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Vasyl Stefanyk Precarpathian
National University

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H.O. Kniazieva, S.A. Kniaziev, R.S. Tomashevskyi, N.O. Kanunnikova, B.V. Vorobiov, O.V. Shestopalov, A.O. Sakun

Corrosion behavior of austenitic and ferritic steels in alkaline and water-salt solutions

National Technical University "Kharkiv Polytechnic Institute", Kharkiv, Ukraine
annapostelnik@ukr.net

The paper presents the results of studies of the corrosion behavior of austenitic and ferritic steels in alkaline, sulfide, and chloride environments. Structural changes on the surface when the steels are kept in solutions at room temperature are shown. The chemical composition of the steels was determined, and the exact phase-structural composition was theoretically predicted and metallographically determined. It was found that austenitic steel is almost not subject to corrosion in a sulfur-containing environment at room temperature. At the same time, ferritic steel, under the same conditions, has significant corrosion damage on the surface, especially in places of mechanical damage.

Keywords: corrosion tests, metallographic studies, corrosion, austenite, ferrite.

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Introduction.

Stainless and corrosion-resistant steels are used in the chemical industry to manufacture various chemical equipment, and in the oil industry to make tubes for cracking plants and oil refining equipment [1-4]. In the metallurgical and machine-building industries, heat-resistant steels and alloys are used in the manufacture of furnace equipment [5]. Corrosion in a sulfur-containing environment is also relevant in the aqueous environment, for example, for corrosion-resistant materials operating in water, the mechanism of which is described in detail in [6].

The modern energy, gas turbine, oil refining, and organic and synthetic materials industries use stainless steels that have high mechanical properties at elevated temperatures.

There are many industrial processes in which structural materials are exposed to a hot gas atmosphere containing not just one, but a number of different corrosive species. For example, during thermal cracking of man-made resources, alloys suffer from chlorine and simultaneous sulfur-induced high-temperature corrosion. Most commonly used high-temperature alloys resist high-temperature corrosion by forming oxide scales. In the case of Fe-Cr-Ni alloys, this protective oxide layer is mainly Cr_2O_3. However, the initial oxide layer of the alloys is often destroyed in such atmospheres because HCl gas or chlorine can penetrate this protective layer and consistently form volatile metal chlorides with the base material. The result is a loose and unprotected scale. In a reducing atmosphere, the corrosion rate even increases if chlorine is present [7-8].

In addition to the formation of evaporating metal chlorides, sulfidation of materials can be a significant problem. At relatively high sulfur partial pressures and low oxygen partial pressures, sulfidation can become the main corrosion mechanism. In a reducing atmosphere, sulfur, from biological components or fuels, is released as H_2S gas, which is known to be very corrosive compared to SO_2 released in an oxidizing atmosphere. It is well known that in a reducing sulfur-containing combustion atmosphere, corrosion is more severe than in an oxidizing environment, as cation diffusion in sulfides is much faster than in the corresponding oxides. Due to the greater disorder in the lattice, sulfide flakes grow faster and chip more easily than oxide flakes. Thus, the sulfide scales of alloys, which are often multilayered and complex, do not provide protection for the base material and, therefore, lead to severe corrosion attack [4, 9].

However, studies of the effect of sulfur pressure on the high-temperature corrosion behavior of alloys in chlorine-containing and reducing atmospheres are rare and not yet fully understood due to the lack of accurate and systematic analysis of real reactions in these complex multireaction environments. The studies conducted in various sources devoted to this topic, in some cases, have discrepancies in the results. These authors have found an increase in the speed of corrosion with increasing concentrations of H_2S [10], while others reported a decrease in the corrosion effect when H_2S was added to chlorine-containing atmospheres [11]. Thus, further research is needed to evaluate the corrosion behavior.

In sulfidizing atmospheres, chromium is considered to be the most useful alloying element against sulfidization. H.Wang et al. reported a decrease in the corrosion rate in an HCl-H_2S atmosphere with increasing chromium content, especially in the range of 8-12 wt % Cr, which is associated with an increase in the volume fraction of Cr_2O_3 in the scale [7, 12].

I. Materials and methods of research

The research was conducted on steels of two different classes: austenitic class - steel 08Cr18Ni9Ti (AISI301; 1.4310) and ferritic class - steel 12Cr17 (AISI430; 1.4016). Samples measuring 30x30 mm are cut from cold-rolled steel. The polished surface of the samples was used in the initial state for testing. Corrosion tests were carried out for 3 weeks in the following solutions:

1. Saturated aqueous alkaline KOH solution;
2. Aqueous salt solution 5% Na_2SO_3 + 5% NaCl;
3. In a corrosive environment of 5% S + 5% NaCl.

