

SURFACE CHARACTERIZATION AND PICKLING CHARACTERISTICS OF THE OXIDE SCALE ON DUPLEX STAINLESS STEEL

POVRŠINSKA KARAKTERIZACIJA IN LASTNOSTI LUŽENJA OKSIDNE PLASTI NA DUPEKSNEM NERJAVNEM JEKLU

Črtomir Donik

Institute of metals and technology, Lepi pot 11, SI-1000 Ljubljana, Slovenia
crtomir.donik@imt.si

Prejem rokopisa – received: 2011-05-03; sprejem za objavo – accepted for publication: 2011-07-05

Mixtures of hydrofluoric ($\text{HF}_{(\text{aq})}$) and nitric acids (HNO_3) used for the pickling of stainless steels to remove thick oxide scale generate waste liquids with a high HF concentration. The oxide formation during production annealing and the subsequent pickling response in mixed acids have been studied. A cost reduction and a procedure optimization can be achieved by the use of the proper concentration of mixed acids and a low pickling temperature. In this work, new mixtures of both with a high pickling efficiency for solutions designed for duplex stainless steel are checked. The experiments were carried with mixtures consisting of mass fractions 0.5–4.0 % $\text{HF}_{(\text{aq})}$ and 12.5–22.0 % HNO_3 at room and elevated temperatures. The goal of the presented work was to determine the optimal pickling time with respect to the temperature and the acid mixture concentration.

Keywords: duplex stainless steel, pickling, oxide scale, HF, HNO_3

Mešanice fluorovodikove in dušikove(V) kisline z visoko koncentracijo fluorovodikove kisline se uporablja za luženje nerjavnega jekla, ko po žarjenju ostanejo na površini visokotemperaturni oksidi. Raziskovali smo tvorjenje visokotemperaturnih oksidov pri žarjenju in posledično vpliv kislinskih mešanic pri odstranjevanju le-teh. Z optimizacijo postopkov uporabe kislinskih mešanic in procesov, povezanih s tem, ter uporabo najprimernejše mešanice pri najnižji temperaturi lahko zelo zmanjšamo stroške, povezane s končno pripravo nerjavnih jekel. V predstavljenem delu smo preiskovali, kako in katere kislinske mešanice fluorovodikove ($\text{HF}_{(\text{aq})}$) in dušikove(V) kisline (HNO_3) so najugodnejše za luženje dupleksnih nerjavnih jekel. Preiskave smo naredili pri mešanicah 0.5–4.0 % $\text{HF}_{(\text{aq})}$ in 12.5–22.0 % HNO_3 pri sobni in povišanih temperaturah. Cilj predstavljenega dela je bila povezava med sestavo oksidne plasti na površini DSS 2205 in hitrostjo odstranjevanja le-te v povezavi s temperaturo in sestavo kislinske mešanice za optimalno dekapirno raztopino.

Ključne besede: dupleksno nerjavno jeklo, luženje, oksidna plast, HF, HNO_3

1 INTRODUCTION

Stainless steels are widely used materials and they have many different applications.^{1–9} Duplex stainless steels with a ferrite/austenite volume ratio of about 1:1 have been recognized as good corrosion-resistant materials in various aqueous environments. For this reason, these steels are often exposed to different and relatively aggressive media. Different oxides can be formed on the steel surface and these, often complex, oxides may affect the processing and change the mechanical, chemical and physical properties of the material^{10–14}. The alloy selected for this study consisted of the following mass fractions: 22 % chromium, 5–6 % nickel, 3 % molybdenum, 2 % manganese and nitrogen-alloyed duplex stainless steel (DSS 2205). The oxidation and corrosion resistance of the stainless steel have already been the subject of several studies^{9,13,15–18}. The corrosion resistance of stainless steel is known to be due to a passivation layer of chromium oxide (Cr_2O_3) on the surface, which acts as a protective layer against corrosion and has low volume diffusion constants for oxygen and metal ions. It was found that the stabilizing effect of molybdenum on the surface of the passive film

enhances the formation of a layer on duplex stainless steel with a higher Cr/Fe ratio.^{19–21} A well-prepared surface of stainless steel shows its superiority over other steels in terms of the possibility of self-preservation with a protective oxide layer with an excellent ability of re-oxidation after damage^{22–24}.

