Effects of Copper Addition on the Passivity and Corrosion Behavior of 27Cr-7Ni Hyper Duplex Stainless Steels in Sulfuric Acid Solution

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The effect of the Cu addition on the passivation behavior of hyper duplex stainless steels in both the active and passive states was investigated using the electrochemical tests, a scanning electron microscope-energy dispersive spectroscope, a scanning Auger multi-probe analysis and an X-ray photoelectron spectroscopy analysis in sulfuric acid solution. In the active region of $-0.2 V_{SCE}$, the Cu addition to the base alloy has a positive effect on the general corrosion resistance due to the novel Cu enriched on the surface. In the passive region of $0.6 V_{SCE}$, the Cu addition to the base alloy degraded the stability of passive film due to an increase of the formation of Cr enriched inclusion such as (Cr, Mn, Al) oxides and (Cr, Mn, Al, Fe) oxides acting as the defect in the passive film, resulting in deteriorating general corrosion resistance.

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1. Introduction

Duplex stainless steels with nearly equal fractions of ferrite (α) and austenite (γ) phases are being increasingly used for various applications such as fuel gas desulphurization facilities in fossil power plants, desalination facilities, offshore petroleum facilities, and chemical plants due to their high resistance to stress corrosion cracking and pitting corrosion, good weldability, excellent mechanical properties and relatively low cost due to the addition of low Ni, as compared with austenite stainless steels.¹⁻³⁾

Among the minor alloying elements, Cu is well known alloying element which is used to improve the general corrosion resistance of stainless steel in sulfuric acid solution.⁴⁻⁶⁾ It has been reported in previous studies that the mechanism of the beneficial effect of the Cu addition on the stainless steels is based on the suppression of the anodic dissolution by the noble metallic Cu enriched on the surface of stainless steels in the sulfuric acid solution.⁷⁻¹⁰⁾

Many researchers have been reported the positive effects of Cu addition on the passivation behavior of stainless steels. Wilde and Greene¹¹⁾ noted that Cu has a positive effect on the passivation in the acidic solution due to its low hydrogen over potential. Itzhak and Peled¹²⁾ presented that the Cu additions enhance the passivation process of the austenitic stainless steel due to a cathodic depolarization effect of hydrogen evolution and oxygen.

On the other hand, Cu showed detrimental effects on the stability of passive film on the stainless steels. Seo *et al.*¹³⁾ showed that the metallic surface layer of Cu dissolves as cupric ions in the passive potential region which results in a detrimental effect on the stability of the passive film of ferritic stainless steel. Lizlovs¹⁴⁾ found that copper reduces the passive film stability of stainless steels containing 1% Mo, but their the stability was improved by the addition of Cu when the steels contained 3% Mo. Postrach *et al.*¹⁵⁾ claimed that the films of alloys containing Cu, according to the accelerated open circuit breakdown of Cu bearing

samples, are less stable than expected, which is related to a faster removal of the oxide film. Oguzie *et al.*¹⁶⁾ reported that Cu has negative effects on the stability of the passive film of austenitic, ferritic and martensitic stainless steels in the sulfuric acid solution due to the presence of Cu in the passive film as cupric ions increased the donor (N_D) and acceptor (N_A) densities affecting the film stability. These inconsistent results on the passivity of stainless steels revealed a very complex role played by Cu.

The addition of Cu on the various stainless steels shows different behavior in the active and passive region. Therefore, it is essential to confirm the effects of Cu addition on the passivation behavior in the active and passive region separately. Moreover, few studies have been focused on the effect of Cu addition on the passivation behavior of hyper duplex stainless steels.

In this work, the effects of the Cu addition on the general corrosion resistance and passivation behavior in both the active and passive state of hyper duplex stainless steels in the sulfuric acid solution were investigated using a potentiodynamic polarization test, a potentiostatic polarization test, a scanning electron microscope-energy dispersive spectroscope (SEM-EDS), a scanning Auger multi-probe (SAM) analysis and an X-ray photoelectron spectroscopy (XPS) analysis.

