
Regularities of galvanic corrosion of the copper / stainless steel couple in Fe(III) environment

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Nobility inversion and galvanic corrosion regularities in the Cu/AISI 316 stainless steel system caused by Fe(III) were studied by voltammetry and the weight loss method. Stainless steel in Fe(III) environment exhibited typical passive behaviour over a wide potential range, while copper and carbon steel actively dissolved above the open circuit potentials (E_{ocp}). It was demonstrated that depending on the solution temperature and the pH even small Fe(III) concentrations (*ca.* 1 mg/l and lower) caused a significant positive E_{ocp} shift for AISI 316, while it was not the case for copper and carbon steel. Such nobility inversion of copper and stainless steel is of great practical importance when exploring Cu/stainless steel systems in the environments polluted with iron ions.

Key words: stainless steel, copper, ferric ions, nobility inversion, galvanic corrosion

INTRODUCTION

Stainless steels are widely used in many areas of industry and domestic surroundings due to their good maintenance, reasonable cost, good mechanical properties and high resistance to corrosion [1–6]. It is commonly known that galvanic corrosion is one of most dangerous kinds of corrosion, which may cause the failure of equipment [6, 7]. Galvanic corrosion occurs when two metal systems having different electrochemical potentials are coupled and have a contact with a conductive electrolyte. Even a small quantity of condensed moisture (water) is enough for galvanic corrosion to start. When this occurs, the noble metal becomes a cathode and a less noble one acts as an anode, whose dissolution accelerates the corrosion process. Also, two metals of the same nature with a different surface state or alloys with a different content of alloyed additives can be examples of galvanic systems. So, a spontaneous process when positive ions discharge on a more negative metal surface also cause galvanic corrosion (for instance, Cu, Fe on Al surface). Each of these effects represents a serious technical issue.

In this study influence of Fe(III) on galvanic corrosion of the couple copper–stainless steel AISI 316 was investigated. The motivation to carry out this work was real corrosion problems, which emerged when trying to explain corrosion failures of heat ex-

changers in the Vilnius heating networks made of stainless steel sheets connected with copper joints. Such commonly adopted exchangers were stable in pure water; however, the equipment suffered from extensive corrosion attacks and finally failed in the media with increased iron content. The results obtained may be of interest for corrosion scientists and engineers working in any area, where exposure of stainless steels to Fe(III)-enriched media is involved.

EXPERIMENTAL

Samples for measurements were prepared from commercially available plates of AISI 316 stainless steel, whose exact composition according to the electron microprobe analysis was (in mass %): Fe 66.7, Cr 17.5, Ni 10.4, Mo 2.33, Cu – 1.1, rest – Mn, Si, W, Pb and C). The carbon steel used had the following composition: Fe 91.8, Cu 5.35, Ni 0.75, Mn 0.1, Si 0.15, Cr 0.25, C 0.1, rest S, As, P. Copper samples were prepared from a pure copper plate (99.9).

Electrodes for electrochemical measurements had an actual area of 1 cm². The electrode surface before measurements was treated by abrasive SiC emery paper (1000), rinsed with alcohol and water, dried under ambient conditions and mounted in a glass cell. A saturated Ag/AgCl/KCl electrode was used

as reference and all potentials in this paper were referred to that electrode. A salt bridge was used to avoid Cl^- ions to fall into the solution. A platinum foil served as a counter electrode. The cell temperature was maintained by a thermostat.

Distilled water and $\text{Fe}_2(\text{SO}_4)_3$ of analytically grade purity were used to prepare the solutions. Solution pH was adjusted with 0.1 M H_2SO_4 .

Voltammetric measurements were conducted by a PS-305 potentiostat (Elchema, USA) equipped by VOLTSCAN (version 3.8.1) data acquisition and MASTER WINDOWS data processing softwares. The potential scan rate during polarization resistance measurements was 0.1 mV/s.

Corrosion rates of copper and carbon steel coupled either with AISI 316 or copper were determined by the weight loss method. For that purpose, connected tin-plates of the above couples were exposed for 14 days (couple Cu/AISI 316) and for 3 days (couple Cu/carbon steel) to ferric sulphate solutions. The actual contact area of the individual electrode with the solution was 50 cm^2 .