On the other hand, it was found that the high-temperature oxide layer, which forms during heat treatment or welding, has inferior protective properties due to the rapid growth, and the chromium content in such a layer is lower than in the scale formed during high-temperature soaking.¹ The high-temperature oxide layer lowers the surface quality and increases the non-uniformity of the surface to the corrosion process. Thus, a high quality of pickling is required. Pickling is the procedure of removing the oxide scale formed over steel surface, mostly during soaking and the hot rolling and forming processes that take place in pickling baths. The bath is exhausted when the metal concentration rises up to 5 wt% of the total liquid; however, this value depends on the acid mixture and the steel composition. The pickling rate efficiency decreases progressively and the pickling bath must be substituted with a fresh acid mixture. Thus, fresh acids are added to make up for the HF and HNO_3

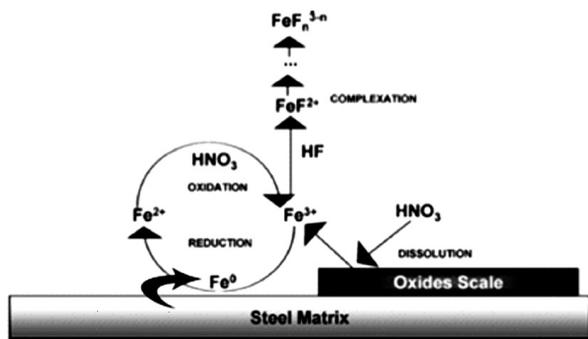


Figure 1: Chemical pickling mechanism proposed by Galvez et al.³³
Slika 1: Mehanizem kemijskega luženja, ki ga predlagal Galvez s sodelavci.³³

consumed in the pickling process. For this reason, it is important to measure frequently and preserve the optimized individual acidic concentrations of the pickling liquid. For a quantitative analysis of the HF and HNO₃ concentrations in the pickling liquid, the method developed by Galvez et al.²⁵ is used. This treatment is more efficient than other scale-removing processes, but it generates a great volume of dangerous and toxic wastes: air pollutants (hydrogen fluoride and NO_x), solid wastes (metal fluorides with descaled chromium oxides) and exhausted pickling liquor are generated^{16,25–32}. Nitric(V) acid oxidizes and dissolves the Fe(II)–oxides scale, while hydrofluoric acid is used because of its great reactivity and the stabilizing capacity of metals in solution with complexes formation in the process.

The pickling process is carried out by submerging steel plates in an aqueous solution of hydrofluoric and nitric acids, pickling baths. The scale-dissolution mechanism depends on the oxidation reactions with nitric acid and it is catalyzed by Fe³⁺, as shown in the simplified reaction scheme (**Figure 1**).³³

The aim of the present work was to investigate the thick high-temperature oxides on the steel DSS 2205 in order to determine the acid mixture for descaling. For the analysis of the scale, energy-dispersive x-ray spectroscopy (EDS) was used.

2 MATERIALS AND METHODS

The DSS 2205 with the composition shown in **Table 1** was obtained from the steel plant Acroni. The chemical analyses were performed using an ICP-AES Perkin Elmer 3300. Before annealing, the stainless-steel slab was soaked at 1200 °C for 3 h, hot-rolled to plates of thickness of 28 mm, and annealed at 1100 °C for 2 min to obtain the certified microstructure. The specimens

were used as received from the steel plant, where these were cut out from plates and already sandblasted. The test specimens were cut into squares of 25 × 25 mm, sunk in pickling solutions with different concentrations of HF and HNO₃ for different times at room and elevated temperatures up to 60 °C. All the as-prepared samples were analyzed by FE-SEM JEOL JSM 6500 F SEM/EDS/WDS. The SEM was operated at primary beam energies of 15 and 5 keV in the EDS mode, corresponding to probing depths of approximately 0.8–1.5 μm and 0.25–0.5 μm in layers with predominantly the Fe/Cr/Ni/Mn-oxide composition. In samples of layer thickness well below 1 μm, the average layer density decreased considerably, due to the oxide nature of the layer. A lower primary beam energy was used because it produced better compositional information from the layer only. All the chemicals used were p.a. quality from Merck, Darmstadt, Germany.

3 RESULTS

Secondary-electron image of the cross-section of the oxide scale on the DSS 2205 is shown in **Figure 2**. The scale is not homogeneous and has many cracks that offer the possibility of penetration of the pickling solution to the interface scale/metal to accelerate the pickling process. The figure also shows the rugosity of the interface oxide layer/metal in the range of 10 μm to 20 μm. The scale has on the same areas a clear two-phase microstructure, as shown in the backscattered-electron image in **Figure 3**. A careful observation shows that the white phase is equal to the base metal and this suggests