2. Experimental Procedures

Ingots weighing 50 kg with dimensions 150 by 150 by 300 mm (width by length by height) were manufactured using a high frequency vacuum induction furnace. After these ingots were hot rolled in the range of 1333 to 1523 K, plates of 6 mm thickness were manufactured. The specimens were cut into dimensions of 15 by 15 by 6 mm (width by length by thickness) and solution heat-treated in air for 5 min per 1 mm thickness at 1090°C and then quenched in water. The chemical compositions of the alloys are presented in Table 1.

The effects of Cu addition on the general corrosion resistance of hyper duplex stainless steels were investigated using a potentiodynamic anodic polarization technique in sulfuric acid solution. The corrosion potential (E_{corr}), the

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Fig. 1 SEM-BSE images of the microstructure in the alloys: (a) Base alloy and (b) 1.5Cu alloy.

Table 1 Chemical composition of the experimental alloys (mass%).

Alloy	C	Cr	Ni	Mo	W	Si	Mn	Cu	N	Fe
Base	0.020	27.01	7.00	2.52	3.28	0.35	0.88	—	0.35	Bal.
1.5Cu	0.017	26.91	6.59	2.50	3.30	0.33	0.94	1.45	0.38	Bal.

passivation current density (I_p) and the corrosion current density (I_{corr}) were obtained from the potentiodynamic polarization curves. The corrosion current density (I_{corr}) was commonly obtained by the extrapolation of the cathodic and anodic curve between 50 and 100 mV away from the corrosion potential. The potentiodynamic anodic polarization test was conducted in a deaerated 2 M H_2SO_4 solution at 333 K according to the ASTM G 5.¹⁷⁾ Test specimens were joined with Cu wire through soldering (95 mass% Sn-5 mass% Sb), and then mounted with an epoxy resin. One side of the sample was ground to 600 grit using SiC abrasion paper. After defining the exposed area of the test specimen as $0.5 \times 10^{-4} m^2$, the remainder was painted with a transparent lacquer. The test was conducted at a potential range of -0.65 V to $+1.1$ V vs. SCE (saturated calomel electrode) and at a scanning rate of $1 \times 10^{-3} V s^{-1}$, using a SCE.

The potentiostatic test was measured in a deaerated 2 M H_2SO_4 solution at 333 K with an respectively applied potential of $-0.2 V_{SCE}$ in the active region and $0.6 V_{SCE}$ in the passive region of the potentiodynamic anodic polarization curves at which a meta-stable pitting can occur.^{18,19)} The current transients were recorded for a duration of 3600 s and 36000 s.

The specimens used for a surface analysis were polished with SiC paper to 2000 grit, then polished with a 1 μm diamond paste, and washed with acetone. The chemical compositions of each phase were analyzed using a SAM after the potentiostatic polarization test. The Ar sputtering rate was approximately 5 nm/min. The chemical species in the outermost surface film formed on the alloy were analyzed using an XPS after the potentiostatic test at the respectively applied with $-0.2 V_{SCE}$ in the active region and $0.6 V_{SCE}$ in the passive region in deaerated 2 M H_2SO_4 solution for 10 h. The energy source was an Al-K α (1486.6 eV) X-ray, and the acquired spectra were calibrated with a binding energy of C 1 s (284.5 eV).

Thermodynamic calculations were carried out using thermodynamic calculating software (FactSage^{TM}).²⁰⁾ The

Fig. 2 SEM-EDS analysis of inclusions in the alloy: (a) Base alloy and (b) 1.5Cu alloy.

temperature was set to 333 K. The E-pH (Pourbaix) diagrams were plotted in Cu- H_2O and Cu-S- H_2O systems. The activity of Cu ions was set to 1×10^{-6} mol/L.

3. Results and Discussion

3.1 Effects of Cu addition on the distribution and formation behavior of inclusions

Figure 1 shows the BSE images of the experimental alloys which were solution heat-treated. The dotted circles of the blackish globular particles appeared to be inclusions. No secondary phases such as sigma (σ) and chi (χ) phases were observed in the experimental alloys.

