M. M. LACHOWICZ*,#, M. B. LACHOWICZ**

THE MECHANISM OF CORROSION OF STEEL 304L IN THE PRESENCE OF COPPER IN INDUSTRIAL INSTALLATIONS

MECHANIZM KOROZJI STALI AUSTENITYCZNEJ 304L W OBECNOŚCI MIEDZI W INSTALACJACH PRZEMYSŁOWYCH

This paper presents the mechanism of corrosion of austenitic steel in the presence of copper. It has been found that when corrosion occurs, the presence of copper in the corrosive solution in the neighbourhood of austenitic steel results in the intensification of the corrosion processes. In the macroscopic scale, austenitic steel constitutes a cathode, but since copper precipitates can deposit on it, the steel can locally pass to the active state and become an anode in the places where copper deposited, which leads to its local corrosion due to galvanic corrosion.

Keywords: austenitic steel, copper, pitting corrosion, mechanism of corrosion

W pracy przedstawiono mechanizm korozji stali austenitycznej w obecności miedzi. Stwierdzono, że w przypadku wystąpienia korozji stali austenitycznej w obecności miedzi, prowadzi to do intensyfikacji zachodzących procesów korozyjnych. W skali makroskopowej stal austenityczna stanowi katodę, jednak możliwość osadzania się na niej wydzieleń miedzi powoduje, że lokalnie może ona przejść w stan aktywny i w tych miejscach stać się anodą, co prowadz do jej lokalnej korozji wskutek wystąpienia korozji galwanicznej.

1. Introduction

Alternate anodic and cathodic processes take place in different places on the surface of a metal exposed to a corrosive solution [1-3]. Even though austenitic steels are resistant to general corrosion, in some environments they undergo pitting corrosion. Then corrosion pits initiated at the nucleation stage grow and new nuclei continuously form. The nucleation of corrosion pits takes place in the weakest places of the passive layer, i.e. in mechanically damaged places, places where nonmetallic inclusions (carbides) occur, on dislocation jogs or on grain boundaries. In the case of alloys which readily undergo passivation, the passive layer is almost immediately restored in the places where corrosion pits form, whereas in the case of alloys which do not readily undergo passivation, open corrosion pits develop. Depending on the corrosion conditions the pits can assume various shapes (from circular to cylindrical). Also the size of the pits varies depending on the corrosion conditions.

Around a corrosion pit factors limiting the development of general corrosion occur. The surface of the pit becomes an anode and metal dissolution takes place inside the pit. The surroundings of the pit become a cathode and oxygen reduction takes place there. Thus the formation of a corrosion pit causes a local shift of the austenitic steel potential towards more negative values. The concentration of aggressive ions inside the pit increases as a result of their migration with the corrosion current. The increase in the concentration of aggressive ions leads to the formation of a corrosion cell inside the pit and to a higher conductivity of the concentrated corrosive solution. As a result of the hydrolysis of the metal ions the solution inside the pit becomes acidified. As the pH decreases, the passivation potential locally increases which makes it difficult for the passivation layer to rebuild. Repassivation is also retarded by the limited oxygen access to the inside of the corrosion pit, due to the poor solubility of oxygen in the concentrated electrolyte [3].

When combining stainless steel with other materials one should bear in mind that galvanic corrosion may occur as the latter takes place at the contact between materials differing in their electrochemical potentials, in the presence of an electrolyte. As a result of such a combination, one of the metals becomes an anode and the other – a cathode. When electrochemical corrosion sets in, the less noble metal (the anode) in such a pair undergoes accelerated corrosion while the more noble material is cathodically protected.

Since in the electrochemical series of metals stainless steel and copper are situated close to each other the risk of galvanic corrosion in such a combination seems to be slight. However, one should bear in mind that a difference of 50

* WROCLAW UNIVERSITY OF TECHNOLOGY, FACULTY OF MECHANICAL ENGINEERING; DEPARTMENT OF MATERIALS SCIENCE, STRENGHT MATERIALS AND WELDING, 25 SMOLUCHOWSKIEGO STR., 50-371 WROCLAW, POLAND

** WROCLAW UNIVERSITY OF TECHNOLOGY, FACULTY OF TECHNOLOGY AND LIFE SCIENCES, 9 BATOREGO STR., 59-220 LEGNICA, POLAND

Corresponding author:: marzena.lachowicz@pwr.edu.pl

mV is sufficient for galvanic corrosion to occur and the potential difference determined in standardized laboratory conditions may differ from the actual potential difference occurring in the real operating conditions. Moreover, the galvanic series was formed by determining the potential relative to the standard hydrogen electrode in the given corrosive medium alone. But it is enough to slightly change the chemical composition of the solution, the rate of flow of the corrosive solution or the temperature to significantly affect the corrosion potential of metals [5,9]. The possibility of occurrence of corrosion in such a combination in different corrosive media has been confirmed by literature reports [4,5,6,8,13,15].