The experiments were performed at room temperature (~ 17 °C).

Elemental analysis was carried out by the optical emission method using a spectro instrument.

Metallographic studies of the samples were carried out in the initial state (to determine metallurgical quality and microstructure), as well as after corrosion tests on a ZESS AIXO Ver.1 metallographic microscope.

Hardness measurements were performed using Rockwell and Brinell hardness testers.

II. Results and discussion

2.1. Examination of samples in the initial state

The first stage of the work was to determine the elemental composition of the samples to be studied. The elemental analysis of the samples is shown in Table 1.

Based on the elemental analysis, we predict the phase composition in the steels using the Scheffler diagram.

According to the Scheffler diagram in Fig. 1, a, it can be seen that the austenitic steel under study contains approximately 8% ferrite in its structure, while the ferritic steel (Fig. 1, b) contains 100% ferrite. There are several theories regarding the influence of ferrite on the corrosion resistance of steels [14], in this case we will focus on the theory that believes that the presence of a small amount of ferrite phase has a positive effect on the corrosion resistance of austenitic steel. The essence of these statements is simple: austenite and ferrite are similar phases in nature, and under conditions when steels have a

Table 1.

Elemental composition of the samples under study

Chemical element	Elemental composition, wt. %							
	AISI301				AISI430			
	Measurements			Average value	Measurements			Average value
	1	2	3		1	2	3	
C	0.0630	0.0492	0.0522	0.0548	0.0274	0.0482	0.0355	0.0370
Si	0.379	0.368	0.377	0.3747	0.260	0.254	0.259	0.2577
Mn	1.12	1.14	1.11	1.1233	0.308	0.316	0.305	0.3097
P	0.0214	0.0195	0.0209	0.0206	0.0191	0.0147	0.0152	0.0163
S	0.0064	0.0041	0.0051	0.0052	<0.0010	<0.0010	<0.0010	<0.0010
Cr	18.49	18.54	18.43	18.4867	16.28	16.40	16.43	16.3700
Mo	<0.0010*							
Ni	8.36	8.30	8.34	8.3333	0.122	0.122	0.122	0.1220
Al	0.0179	0.0108	0.0115	0.0134	0.0166	0.0129	0.0186	0.0160
Co	0.239	0.239	0.242	0.2400	0.0201	0.0203	0.0202	0.0202
Cu	0.0727	0.0739	0.0805	0.0757	0.118	0.114	0.111	0.1143
Nb	<0.0020*							
Ti	0.0087	0.0086	0.0081	0.0085	0.0065	0.0072	0.0062	0.0066
V	0.0999	0.0971	0.0998	0.0989	0.101	0.0054	0.101	0.0691
W	0.0062	<0.0050	0.0064	0.0063	0.0054	<0.0050	0.0068	0.0061
Pb	<0.0010*							
Sn	0.0032	<0.0025	<0.0025	0.0032	<0.0025	<0.0025	<0.0025	<0.0025
Zr	0.0014	0.0015	0.0015	0.0015	0.0013	0.0012	0.0012	0.0012
Fe	71.1	71.1	71.2	71.1333	82.7	82.6	82.6	82.6333

