИСКОРЕНИХ ЕЛЕКТРОХІМІЧНИХ МЕТОДІВ ВИПРОБУВАННЯ НА СТІЙКІСТЬ ДО МІЖКРИСТАЛІТНОЇ КОРОЗІЇ

Т.О. Дергач, Д.А. Сухомлин, Д.Б. Глушкова, А.Є. Балєв

Мета даної роботи є наукове та експериментальне обґрунтування можливості широкого застосування в промисловості прискорених електрохімічних методів випробування на стійкість до міжкристалітної корозії металопродукції з аустенітних нержавіючих сталей як альтернативи тривалим (до 240 годин) методам кип'ятіння зразків у розчинах кислот. Було здійснено масові порівняльні випробування на стійкість до міжкристалітної корозії за двома типами методик: а) у слабко окисних середовищах – прискореним електрохімічним методом потенціостатичного травлення зразків у 1 N $HClO_4$+0,25 N NaCl та тривалим методом шляхом кип'ятіння зразків у 35% H_2SO_4 з додаванням $CuSO_4$ і металевої міді (Практика Е, ASTM A-262); б) у сильно окисних середовищах – прискореним електрохімічним методом анодного травлення металографічних шліфів у 10% $H_2C_2O_4{\cdot}2H_2O$ та тривалим кип'ятінням зразків у 65% HNO_3 (Практики А і С, ASTM A-262, відповідно). Для досліджень використовували зразки сталі типу 304L (0.018–0.05% С), сенсибілізовані за різними режимами, а також металопродукцію з Cr–Ni та Cr–Ni–Mo сталей промислового виробництва. Встановлено збіжність результатів випробувань зразків, отриманих запропонованими прискореними і традиційними тривалими методами, а також визначено кількісні критерії задовільної стійкості сталей до міжкристалітної корозії при випробуванні за методами потенціостатичного травлення і Практики А. Показана висока корозійна стійкість спеціальних двійникових меж зерен $\Sigma3$ у рамках теорії решіток співпадаючих вузлів. Отримані результати дозволяють рекомендувати застосування прискорених методів потенціостатичного травлення та Практики А замість тривалих методик у промисловому виробництві металопродукції з аустенітних нержавіючих сталей.

Ключові слова: аустенітні нержавіючі сталі, міжкристалітна корозія, електрохімічні методи, зернограничая структура, спеціальні межі, решітки співпадаючих вузлів.

SCIENTIFIC AND EXPERIMENTAL JUSTIFICATION FOR THE INDUSTRIAL APPLICATION OF ACCELERATED ELECTROCHEMICAL METHODS FOR TESTING RESISTANCE TO INTERGRANULAR CORROSION

T.O. Derhach [a]***, D.A. Sukhomlyn*** [b, *]***, D.B. Hlushkova*** [a]***, A.Ye. Baliev*** [c]

[a] **Kharkiv National Automobile and Highway University, Kharkiv, Ukraine**

[b] **Dnipro University of Technology, Dnipro, Ukraine**

[c] **«CENTRAVIS PRODUCTION UKRAINE» PJSC, Nikopol, Ukraine**

[*] **e-mail: sukhomlyndmitrij@gmail.com**

The purpose of this work is to provide a scientific and experimental justification for the widespread industrial application of accelerated electrochemical methods for testing the resistance of austenitic stainless steel products to intergranular corrosion as an alternative to prolonged (up to 240 hours) boiling tests in acid solutions. A large-scale comparative study was conducted using standardized methods for assessing the intergranular corrosion resistance: (a) in weakly oxidizing environments – an accelerated electrochemical method of potentiostatic etching in 1 N $HClO_4$+0.25 N NaCl, compared with a prolonged test involving the boiling of samples in 35% H_2SO_4 with the addition of $CuSO_4$ and metallic copper (Practice E, ASTM A-262); and (b) in highly oxidizing environments – an accelerated electrochemical method of anodic etching of metallographic sections in 10% $H_2C_2O_4 \cdot 2H_2O$, compared with a prolonged test involving the boiling of samples in 65% HNO_3 (Practices A and C, ASTM A-262, respectively). The study was conducted on experimental 304L-type stainless steel samples with a carbon content of 0.018–0.05%, sensitized under different conditions, as well as on industrially manufactured Cr–Ni and Cr–Ni–Mo stainless steel products. A strong correlation was found between the results obtained using the proposed accelerated methods and the traditional prolonged tests. Additionally, quantitative criteria for satisfactory intergranular corrosion resistance were established when testing by the potentiostatic etching and Practice A methods. The study demonstrated the high corrosion resistance of special $\Sigma 3$ twin grain boundaries when using method A, as described in the coincident site lattice theory. The obtained results support the recommendation of using the accelerated potentiostatic etching and Practice A methods as viable alternatives to prolonged testing procedures in industrial production of austenitic stainless steel products.