The combination of stainless steel and copper is used in many industrial applications [4,6,13,15], e.g. in solar collectors in which a copper coil is set in a tank made of stainless steel. Owing to the high thermal conductivity of copper, in heat exchangers (from coolers or refrigerators to heaters) copper coils are used. Figure 1 shows an example of the corrosion of steel 5CrNi18-10 caused by the presence of copper.
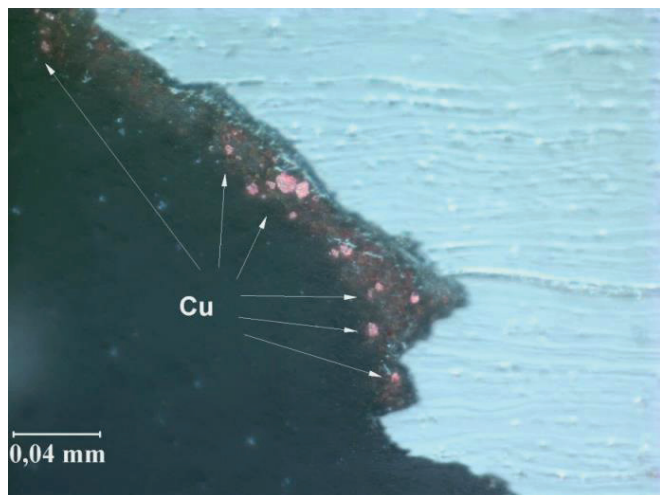
TABLE 1

Chemical composition of tested steel of grade 5CrNi18-10 acc. to PN-EN 10088-1.

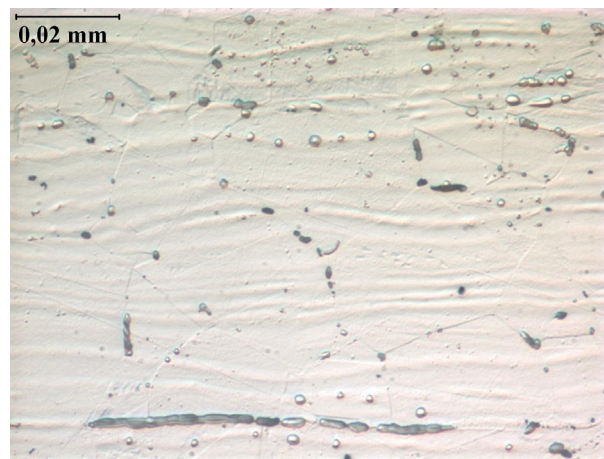| Element	Content [% weight]
C	0,01
Si	0,35
Mn	1,63
P	0,027
S	0,003
Cr	18,31
Ni	8,07
N	-
V	0,13
Cu	0,27
Al	0,01
Mo	0,26
Co	0,16
W	0,06
Nb	0,006
Fe	balance

Fig. 1. Microstructure of tested material. Visible band of ferrite δ and carbides in austenite matrix. Optical microscopy

Fig. 1. Corrosion of steel 5CrNi18-10. Light copper particles (indicated by arrows) are visible in corrosion products. Optical microscopy

2. Material and test methodology

Steel of grade X5CrNi18-10 acc. to PN-EN 10088-1 (304L acc. to ASTM) and CW008A copper in as supplied condition were used in electrochemical tests. The chemical composition of the tested austenitic steel is presented in table 1 while its microstructure is shown in figure 2. According to EN-12165:1998, the chemical composition of copper includes at least 99.95% of copper.

An analysis of the chemical composition of the steel was carried out using a LECO GDS-750-QDP spectral analyzer. Microscopic examinations were performed using a JEOL JSM-5800LV microscope and a Phenom proX microscope. A microanalysis of the chemical composition was carried out using a JEOL JSM-5800LV scanning electron microscope coupled with an Oxford LINK ISIS-300.