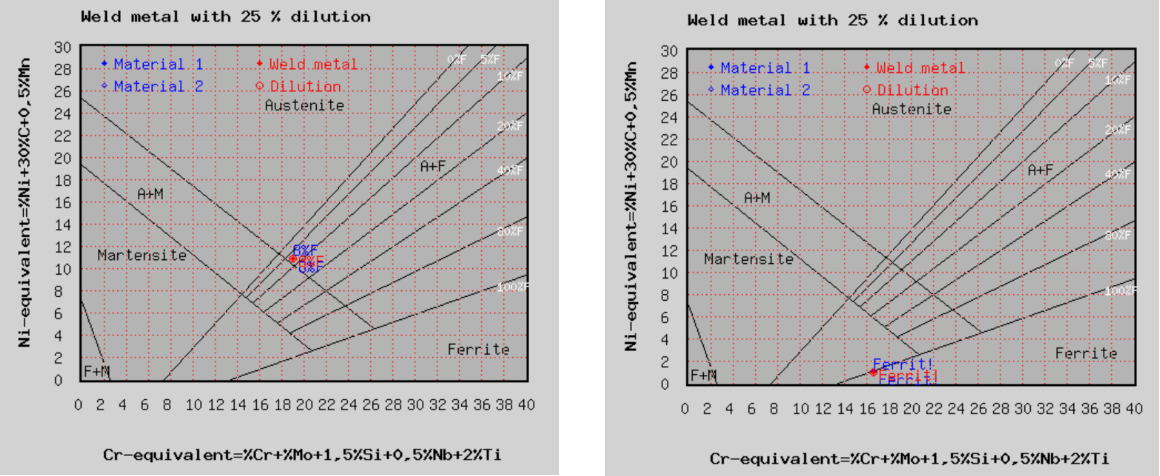
* beyond the sensitivity of the device

very low carbon content, its concentration in solid solutions is close. Therefore, the chemical gradient of these elements will be minimal, which means that the negative role of phases on corrosion resistance is reduced. On the other hand, the placement of a small amount of ferrite phase along the boundaries of austenite grains serves as a kind of barrier to the diffusion of carbon and alloyed elements, primarily Cr, from the middle of the austenite grain to its periphery. Thus, according to this theory, ferrite prevents carbide formation at grain boundaries and the outflow of Cr from the solid solution. All this has a favorable effect on the increased stability of intergranular corrosion boundaries.

Metallographic analysis of the samples in their original state fully confirms the phase composition predicted by the Scheffler diagram (Fig. 1).

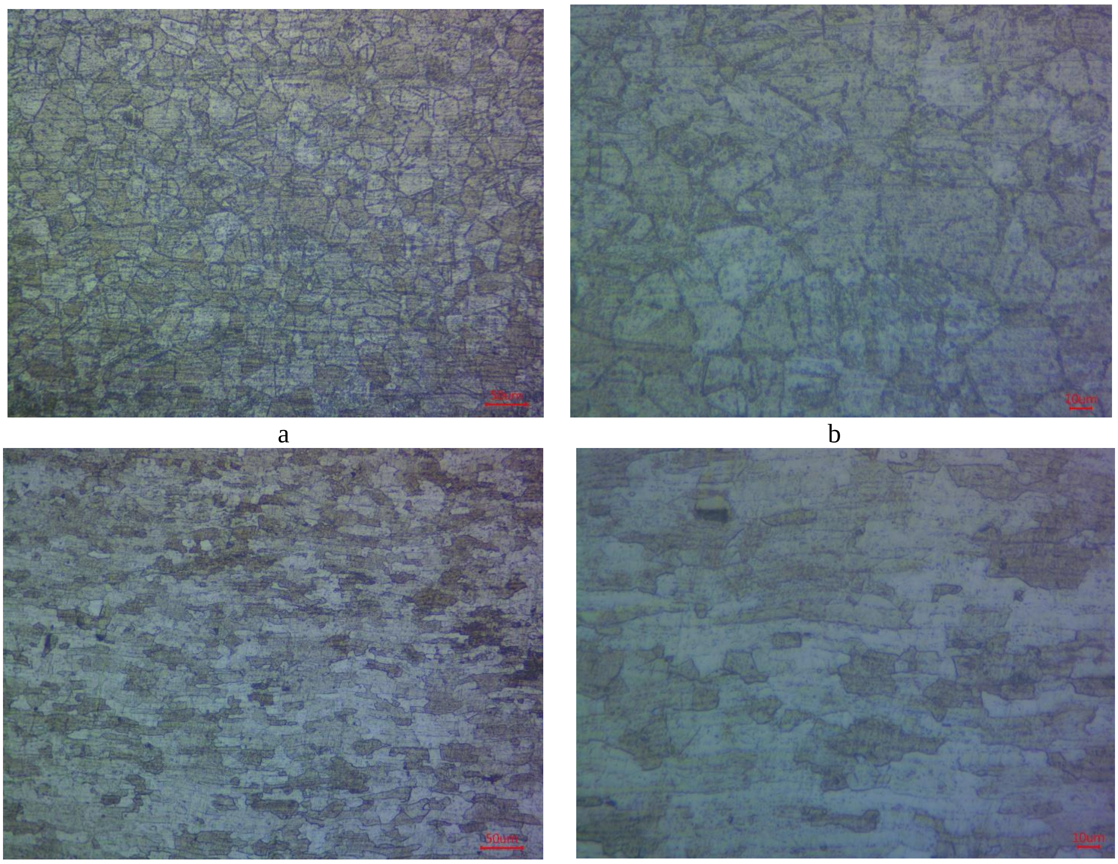
Figure 2 shows that AISI430 steel is in a riveted state, which confirms a high level of hardness (65 HRB or 109 HB). The average hardness of austenitic steel is 42 HRB or 81 HB.