Figure 2 shows the BSE images of the inclusions in the experimental alloys. The chemical compositions of the

Fig. 3 The number, area and distribution of inclusions per frame area of the alloys: (a) the number and area of inclusions and (b) the distribution of inclusions.

inclusions were analyzed using SEM-EDS. As presented in Fig. 2 (a), the inclusions in the base alloy were composed of the main type of (Cr, Mn, Al) oxides and (Cr, Mn, Fe, Al) oxides. Figure 2 (b) shows that the inclusions in the 1.5Cu alloy were composed of the main type of (Cr, Mn, Al) oxides and (Cr, Mn, Fe, Al) oxides. The chemical composition of inclusions in the 1.5Cu alloys was similar to those in the base alloy.

Figure 3 presents the effects of Cu addition on the number, area, and distribution of inclusions per frame area of the experimental alloys. Cu addition to the base alloy increased the number of inclusions per frame area (Fig. 3 (a)). The area of inclusions per frame area in the 1.5Cu alloy was increased by about 2.6 times, compared with that of the base alloy (Fig. 3 (a)). Cu addition to the base alloy increased the number of coarse inclusions and decreased the number of fine inclusions (Fig. 3 (b)).

In the previous work, The Cu addition to the duplex stainless steels increased the amount of Cr oxides and oxysulphides that acted as pitting initiators by increasing the activity of Cr, and resulted in decreasing the pitting corrosion resistance.²¹⁾

3.2 Effects of Cu addition on potentiodynamic and potentiostatic polarization behaviors

Figure 4 shows the effect of Cu addition on the potentiodynamic polarization behavior of the experimental alloys in a deaerated 2M H_2SO_4 solution at 333 K according to ASTM G 5. Table 2 shows the effect of Cu addition on the corrosion potential (E_{corr}), the corrosion current density (I_{corr}),

Fig. 4 Potentiodynamic anodic polarization behaviors of the alloys in the deaerated 2M H_2SO_4 solution at 333 K.

Table 2 Electrochemical parameters for the experimental alloys in deaerated 2M H_2SO_4 solutions at 333 K obtained from the potentiodynamic anodic polarization curves.

Alloy	E_{corr} (mV _{SCE})	I_{corr} ($\mu\text{A}/\text{cm}^2$)	I_c ($\mu\text{A}/\text{cm}^2$)	I_p at 0.6 V _{SCE} ($\mu\text{A}/\text{cm}^2$)	Corrosion rate (mpy)
Base	-241	61.4	121.5	10.2	24.8
1.5Cu	-232	21.8	45.3	12.7	8.8

the critical current density (I_c) and the passivation current density (I_p) obtained from Fig. 4. Based upon a decrease of the I_c and I_{corr} in active region, the active corrosion resistance of the 1.5Cu alloy in a deaerated 2M H_2SO_4 solution at 60°C was higher than that of the base alloy. In particular, the active corrosion resistance in active region of the 1.5Cu alloy was much higher than that of the base alloy because I_c ($0.0453 \text{ mA}/\text{cm}^2$) of 1.5Cu alloy is much smaller than that ($0.1215 \text{ mA}/\text{cm}^2$) of the base alloy. The addition of Cu lowers the I_c and facilitates the formation of passivation. This result can be related to the tendency of Cu to reduce the overpotential of the cathodic reaction, thus promoting active-passive transition.²²⁾ An additional factor is the affinity of Cu for oxygen, which could facilitate adsorption of oxygen and enhance the passivation process.⁸⁾ Hence, it is concluded that the Cu addition has a positive effect on the active corrosion resistance of the alloys in the sulfuric acid solution. On the other hand, in the passive region, I_p ($12.7 \mu\text{A}/\text{cm}^2$) of 1.5Cu alloy is larger than that ($10.2 \mu\text{A}/\text{cm}^2$) of the base alloy. Based upon the increase of the I_p , the addition of Cu to the base alloy has a negative effect on the passivation behavior.

Figure 5 presents the effect of the Cu addition on the potentiostatic test for the experimental alloys at the applied potential of $-0.2 \text{ V}_{\text{SCE}}$ in the active region of the potentiodynamic polarization curves of Fig. 4 in the deaerated 2M H_2SO_4 at 333 K. The potentiostatic test was performed in order to observe the current transients at a primary passivation potential (E_{pp}) that corresponds to the critical current density at the potentiodynamic anodic polarization curves. The addition of Cu to the base alloy decreases the critical current density.