3. Tests

Polarization curves for steel 304L and copper CW008A (Fig. 2) were determined by carrying out electrochemical tests. The curves show that corrosion potential $E_{corr \text{ (relative to Ag/AgCl)}}$ = -189 ±15 mV of the copper was lower than that of the austenitic steel. The latter was characterized by corrosion potential $E_{corr \text{ (relative to Ag/AgCl)}}$ = -93 ±9 mV and breakthrough potential $E_{np \text{ (relative to Ag/AgCl)}}$ =+360 ±11 mV. This is consistent with studies [4, 5, 6, 8] in which copper paired with steel 304 or 304L showed an anodic character. Moreover, in [4,7] it was found that the current density of this corrosion pair increases with temperature and with the Reynolds number of the aqueous LiBr solution used in the tests.

Also a sample in the form of a corrosion pair was produced as described in Polish patent No. 213916 for the purpose of the investigations. In this way a galvanic cell in which electric charges could be transferred between the electrodes by the ions present in the corrosive solution was created. The transfer of the charges is connected with the oxidation and reduction processes

taking place on the surface of the electrodes. In the case of the austenitic steel connected to the more negative potential of the copper anode, corrosion potential $E_{corr\,(relative\,to\,Ag/AgCl)}$ amounted to -186± 12 mV. This means that the contact between the austenitic steel and the copper causes strong cathodic polarization of the steel, resulting in a shift of the corrosion potential towards values close to those for copper (Fig. 2).
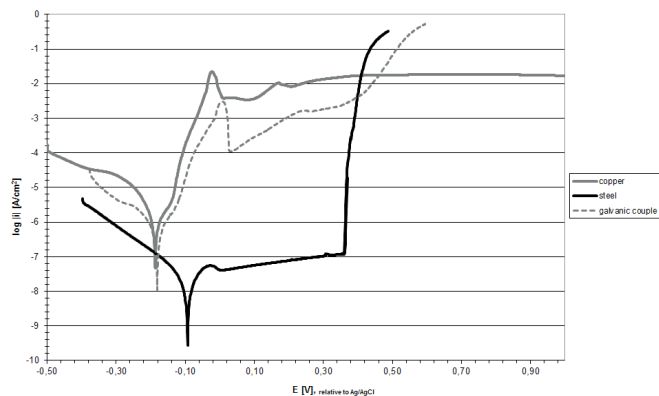

Fig. 2. Typical potentiodynamic curves obtained for tested materials; potentials measured relative to Ag/AgCl

After the electrochemical tests the surface of the samples was subjected to microscopic examinations which revealed corrosion pits on the surface of austenitic steel 304L (Fig. 3). The width of the corrosion pits, measured in the widest place and determined on the basis of measurements performed for 50 pits, ranged from 90 μm for circular pits to about 2 mm for elliptical pits. Their depth ranged from 58 to 226 μm.
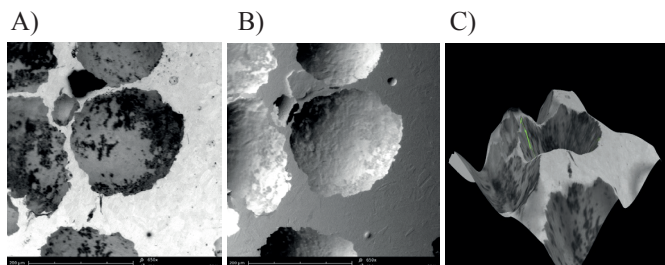

Fig. 3. Corrosion pits on steel surface without copper after polarization to potential of 500 mV: a) SE, b) BE, c) 3D reconstruction. SEM