Samples of ferritic steel are harder, which is explained by the riveted condition. Since the Rockwell hardness values for AISI301 steel are within a large margin of error



a b

Fig. 1. Theoretical phase composition of austenitic and ferritic steel on the Scheffler diagram:
a - AISI301 steel, b – AISI430 steel [13].



a b

c d

Fig. 2. Microstructure of the samples in the initial state: a, b - AISI301 steel,c, d – AIS4301 steel:
a, c - x200 magnification; b, d - x500 magnification.

due to the methodology of hardness determination, an additional Brinell hardness measurement was performed.

2.2. Examination of samples after corrosion tests

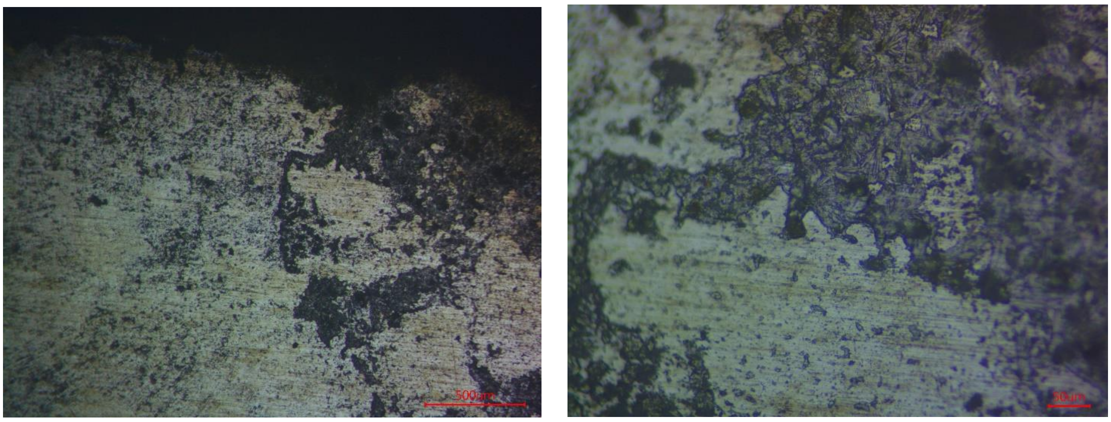
Laboratory corrosion tests were carried out in three aqueous solutions.

Both steels under study are resistant in alkaline KOH aqueous solution. However, for ferritic steel, the surface was observed to be cleaned of traces of scale.

Aqueous saline solutions of 5% Na_2SO_3 + 5% NaCl and 5% S + 5% NaCl on austenitic steel do not lead to significant corrosion damage, only in the solution of 5% S + 5% NaCl a slight plaque is observed at the edges of the tested samples.

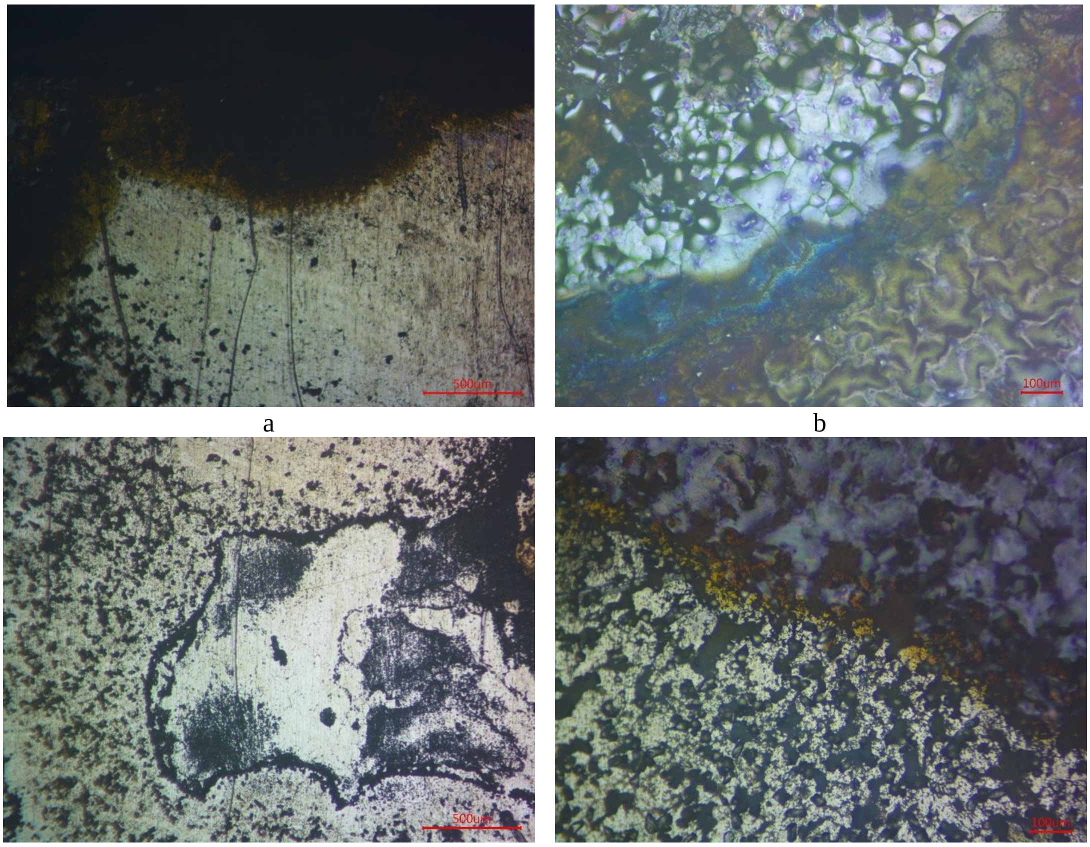
Aqueous saline solutions of 5% Na_2SO_3 + 5% NaCl and 5% S + 5% NaCl have a significant effect on ferritic steel. Thus, in the solution of 5% Na_2SO_3 + 5% NaCl, a plaque formed on the surface and significant corrosion damage was observed (Fig. 3).