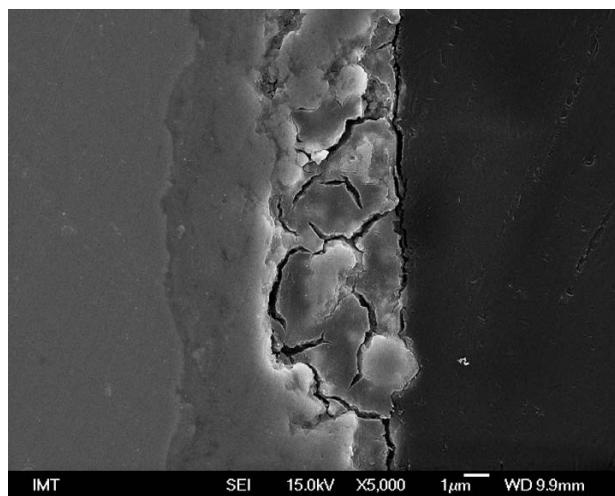


Figure 2: SEM image of cross-section of the oxide scale on DSS 2205
Slika 2: SEM slika prečnega preza oksidne plasti na DSS 2205

Table 1: Chemical composition of the duplex stainless steel in mass fractions w/%
Tabela 1: Kemijska sestava preiskovanega dupleksnega jekla v masnih deležih w/%

w/%	Cr	Ni	Mn	Si	P	S	C	Mo	N	Fe
	22.52	5.14	1.47	0.43	0.032	0.001	0.029	3.17	0.17	balance

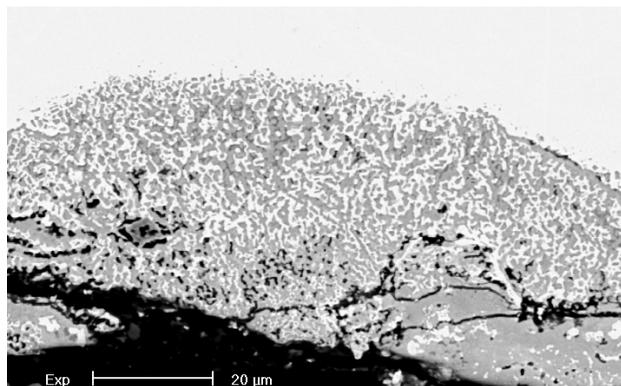


Figure 3: BE image of cross-section of oxide scale on DSS 2205
Slika 3: BE slika prečnega prereza oksidne plasti na DSS 2205

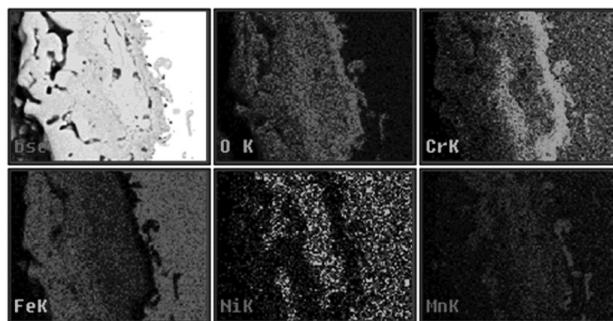


Figure 4: BE image with additional EDS mapping (O, Cr, Fe, Ni and Mn) of the scale on the DSS 2205

Slika 4: BE slika z EDS površinsko porazdelitvijo elementov (O, Cr, Fe, Ni in Mn) na prečnem prerezu oksidne plasti na DSS 2205

that the gray phase is oxidized metal, very probably it is mostly chromium oxide. In areas with less or without white inserts the content of iron is probably higher. This conclusion is made by the high Gibbs energy of formation for the Cr_2O_3 , while it is much lower for oxides like FeO , Fe_2O_3 and Fe_3O_4 and still lower than for NiO , which are presented on Ellingham-Richardson diagram.¹ **Figure 4** shows the EDS mapping, which shows the distribution of elements on the cross-section of the scale. The distribution of oxygen is shown on the second-top image. As expected, oxygen is found only in the oxide layer. The third-top image shows the chromium distribution with an increased chromium concentration in the thin layer in the contact with the metal matrix. In this layer, chromium is enriched; iron and nickel are depleted at the metal of the interface

In the top layer of the oxide scale the chromium content is, as shown later, very similar to the content of chromium in the steel. The lower content of chromium may increase the scale solubility in the pickling solution. It also indicates that the difference in the Gibbs free energy of formation for chromium and iron oxides is efficient and stronger in internal parts of the scale, where the effect of the diffusion of the oxygen is lower. This explanation is confirmed by the image Fe K, which shows the distribution of iron in the scale with a higher content of iron on the upper part and a gradual decrease of iron towards the steel surface and the increase of chromium content in the opposite direction. This demonstrates the competition of these two elements in forming the oxides inside the oxide layers, which is due to the difference in the Gibbs free energies¹. The last two images of nickel and manganese show the distribution of these elements and no particular pattern is shown. An increase in the manganese content is found in the intermediate layer between the metal and the oxide, probably due to its diffusion characteristics.