In the case of the samples tested in the presence of copper, examinations of their surface after the electrochemical tests revealed a different character of the pitting corrosion (Figs 4 and 5). It was found that all the pits were characterized by developed surface with visible areas of local steel solubilisation centred around the formed pit. The width of the corrosion pits, measured in the widest place and determined on the basis of measurements performed for 50 pits, ranged from 148 μm for circular pits to 2.3 mm for elliptical pits. Their depth ranged from about 27 to 299 μm. Thus a trend towards the formation of corrosion pits with a more developed surface was also detected.
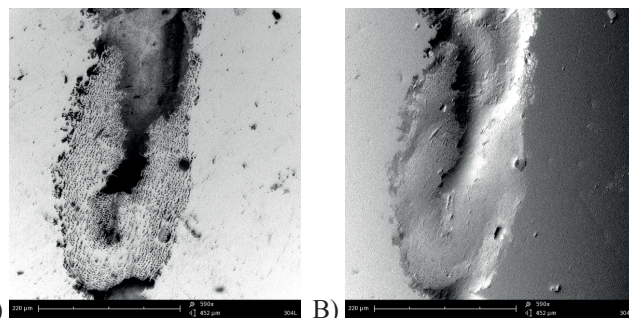

Fig. 4. Corrosion pits formed on steel surface in presence of copper after polarization to potential of 500 mV: a) SE, b) BE
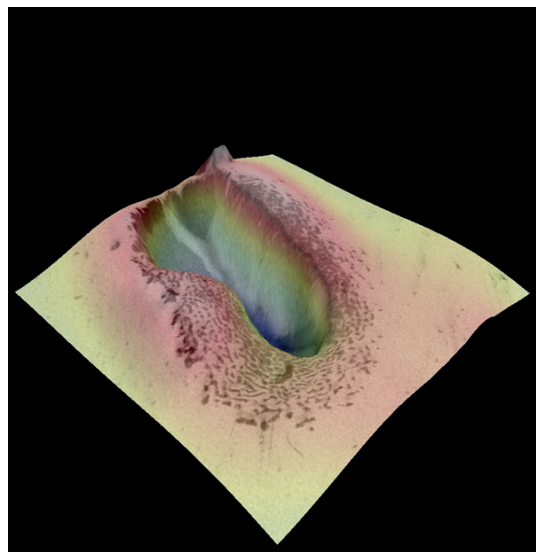

Fig. 5. Corrosion pits formed on steel surface in presence of copper after polarization to potential of 500 mV: a) SE, b) BE. SEM

The microscopic examinations also showed the cathodic deposition of copper from the anodic surface onto the austenitic steel surface constituting a cathode. This indicates that the ions produced as a result of copper solubilisation, contained in the electrolyte would deposit on the surface of the austenitic steel. This process is the consequence of electrolytic deposition and proceeds via the coating of the metal constituting the cathode with metal ions undergoing reduction and forming the tarnish, when a direct current flows through the electrolyte during electrolysis. Because of the lower electrochemical potential, oxidation takes place on the surface of the copper and the latter sulubilizes in accordance with the equation: $M0 \rightarrow Mz+ + z\,e-$. (i.e. $Cu \rightarrow Cu^{2+}+2e^-$), which means that Cu^{2+} ions penetrate into the corrosive solution. Thus copper atoms pass into the electrolytic solution and the released electrons are used up in the cathodic process. Reduction and coating with the metal ions present in the electrolyte take place on the surface of the austenitic steel. Metal deposition on the cathode proceeds in accordance with the equation: $Mz+ + z\,e- \rightarrow M0$ (i.e. $Cu^{2+}+2e^- \rightarrow Cu$). The Pourbaix diagram for copper in a solution with pH= 6.5 shows that at this pH copper forms Cu^{2+} ions at a potential of about 1 V.
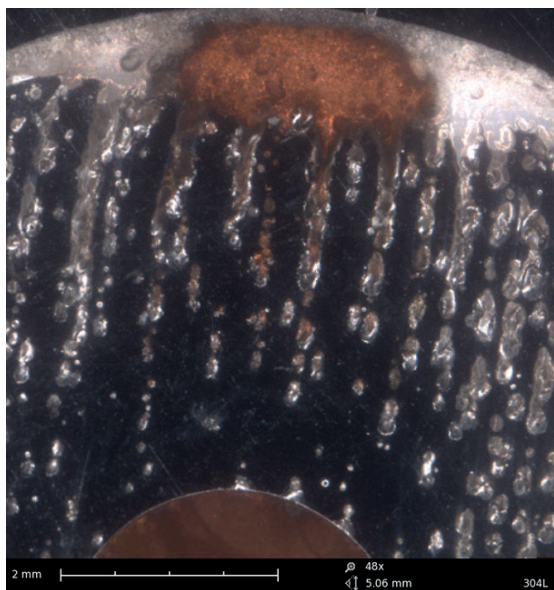
Fig. 6. General view of sample after electrochemical tests. Macroscopically visible deposition of copper on austenitic steel surface