Fig. 5 The potentiostatic polarization tests at an applied potential of $-0.2 V_{SCE}$ (active region) of the alloys in deaerated 2 M H_2SO_4 solution at 333 K.

Fig. 6 The potentiostatic polarization tests at an applied potential of $0.6 V_{SCE}$ (passive region) of the alloys in deaerated 2 M H_2SO_4 solution at 333 K.

Fig. 7 SEM image of the inclusions in the alloys after the potentiostatic test in deaerated 2 M H_2SO_4 solution at 333 K: (a) at an applied potential of $-0.2 V_{SCE}$ and (b) at an applied potential of $0.6 V_{SCE}$.

Figure 6 presents the effect of the Cu addition on the potentiostatic test for the experimental alloys at the applied potential of $0.6 V_{SCE}$ in the passive region of the potentiodynamic polarization curves of Fig. 4 in the deaerated 2 M H_2SO_4 at 333 K. The I_p of the 1.5Cu alloy is higher than that of the base alloy. Furthermore, numerous current transients that indicate the metastable pitting and repassivation at the inclusions occurring in test period from 3000 s to 6000 s in the potentiostatic curve of the 1.5Cu alloy, compared with that of the base alloy.

Figure 7 presents the SEM image of the surface morphologies after potentiostatic tests at the applied potential of -0.2 and $0.6 V_{SCE}$ of the experimental alloys in deaerated 2 M H_2SO_4 solutions at 333 K. In the active region, the base alloy without Cu is more corroded than 1.5Cu alloy (Fig. 7 (a)). As presented in Fig. 7 (b), the 1.5Cu alloy was corroded more

than that of the base alloy. Considering the I_p and surface morphology after the potentiostatic test, the passivity of the 1.5Cu alloy was inferior to the base alloy. The deterioration of the general corrosion resistance in passive region as a result of an increase in the Cu addition seems to be associated with the increase in the area fraction of the inclusions per frame area in the alloy.^{21,23–25} That is, as the interface areas between the inclusion and the matrix in the alloy increased with an increase in the Cu addition, the preferential sites for the initiation of corrosion in the alloy were increased.

In summary, based upon a decrease of the I_{corr} and I_c , the addition of Cu to the base alloy considerably enhanced the general corrosion resistance in the active region. In the passive region, based upon the increase of the I_p , the addition of Cu to the base alloy deteriorated the corrosion resistance.

Fig. 8 The Cu of Auger depth profile in the 1.5Cu alloy after the potentiostatic polarization test at an applied potential of $-0.2 V_{SCE}$ in the deaerated 2 M H_2SO_4 solution at 333 K.

Table 3 The binding energies of some chemical species for the XPS analysis.

Species	Binding energies (eV)	Species	Binding energies (eV)
Fe(M) $2p_{3/2}$	706.7	Cu(M) $2p_{3/2}$	932.5
FeO $2p_{3/2}$	709.4	CuO $2p_{3/2}$	933.6
Fe ₂ O ₃ $2p_{3/2}$	710.9	Cu(OH) ₂ $2p_{3/2}$	934.4
Fe ₂ O ₃ $2p_{3/2}$	715.4	Cu(OH) ₂ $2p_{3/2}$	935.1
Cr(M) $2p_{3/2}$	573.8	FeSO ₄ $2p_{3/2}$	168.3
Cr ₂ O ₃ $2p_{3/2}$	576.4	CuSO ₄ $2p_{3/2}$	169.1
Cr(OH) ₃ $2p_{3/2}$	577.3	CuSO ₄ ·5H ₂ O $2p_{3/2}$	169.5
CrO ₃ $2p_{3/2}$	578.1		

Fig. 9 Deconvolution of Cu and S related chemical species by the XPS in the outer surface film formed on the 1.5Cu alloy after the potentiostatic test for 10 h in deaerated 2 M H_2SO_4 solutions at 333 K: (a) at an applied potential of $-0.2 V_{SCE}$ (active region) and (b) at an applied potential of $0.6 V_{SCE}$ (passive region).