Atomic absorption spectroscopy (AAS) was applied to determine the concentration of the elements

released into solution during exposure using a Perkin Elmer AAS 603 machine (USA).

RESULTS AND DISCUSSION

Figure 1 shows the open circuit potential E_{ocp} vs. time for copper, AISI 316 and carbon steel in solutions containing different Fe(III) concentrations ($c_{\text{Fe(III)}}$). Under ambient conditions the Cu potential is more positive than that of AISI 316 at $c_{\text{Fe(III)}} \leq 1 \text{ mg/l}$. At higher additive concentrations, however, the potential of AISI 316 shifts considerably in the positive direction, while that of copper remains actually unaffected. Thus, when increasing Fe(III) concentration, a nobility inversion is observed: Cu is nobler at lower Fe(III) concentrations, whereas AISI 316 becomes nobler at higher contents of the additive. Ferric ions' impact on the stainless steel surface state is rather strong: E_{ocp} values of AISI 316 stainless steel extracted from 10 mg/l solution of $\text{Fe}_2(\text{SO}_4)_3$ and located into that of nonferric water remain unchanged (Fig. 1 d). The carbon steel is a less noble sample, whose potential is only slightly affected by Fe(III) concentration.

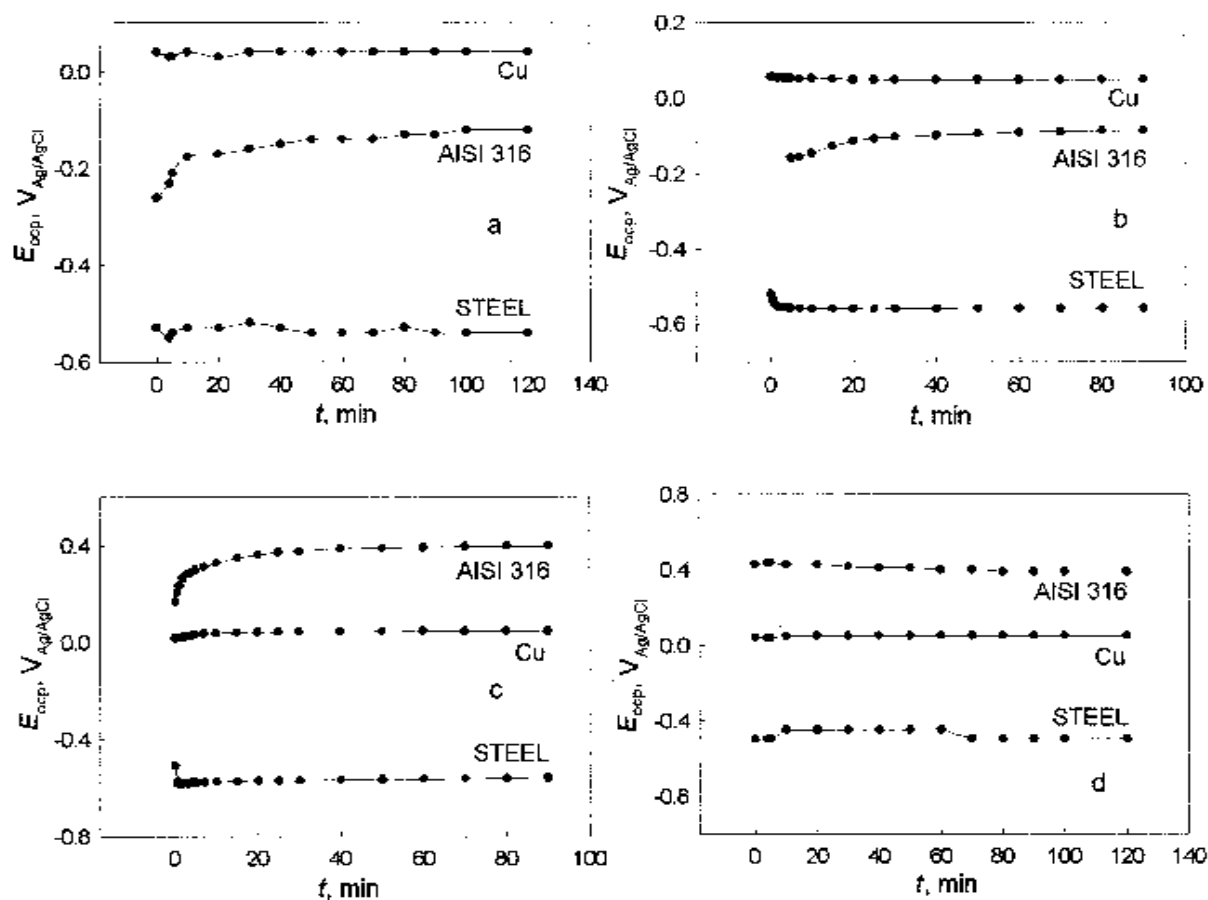


Fig. 1. Dependences of E_{ocp} of AISI 316, carbon steel and Cu electrodes on time in ferric solutions, pH 2.7, 20 °C. Fe(III) concentration: a – nonferric, b – 1 mg/l, c – 10 mg/l, d – nonferric, electrodes before measurements were for 2 h exposed to 10 mg/l $\text{Fe}_2(\text{SO}_4)_3$ solution

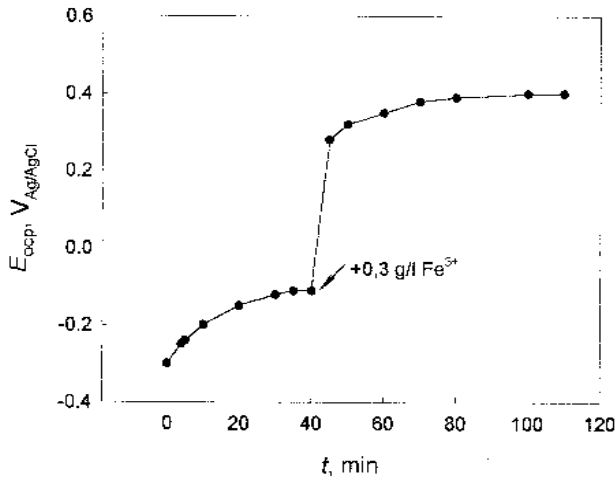


Fig. 2. Influence of introduction of ferric ions into a non-ferric solution on E_{ocp} of AISI 316 stainless steel at pH 2.7, 20°