The observable deposition was visible in both the macroscopic scale (Fig. 6) and the microscopic scale (Figs 7-10). Copper deposition on the surface of austenitic steel was also observed in [10, 11, 14]. Corroding copper sends its ions to the solution, which travel towards the steel surface and deposit on it as metallic copper. Numerous studies have shown that the copper ions in the corrosive solution can also come from the solubilisation of austenitic steel containing copper in its chemical composition [10, 11, 14]. The microscopic examinations showed that copper deposition occurred mainly on the surface damaged by corrosion around the sensitized points where the process of anodic solubilisation had begun in the corrosion-affected places, i.e. in active places lacking the passive layer. The migration of Cu^{2+} ions with the corrosion current to these areas is most probably caused by the difference in concentration arising due to an increase in the concentration of aggressive ions in the pit areas and connected with the increase in the corrosion current. It has been found that within the corrosion pits copper deposits on their entire surface, whereas around them copper deposition has a dispersed character.

Figure 7 shows an example of a corrosion pit with copper deposited inside it. The characteristic X-ray radiation spectrum obtained from this area is shown in fig. 8 while the results of point microanalyses are presented in table 2. Within the pit, where copper covers its entire area, the action of the copper is similar to that of a cathodic coating, consisting in insulating the austenitic steel from the corroding medium and so preventing its corrosion, regardless of whether the steel is in the active or passive state and thus regardless of the its electrochemical potential at a given moment.
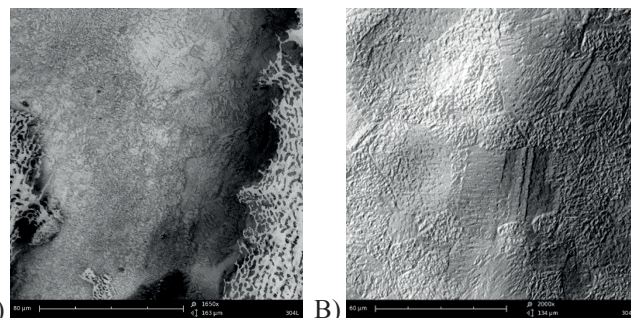

Fig. 7. A) Copper deposition (reflecting austenite structure) in place where corrosion pits occur: SEM, SE. B) Close-up of fragment shown in fig. 7A. Visible structure oriented by substrate: SEM, BE
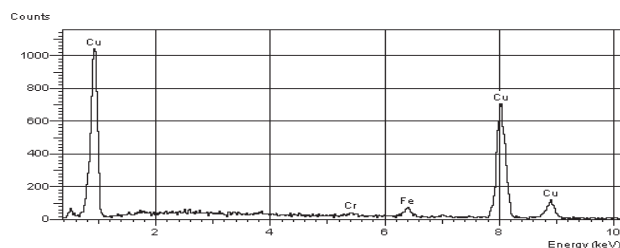

Fig. 8. Characteristic X-ray radiation spectrum obtained from surface of corrosion pit shown in fig. 7, in place of copper deposition

TABLE 2

Elemental content determined by point microanalysis in place marked in fig. 7B

Element	Content [% weight]		
O	6,91	19,23	6,77
Cr	0,73	2,29	1,1
Fe	3,41	2,34	1,78
Cu	88,95	67,46	88,01
Cl	-	-	1,53
Si	-	8,69	-