In an aqueous salt solution of 5% S + 5% NaCl, samples of 12Cr17 steel show a rust deposit from the cut edge, which develops mainly in the areas of non-metallic inclusions (Fig. 4 c, d). Further, it develops intensively, turning into a continuous zone of corrosion damage with cracking of micro-volumes of corrosion products (Fig. 4 a, b).



a b

Fig. 3. The microstructure of ferritic steel after testing in an aqueous solution of 5% Na_2SO_3 + 5% NaCl: a - magnification x50; b - magnification x200.



a b

c d

Fig. 4. The microstructure of ferritic steel after testing in an aqueous solution of 5% S + 5% NaCl: a, c - magnification x50; b, d - magnification x100.

Conclusions

1) Saturated aqueous solutions of KOH at room temperature do not provoke corrosion processes. At the same time, they clean the surface of ferritic steel sheets.

2) Austenitic steel is preferred for sulfide corrosion at room temperature in aqueous solutions. Local corrosion develops intensively on ferritic steel, which subsequently turns into continuous corrosion. First of all, the cut and deformed edges of the sheet material, as well as the riveted surface with scale formed during the rolling process, are subject to destruction.

Kniazieva H.O. – PhD, associate professor of the Department of Materials Science;
Kniaziev S.A. – candidate of technical sciences, doctoral student of the Department of Materials Science;
Tomashevskyi R.S. – candidate of technical sciences, associate professor of the department of industrial and biomedical electronics;
Kanunnikova N.O. – PhD;
Vorobiov B.V. – PhD, Head of the Department of Automated Electrochemical Systemsж
Shestopalov O.V. – candidate of technical sciences, associate professor, head of the department of chemical engineering and industrial ecology;
Sakun A.O. – PhD, associate professor of the department of chemical engineering and industrial ecology.

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Г.О. Князєва, С.А. Князєв, Р.С. Томашевський, Н.О. Канунnікова, Б.В. Воробйов,
О.В. Шестопалов, А.О. Сакун

Корозійна поведінка сталей аустенітного та феритного класів в лужних та водно-сольових розчинах

Національний технічний університет «Харківський політехнічний інститут», м. Харків, Україна *annapostelnik@ukr.net*

Представлені результати досліджень корозійної поведінки сталей аустенітного та феритного класів в середовищах лугів, сульфідних та хлоридних речовинах. Показано структурні зміни на поверхні при знаходженні сталей у розчинах при кімнатній температурі. Визначено хімічний склад сталей, теоретично спрогнозовано і металографічно встановлено точний фазово-структурний склад. Встановлено, що сталь аустенітного класу майже не піддається корозії в сірковмісному середовищі при кімнатній температурі. В той же час сталь феритного класу, в цих же умовах, має суттєві корозійні ушкодження на поверхні, особливо у місцях механічних пошкоджень.

Ключові слова: корозійні випробування, металографічні дослідження, корозія, аустеніт, ферит.