3.3 Effects of Cu addition on the passivation behaviors

Figure 8 shows Auger depth profile of the α -phases and γ -phases in the 1.5Cu alloy after the potentiostatic polarization test at an applied potential of $-0.2 V_{SCE}$ (active region) in the deaerated 2 M H_2SO_4 solution at 333 K. As shown in the Fig. 8 the Cu which act as γ -stabilizers, are enriched in the γ -phase and are diluted in the α -phase, while the atomic concentration of the Cu in the outermost surface film of both the α -phases and γ -phases film increased significantly compared with that of the substrate. This indicates that the novel metals such as Cu can be enriched on the alloy surface due to the selective dissolution of the active metals such as Fe, Cr, and Ni in the alloy. Consequently, Cu can contribute to the general corrosion resistance. In particular, the Cu on the outermost surface film of the γ -phase was enriched by approximately 11.8 at%, which is much larger than that of the substrate and that of the α -phase was enriched by approximately 4.2 at%, which is also larger than that of the substrate.

Figure 9 shows that the deconvolution of Cu and S related chemical species by the XPS in the outer surface film formed on the 1.5Cu alloy after the potentiostatic test at the applied potential of $-0.2 V_{SCE}$ (active region) and $0.6 V_{SCE}$ (passive region) for 10 h in deaerated 2 M H_2SO_4 solutions at 333 K. In the active region of $-0.2 V_{SCE}$, the chemical species related to Cu and S in the outermost surface film were analyzed using XPS (Fig. 9 (a)). The binding energy of each chemical element used for the XPS analysis is given in Table 3. For 1.5Cu alloy, existed as Cu (M), cupric oxide (CuO) and copper hydroxide (Cu(OH)₂); S existed as copper sulfate (CuSO₄) and iron sulfate (FeSO₄) (Fig. 9 (a)). Based on the results of the XPS analysis, the contribution of the Cu addition to the enhancement of active corrosion resistance can be explained as the followings. The novel metals such as Cu can be enriched on the alloy surface due to the selective dissolution of the active metals such as Fe, Cr, and Ni in the alloy. Consequently, Cu can contribute to the corrosion

Fig. 10 E-pH diagram for the (a) Cu-H₂O system at 333 K and (b) Cu-S-H₂O system at 333 K.

Fig. 11 Deconvolution of Cr and Fe related chemical species by the XPS in the outer surface film formed on the alloys after the potentiostatic test for 10 h at an applied potential of $0.6 V_{SCE}$ in deaerated 2 M H₂SO₄ solutions at 333 K.

resistance. In addition, Cu addition to the base alloy forms the insoluble CuO in the relative oxide state and Cu(OH)₂, which greatly enhances the active corrosion resistance, compare with that of base alloy.

In the passive region of $0.6 V_{SCE}$, the chemical species related to Cu and S in the outermost surface film were analyzed using XPS (Fig. 9 (b)). As Cu added, the Cu (M) is not existed and it is dissolved from the passive film due to its oxidation from Cu to Cu²⁺ in the potentiostatic polarization test region. The binding energy of each chemical element used for the XPS analysis is given in Table 3. For 1.5Cu alloy, S existed as hydrous copper sulfate (CuSO₄·5H₂O), copper sulfate (CuSO₄) and iron sulfate (FeSO₄) (Fig. 9 (b)).

Figure 10 shows the E-pH (Pourbaix) diagram of the Cu-H₂O and Cu-S-H₂O systems at 333 K calculated by FactSage software,²⁰⁾ respectively. As presented in Fig. 10 (a), the E-pH diagram for the Cu-H₂O at 333 K and the potential values are given with respect to SHE (standard hydrogen electrode) at 333 K supporting the dissolution of Cu in the passive

region. Cu did not exist as the noble metal state because it was oxidized as Cu²⁺ in the potentiostatic polarization test region ($0.6 V_{SCE} = 0.841 V_{SHE}$). However, as presented in Fig. 10 (b), the Cu was oxidized as the CuSO₄ in the sulfuric acid solution as following reaction.