The data in Fig. 2 give another evidence of the influence of ferric ions on the AISI 316 open circuit potential. Introduction of a small quantity of ferric ions (0.1 ml of 0.3 g/l ferric sulphate solution) into solution led to a sharp increase in the open circuit potential of AISI 316.

The character of Fe(III) influence on E_{ocp} depends also on the solution pH and temperature. In the solution with pH 4.7 and 0.3 mg/l Fe(III), E_{ocp} of stainless steel continually shifted in the positive direction (Fig. 3a). An inversion in stainless steel and Cu nobility is observed after ca. 1.5 h of exposure.

An increase in solution temperature had a similar influence upon E_{ocp} (Fig. 3b). Even at a low Fe(III) concentration (0.1 mg/l) the E_{ocp} of stainless steel shifts in the positive direction and after 1.5 h of exposure the E_{ocp} values of AISI 316 and Cu become similar. E_{ocp} of carbon steel moved towards more negative values when the solution temperature was increased. It should be noted that precipitation of barely soluble iron compounds was observed during the measurements even in the solutions with a very low ferric concentration.

A voltammetric diagram for Cu, AISI 316 and carbon steel is shown in Fig. 4. One can see that the anodic activity of all the samples under study was increased when Fe(III) was added. The AISI 316 exhibits a typical passive behaviour over a wide potential range ($E \approx -0.4 \pm 0.8$ V). By contrast, both carbon steel and Cu do not exhibit passivity and actively dissolve above the open circuit potentials. Thus, one can conclude that even an insignificant corrosion acceleration by Fe(III) will cause a great positive shift of E_{ocp} of AISI 316 due to the curve flatness. Contrary to that, the same corrosion acceleration will only slightly affect the potentials of Cu