The situation is different in the areas surrounding the corrosion pits. The dispersed deposition of copper around the corrosion pits results in local places with a lower corrosion potential (places coated with copper) around which places with a higher corrosion potential (austenitic steel) are situated. However, detailed microscopic examinations revealed that small active galvanic cells form in the areas of dispersed copper deposition on the surface of the austenitic steel, causing local corrosion of the latter (Figs 9 and 10). This indicates that due to the presence of copper precipitates on the surface of the austenitic steel its matrix locally becomes an anode and consequently undergoes solubilisation in such places. In the literature on the subject this phenomenon is referred to as intermediate galvanic corrosion [3]. Thus locally the reversal of the situation observed in the macroscale takes place. Therefore, in order for the copper to become an anode a decrease in corrosion potential of the steel relative to the passive state must occur in such places.
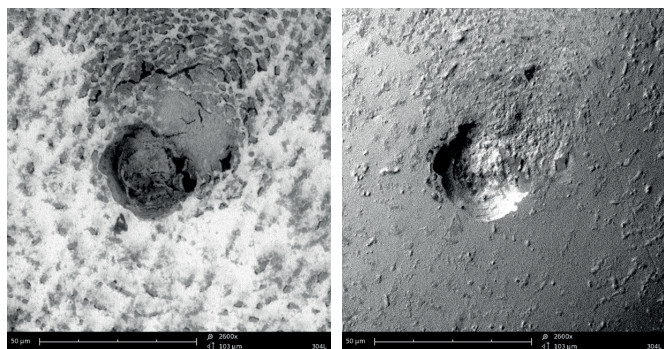
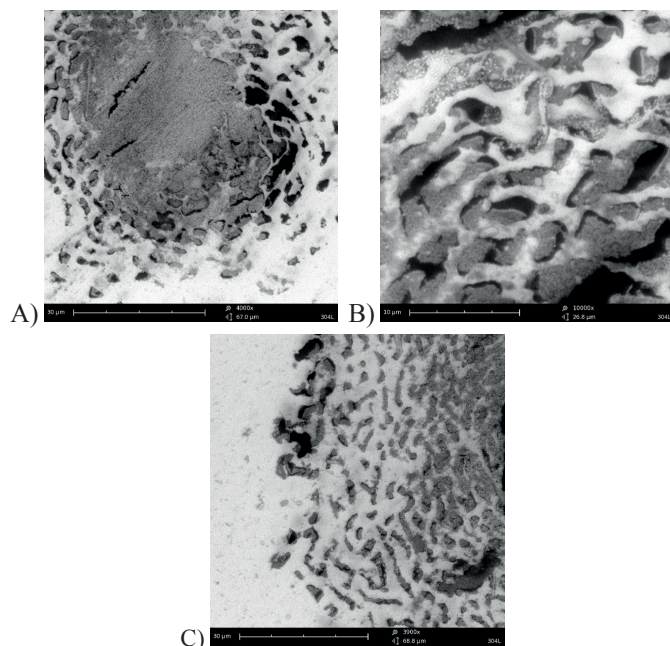Fig. 9. Corrosion pits on steel surface in presence of copper: a) SE, b) BE

Fig. 10. Solubilisation of austenite due to presence of copper deposited on surface of austenitic steel: SEM, SE

It is known that the cathodic polarization of a passivated metal or its contact with another metal with a more negative potential disturbs its passive state [2], which can explain the observed phenomenon. Locally, as a result of the weakening of the passive layer due to the contact of the austenitic steel with the copper the former passes into the active state whereby its electrochemical potential decreases. The decrease is significant enough for the situation to change, i.e. the copper becomes an anode while the austenitic steel becomes a cathode, as evidenced by the solubilisation of the steel in the places of dispersed copper deposition on the austenitic steel, observed in the microscopic image. An additional contributing factor is the low oxygen content due to the fact that oxygen access to the substrate of the steel is rendered difficult by the deposition of copper on its surface, which makes the restoration of the passive layer and the transition of the steel to the passive state difficult. In [12] it was found that the dissolution of austenitic steel in the presence of copper proceeds more readily when Cl ions are present in the corrosive solution. The multiplication of the processes leads to the heavy corrosion of austenite in the neighbourhood of copper precipitates (Fig. 10). Since the

local deposition of copper takes place around the pits, the latter grow in size and assume a characteristic shape (Fig. 4).

4. Conclusion

Although the risk that stainless steel in many corrosive solutions will corrode in the presence of copper can be slight, the studies have shown that when austenitic steel does undergo pitting corrosion, the proceeding corrosion processes intensify in the presence of copper in its neighbourhood. In the macroscopic scale austenitic steel constitutes a cathode, but since copper precipitates can deposit on it, the steel may locally pass to the active state and become an anode in the places where copper deposited, which leads to its local corrosion due to galvanic corrosion. As a result, corrosion pits with a very well developed characteristic surface form. There have been reports about the (disputable) influence of alloying austenitic steel with copper on the corrosion resistance of the former [10, 11, 12]. It has been found that during the corrosion of austenitic steel the ions passing into the corrosive solution can intensify the corrosion process. The mechanism of corrosion of austenitic steel in the presence of copper presented in this paper can explain also this phenomenon.

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