In the passive region of $0.6 V_{SCE}$, the chemical species related to Cr and Fe in the outermost surface film were analyzed using XPS. The results are presented in Fig. 11. The binding energy of each chemical element used for the XPS analysis is given in Table 3. For the experimental alloys, Fe existed as Fe (M), iron(III) oxide (Fe₂O₃) and iron(II) oxide (FeO); Cr existed as Cr (M), chromium(III) oxide (Cr₂O₃), chromium trioxide (CrO₃) and chromium hydroxide (Cr(OH)₃). Table 4 shows the elemental ratios of Cr to Fe calculated from the XPS analysis of Fig. 11 for the experimental alloys after the potentiostatic test of the experimental alloy at the applied potential of $0.6 V_{SCE}$ in

Table 4 Elemental ratios of Cr to Fe calculated from the XPS survey spectrum for the experimental alloys after the potentiostatic test for 10 h at an applied potential of $0.6 V_{SCE}$ in deaerated 2 M H_2SO_4 solutions at 333 K using peak area and atomic sensitivity factors.

Alloy	Peak area				Elemental atomic %		Atomic ratio of Cr/Fe
	Cr		Fe		Cr	Fe	
	Total area	Area /ASF (Cr; 1.5)	Total area	Area /ASF (Fe; 2)			
Base	10820	7213	10531	5266	57.8	42.2	1.37
1.5Cu	11100	7400	11905	5953	55.4	44.6	1.24

the deaerated 2 M H_2SO_4 solutions at 333 K. The addition of Cu to the base alloy decreased the elemental ratio of Cr to Fe of the passivated alloys.

It is necessary to verify the mechanism of the effects of Cu addition on the general corrosion behavior in the active and passive region separately. In the active region, based on the results of the XPS analysis after the potentiostatic test at an applied potential of $-0.2 V_{SCE}$ for 10 h of the 1.5Cu alloy in the deaerated 2 M H_2SO_4 solutions at 333 K, the contribution of the Cu addition to the enhancement of corrosion resistance can be explained as the followings. The novel metals such as Cu can be enriched on the alloy surface due to the selective dissolution of the active metals such as Fe, Cr, and Ni in the alloy. Consequently, Cu can contribute to the general corrosion resistance. For the Cu added alloy, existed as Cu (M), cupric oxide (CuO) and copper hydroxide ($Cu[OH]_2$); S existed as copper sulfate ($CuSO_4$) and iron sulfate ($FeSO_4$). The layer of oxidized products is composed mainly of Cu (M), CuO , $Cu[OH]_2$, $CuSO_4$ and $FeSO_4$ (Fig. 9 (a)). The deposition of these elements and compounds reduces the corrosion rate of Cu added alloy in deaerated 2 M H_2SO_4 solutions at 333 K.

In the passive region, based on the results of XPS surface analysis after the potentiostatic test of the experimental alloy at the applied potential of $0.6 V_{SCE}$ in the deaerated 2 M H_2SO_4 solutions at 333 K, the reasons that the corrosion resistance with the addition of Cu decreased are as follows: the Cr metal, oxides and hydro-oxide such as metallic Cr (M), Cr_2O_3 , CrO_3 , and $Cr[OH]_3$ to enhance the corrosion resistance at the passive region decreased (Fig. 11). The decrease of the Cr (M), oxide and hydro-oxide as the result of the Cu addition seems to be associated with the inclusions in the alloy. That is, the addition of Cu enhanced the driving force of the formation reaction of Cr containing oxide phases during melting and solidification processes, thereby increasing the formation of Cr enriched oxide inclusions. As the interface areas between the Cr enriched oxide inclusion and the matrix in the alloy increased with an increase in the Cu addition, the preferential sites for the initiation of corrosion in the alloy were increased. Hence, it is clarified that Cu addition to the base alloy degraded the passivity of the alloy due to increasing the formation of Cr enriched oxide inclusions acting as the defect in the passive film, resulting in deteriorating the corrosion resistance.