Keywords: austenitic stainless steels; intergranular corrosion; electrochemical methods; grain boundary structure; special boundaries; coincident site lattices.

REFERENCES

1. Lo KH, Shek CH, Lai JKL. Recent developments in stainless steels. *Mater Sci Eng R Rep.* 2009; 65: 39-104. doi: 10.1016/j.mser.2009.03.001.

2. Vakhrusheva VS, Dergach TA, Sukhomlin GD. O sovremennykh trebovaniyakh k korrozionnoi stoikosti trub iz osobo nizkouhlerodistykh nerzhaveiushchykh stalei dlya atomnoi enerhetiki [On the modern requirements to the corrosion resistance of pipes made of especially low-carbon stainless steels for the nuclear power generating industry]. *Probl At Sci Technol.* 2008; 2(92): 73-77. (*in Russian*).

3. Dergach TO. *Teoretychni ta tekhnologichni osnovy keruvannya strukturoyu dlya pidvyshchennya koroziinoyi stiikosti trub z nyzkolegovanykh i vysokolegovanykh stalei* [Theoretical and technological foundations of structure control for improving the corrosion resistance of low-alloy and high-alloy steel pipes]. [dissertation]. 2018. 391 p. (*in Ukrainian*).

4. Maziasz PJ, Busby JT. Properties of austenitic steels for nuclear reactor applications. *Compr Nucl Mater.* 2012; 2: 267-283. doi: 10.1016/B978-0-08-056033-5.00019-7.

5. Joshi A, Stein DF. Chemistry of grain boundaries and its relation to intergranular corrosion of austenitic stainless steel. *Corrosion.* 1972; 28(9): 321-330. doi: 10.5006/0010-9312-28.9.321.

6. Mou L, Bian T, Zhang S, Liu B, Wu P, Zhang J, et al. New sights on intergranular corrosion resistance mechanism of type 304 austenitic stainless steel by adjusting carbon contents. *J Mater Res Technol.* 2023; 26: 666-680. doi: 10.1016/j.jmrt.2023.07.220.

7. Dergach TO, Sukhomlin GD, Deyneko LM, Jiang ZH, Tian J. The influence of surface-active elements on grains boundary structure and resistance against intergranular corrosion of austenitic Cr–Ni and Cr–Ni–Mo steels. *Mater Sci.* 2023; 59: 56-61. doi: 10.1007/s11003-023-00743-w.

8. Dergach TO, Suhomlin GD, Baliev AYe, Suhomlyn DA. Pryskoreni elektrokhimichni metody viprobuvannia austenitnykh koroziinostiikykh stalei na stiikist' proty mizhkrystalichnoi korozii [Accelerated electrochemical testing methods for the durability of austenitic corrosion-resistant steels against intergranular corrosion]. *Visnyk Pridniprovskoi Derzhavnoi Akademii Budivnytstva ta Arhitektury.* 2020; 3(229-230): 46-56. (*in Ukrainian*). doi: 10.30838/J.BPSACEA.2312.070720.46.640.

9. Medvedeva LA, Knyazheva VM, Kolotyrkin YM. To the question of choosing a standard corrosive medium for obtaining the anodic potentiodynamic curve of steels of type 18-10. *Prot Met.* 1986; 21(3): 24-26. (*in Russian*).

10. Bolshakov VI, Sukhomlin GD, Dergach TO. Metodichni osnovi doslidzhennya zernogranychnoi struktury v staliakh z γ, α i $\alpha+\gamma$ fazovym stanom [Methodological bases for investigation of the grain-boundary structure in steels with α, γ and $\alpha+\gamma$ phase state]. *Visnyk Pridniprovskoi Derzhavnoi Akademii Budivnytstva ta Arhitektury.* 2017; 3: 10-21. (*in Ukrainian*).

11. Murr LE. *Interfacial phenomena in metals and alloys.* United States: Addison-Wesley Publishing Company; 1975. 387 p.

12. Hu C, Xia S, Li H, Liu T, Zhou B, Chen W, et al. Improving the intergranular corrosion resistance of 304 stainless steel by grain boundary network control. *Corros Sci.* 2011; 53: 1880-1886. doi: 10.1016/j.corsci.2011.02.005.

13. Hsieh CC, Wu W. Overview of intermetallic sigma (σ) phase precipitation in stainless steels. *Int Sch Res Notices.* 2012: 2012: 732471. doi: 10.5402/2012/732471.