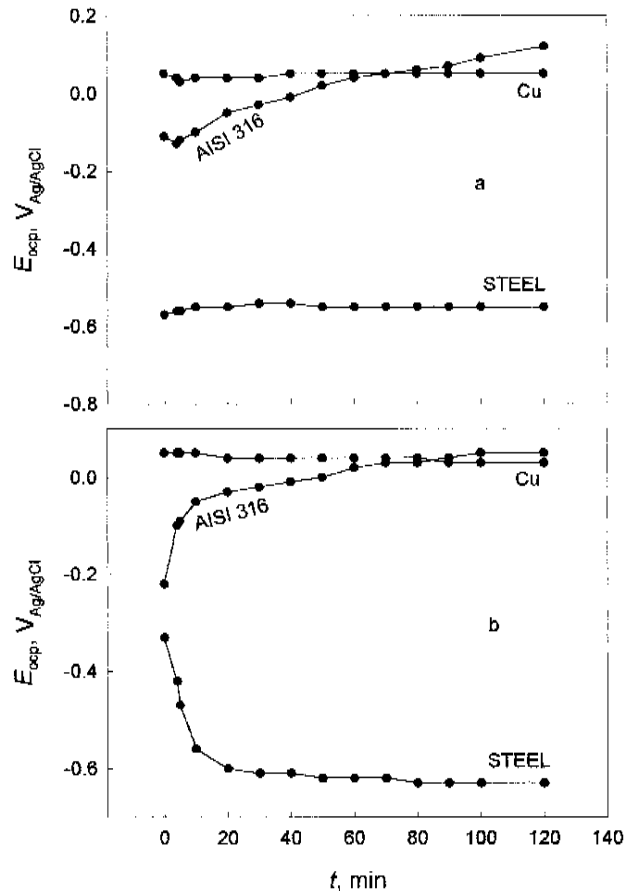


Fig. 3. Dependence of E_{ocp} of AISI 316, carbon steel and Cu electrodes on time in 0.3 mg/l ferric sulphate solution, pH 4.7, 20 °C (a) and in 0.1 mg/l ferric sulphate solution at pH 2.7, 70 °C (b)

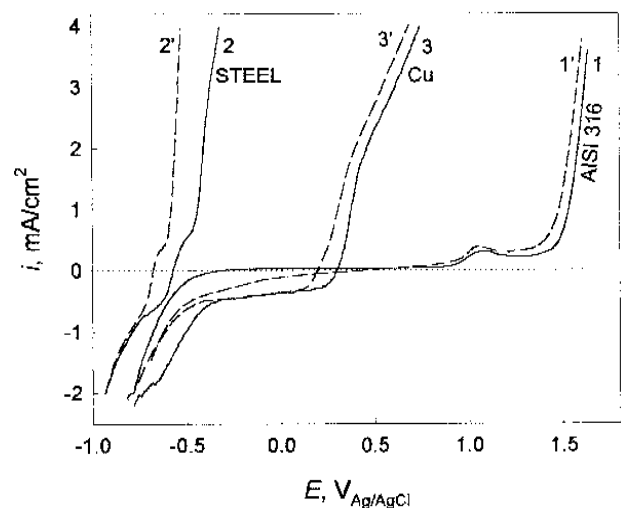


Fig. 4. Polarization curves of the studied electrodes in nonferric solution (1-3) and in 10 mg/l ferric sulphate solution (1'-3'), pH 2.7, 20 °C. AISI 316 (1, 1'), carbon steel (2, 2') and Cu (3, 3')

and carbon steel owing to the ascending character of the voltammetric curve above E_{ocp} . These data

clearly explain why even small quantities of Fe(III) lead to the nobility inversion of Cu and stainless steel.

The observed nobility inversion of Cu and stainless steel is of practical importance. So, in an iron-free environment or in that with minor Fe(III) concentrations copper will be stable in the couple with stainless steel, because copper will act as a cathode and stainless steel will be an anode. In other words, more noble Cu will be protected by less noble stainless steel. The situation is reversed to opposite in a Fe(III)-enriched environment: due to the potential inversion discussed above, Cu becomes an anode and it will actively dissolve (galvanic pair effect).