4. Conclusions

- (1) In the active region of $-0.2 V_{SCE}$, the Cu addition to the base alloy has a positive effect on the general corrosion resistance of the alloys in the sulfuric acid solution. Based on the results of the XPS analysis, the novel metallic Cu enriched on the alloy surface enhances the active corrosion resistance. In addition, the deposition of CuO , $Cu(OH)_2$, $CuSO_4$ and $FeSO_4$ reduces the general corrosion rate of the Cu added alloy in the deaerated 2 M H_2SO_4 solutions at 333 K.
- (2) In the passive region of $0.6 V_{SCE}$, the addition of Cu to the base alloy has a negative effect on the passivation behavior. The Cu addition to the alloy degraded the passivity due to the increase of the formation of the Cr enriched oxide inclusions acting as the defect in the passive film, resulting in the deterioration of the corrosion resistance.

REFERENCES

- 1) J. Olson and S. Nordin: Duplex Stainless Steel. Proc., The Hague, (1986) p. 219.
- 2) E. Perteneder, J. Tosch, P. Reiterer and G. Rabensteiner: Duplex Stainless Steel. Symp. Proc., The Hague, (1986) p. 48.
- 3) J.-O. Nilsson: *Mater. Sci. Technol.* **8** (1992) 685.
- 4) M. Seo, G. Hultquist, C. Leygraf and N. Sato: *Corros. Sci.* **26** (1986) 949.
- 5) Y. Jiangnan, W. Lichang and S. Wenhao: *Corros. Sci.* **33** (1992) 851.
- 6) G. Hultquist, M. Seo, T. Leitner, C. Leygraf and N. Sato: *Corros. Sci.* **27** (1987) 937.
- 7) T. Ujiro, S. Satoh, R. W. Staehle and W. H. Smyrl: *Corros. Sci.* **43** (2001) 2185.
- 8) H. T. Lin, W. T. Tsai, J. T. Lee and C. S. Huang: *Corros. Sci.* **33** (1992) 691.
- 9) J. Banas and A. Mazurkiewicz: *Mater. Sci. Eng. A* **277** (2000) 183.
- 10) A. Pardo, M. C. Merino, M. Carboneras, F. Viejo, R. Arrabal and J. Munoz: *Corros. Sci.* **48** (2006) 1075.
- 11) B. E. Wilde and N. D. Greene, Jr.: *Corrosion* **25** (1969) 300.
- 12) D. Itzhak and P. Peled: *Corros. Sci.* **26** (1986) 49.
- 13) M. Seo, G. Hultquist, C. Leygraf and N. Sato: *Corros. Sci.* **26** (1986) 949.
- 14) E. A. Lizovs: *Corrosion* **22** (1966) 279.
- 15) B. Postrach, I. Garz and H. H. Strehblow: *Mater. Corros.* **45** (1994) 508.
- 16) E. E. Oguzie, J. Li, Y. Liu, D. Chen, Y. Li, K. Yang and F. Wang: *Electrochim. Acta* **55** (2010) 5028.
- 17) ANNUAL BOOK of ASTM STANDARDS, ASTM G 5.
- 18) G. T. Burstein, P. C. Pistorius and S. P. Mattin: *Corros. Sci.* **35** (1993) 57.
- 19) P. C. Pistorius and G. T. Burstein: *Corros. Sci.* **33** (1992) 1885.
- 20) C. W. Bale, E. Bélisle, P. Chartrand, S. A. Decterov, G. Eriksson, K. Hack, I. H. Jung, Y. B. Kang, J. Melançon, A. D. Pelton, C. Robelin and S. Petersen: *Calphad* **33** (2009) 295.
- 21) S. H. Jeon, S. T. Kim, I. S. Lee, J. H. Park, K. T. Kim, J. S. Kim and Y. S. Park: *Corros. Sci.* **53** (2011) 1408.
- 22) J. Banas and A. Mazurkiewicz: *Mater. Sci. Eng. A* **277** (2000) 183.
- 23) J. Stewart and D. E. Williams: *Corros. Sci.* **33** (1992) 457.
- 24) S. T. Kim, S. H. Jeon, I. S. Lee and Y. S. Park: *Corros. Sci.* **52** (2010) 1897.
- 25) S. H. Jeon, S. T. Kim, I. S. Lee and Y. S. Park: *Corros. Sci.* **52** (2010) 3537.