The contribution of galvanic corrosion to the overall corrosion process of the metals studied is evaluated below. In Table 1 the measured values of polarization resistance (R_p), sum polarization resistances R_a and R_c of the anode and the cathode, respectively, the calculated values of the “own” corrosion current densities (j_{corr}) and the galvanic corrosion values (i_{cg}) of Cu/AISI 316 and AISI 316/carbon steel couples are presented. The “own” corrosion rates of metals, *i.e.* those without the contribution of galvanic part, were calculated according to the approximate equation for uniform corrosion [6, 7]:

$$i_{cg} = \Delta E / (R_a + R_c) \tag{2}$$

where ΔE , V is the difference of corrosion (open circuit) potentials of uncoupled metals. It must be noted that equation (2) is strictly valid for the case of equal anode and cathode areas, the same electrolyte conductivity throughout the bulk, *etc.* The above relation can give a pretty good forecast of galvanic corrosion possibility in the locations most significant from the practical point of view *e.g.* on the boundary of two metals.

The calculated “own” corrosion rates of AISI 316 stainless steel are the lowest of all the electrodes because of high values of R_p . But when AISI 316 makes a couple with copper in ferric-free solution its corrosion rate can grow up several times due to the contact corrosion contribution. In ferric solutions, when the E_{ocp} of stainless steel is more positive than that of copper, galvanic contact leads to an increase in copper corrosion rate. Obviously in the both cases the “galvanic” contribution is maximum nearby the location contact. For the AISI 316 / carbon couple, ferric ions do not change the character of corrosion: the shift of E_{ocp} of stainless steel in the positive direction leads to a further increase in carbon steel dissolution. It should be mentioned that for the latter

couple the difference in corrosion potentials reaches $-0.8-0.95$ V and can produce $i_{cg} \sim 8.0 \cdot 10^{-6}$ A cm^{-2} . In any case, from the practical point of view, any galvanic contact of different metals is undesirable.

The calculated data on the galvanic corrosion contribution to overall corrosion process were confirmed by direct measurements: the corrosion rates of copper and carbon steel coupled with AISI 316 and copper, respectively, were determined by the weight loss method (Table 2). The

tightly connected couples of metals were exposed for 3–14 days to the solutions. The quantities of metals transmigrated into the solution bulk were determined by the AAS method. The overall weight losses were converted to corrosion rates ($g/m^2 \times 24$ h). As one can see, in water with a relatively low concentration of ferric sulphate (0.3 mg/l) copper connection with AISI 316 led to a decrease in copper corrosion rate from 0.053 to 0.042 ($g/m^2 \times 24$ h). Such an effect is induced

Table 1. Polarization resistance, sum polarization (in parentheses), corrosion potential difference (ΔE) for the AISI/Carbon steel and Cu/AISI couples, the calculated “own” corrosion currents of studied metals and galvanic ones (in parentheses) in $Fe_2(SO_4)_3$ solutions, pH 2.7.

Metal	Fe(III), mg/l	R_p ($R_{c,a}$), Ω cm^{-2}	ΔE , V	j_{corr} (i_{cg}), A cm^{-2}
AISI 316	0	$0.19 (0.14) \times 10^6$		0.27×10^{-6}
	1	$0.21(0.15) \times 10^6$		0.25×10^{-6}
	10	$0.17(0.12) \times 10^6$		0.25×10^{-6}
Carbon steel	0	230 (125)	~ -0.35	$0.10 \times 10^{-3} (2.5 \times 10^{-6})$
	1	180 (110)	~ -0.45	$0.13 \times 10^{-3} (3.0 \times 10^{-6})$
	10	220 (100)	~ -0.95	$0.11 \times 10^{-3} (8.0 \times 10^{-6})$
Cu	0	1430 (530)	~ -0.2	$12.0 \times 10^{-6} (-1.4 \times 10^{-6})$ AISI 316 dissolves
	1	1350 (500)	~ -0.15	$12.5 \times 10^{-6} (-1.0 \times 10^{-6})$ AISI 316 dissolves
	10	1450 (540)	~ -0.3	$11.7 \times 10^{-6} (2.5 \times 10^{-6})$ copper dissolves

$$j_{corr} = B / R_p \tag{1}$$

where B , V is the value which characterises the kinetics of both cathodic and anodic processes. According to [8], $B \approx 0.052$ V for stainless steel in the ferric solution, $B \approx 0.024$ V for carbon steel, and $B \approx 0.017$ V for copper. The galvanic corrosion current i_{cg} between two metals was approximately evaluated according to the equation [6, 8]:

Table 2. Corrosion rates ($\text{g/m}^2 \times 24 \text{ h}$) of copper and carbon steel in the couple with AISI 316 in $\text{Fe}_2(\text{SO}_4)_3$ solutions, $\text{pH} = 2.7$.

Metal	Concentration of Fe (III)	
	0.3 mg/l	0.3 g/l
Cu	0.053	4.13
Couple Cu/AISI 316	0.042	5.32
Carbon steel	0.82	
Couple Cu/Carbon steel	1.4	

by the so-called “galvanic protection mechanism”, *i.e.* in galvanically coupled metals a more positive one dissolves more slowly (Fig. 1 a, b). Conversely, in a highly concentrated ferric sulphate solution (0.3 g/l) the copper corrosion rate increased from 4.13 to 5.32 ($\text{g/m}^2 \times 24 \text{ h}$). For the Cu/carbon steel couple the increase in steel corrosion rate was determined in the solution with a relatively low ferric concentration.

CONCLUSIONS

Fe(III) ions as strong corrosion accelerators caused nobility inversion in the Cu-AISI 316 stainless steel system. Stainless steel in Fe(III)-containing solutions exhibited a typical passive behaviour over a wide potential range, while copper and carbon steel actively dissolved above the open circuit potentials E_{ocp} . It was demonstrated that depending on the solution pH and temperature even low Fe(III) concentrations (*ca.* 1 mg/l and lower) caused a significant positive E_{ocp} shift for AISI 316, while it was not the case for Cu and carbon steel. Such nobility inversion of Cu and stainless steel is of great practical importance when exploring Cu/stainless steel systems in the environments polluted with iron ions. From the practical point of view, any galvanic contacts of stainless steel, carbon steel and copper in water are undesirable.

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References

1. *Corrosion of stainless steel* (Ed. by A. J. Sedkris), Wiley, New York (1979).
2. Z. Szklarska-Smialowska, *Pitting Corrosion of Metals*, NACE, Houston, TX, (1986).
3. *Metals Handbook: Corrosion*, 13, 9th edition, ASM International, Cleveland, OH, (1989).
4. M. Femenia, J. Pan, C. Leygraf and P. Luukkonen, *Corr. Sci.*, **43**, 1939 (2001).
5. Y. Zuo, H. Wang, J. Zhao and J. Xiong, *Corr. Sci.*, **44**, 13 (2002).
6. G. Kaesche, *Die Korrosion der Metalle*, Berlin, Springer-Verlag, (1990).
7. *Advances in Corrosion Science and Technology* (Ed. by M. G. Fontana and R. W. Staehle), 6, New York, Plenum Publ. Comp., (1976).
8. R. Akid and D. J. Mills, *Corr. Sci.*, **43**, 1203 (2001).

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ELEKTROCHEMINĖS POROS VARIS/NERŪDIJANTIS PLIENAS GALVANINĖS KOROZIJOS DĖSNINGUMAI TERPĖJE SU FE(III) JONAIŠ

S a n t r a u k a

Sistemos Cu/AISI 316 nerūdijantis plienas korozijos potencialų inversija ir galvaninės korozijos dėsninčiai, sąlygoti Fe(III) jonų poveikio, ištirti voltamperometriniais ir svorio nuostolių metodais. Nustatyta, kad terpėje, turinčioje Fe(III) jonų, nerūdijantis plienas plačiame potencialų diapazone yra pasyvus, o Cu ir anglinis plienas aktyviai anodiškai tirpsta, kai potencialas didesnis už atviros grandinės potencialą (E_{ocp}). Parodyta, kad priklausomai nuo terpės pH ir temperatūros netgi nedidelės Fe(III) koncentracijos ($\cong 1 \text{ mg/l}$ ir mažiau) sukelia AISI 316 E_{ocp} poslinkį į teigiamą pusę, bet praktiškai neturi įtakos Cu ir anglinio plieno E_{ocp} . Tokia korozijos potencialų inversija sistemoje Cu/AISI 316 sąlygoja kontaktinių korozijos srovių atsiradimą, o tai turi didelės praktinės reikšmės, kai įranga eksploatuojama geležies jonais užterštoje aplinkoje.