Figures 5 and **6** show the pretreated surface with sandblasting just before the stainless-steel sheets were placed in the pickling baths. Sandblasting in the Acroni steel plant is used to reduce the time and consumption of

acid pickling solutions. **Figure 5** shows the aim of sandblasting of the surface – the formation of the cracks that are marked in **Figure 5**, the complex oxide scale on stainless steels consisting of Fe_2O_3 , Fe_3O_4 , FeCr_2O_4 , Cr_2O_3 , CrO_3 , FeCrO_3 and MnO_2 , as confirmed in our previous work^{34–37} and allowing a faster reaction of the acid mixture with the oxides in the scale and more importantly, the acid mixture penetrates between the scale and the steel surface, making possible a rapid dissolution of a thin layer of steel that separates the un-dissolved scale from the metal. **Figure 5** also confirms, as reported by Riquier^{17,38}, that if the DSS 2205 is normally cooled down, the top layer of duplex stainless steel consists of more austenite grains than the matrix material where the ratio of austenite to ferrite is 1:1. Its presence shows that the share of oxidation of the chromium is greater than that of iron, as expected from the difference of the Gibbs free energy for the formation of the oxides of both metals. This layer has to be removed with the pickling process to gain the certified properties of DSS 2205.

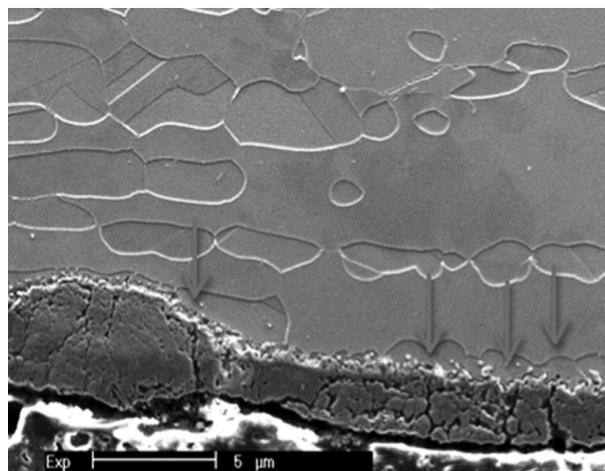


Figure 5: SEM image of cross-section of oxide scale on DSS 2205 after sandblasting

Slika 5: SEM slika prečnega prereza oksidne plasti na DSS 2205 po peskanju

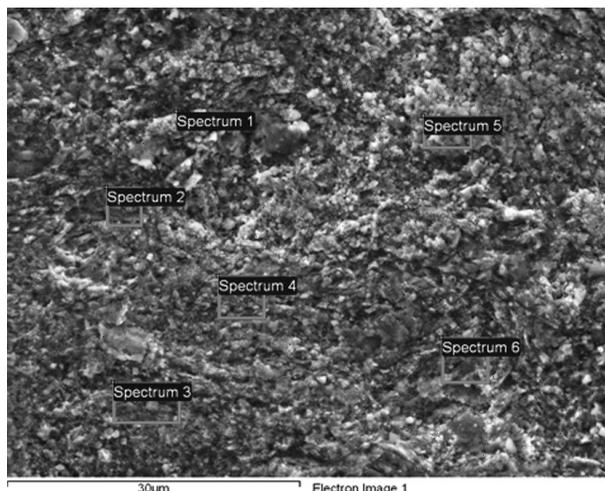


Figure 6: SE image of the sandblasted surface of as-received sample
Slika 6: SE slika peskane površine prejetega vzorca

Figure 6 shows a sandblasted surface of DSS 2205 just before the stainless-steel sheets were placed in the pickling baths to decrease the pickling time and the consumption of the pickling solutions. The surface is rough and from the analyzed areas in **Table 2** it is concluded that the top layers were not completely removed since the content of iron is high. From the results in **Table 2** it can be concluded that after sandblasting the remaining scale contains oxygen iron, chromium and nickel in different contents. From the data in **Table 3** it is concluded that with sandblasting approximately the upper half of the scale layer in Figure 5 is removed. From the data in **Table 2** we can also conclude that the increase in manganese up to more than twice is an artifact that was also observed in our previous works.^{35,36}

Table 2: Content of elements on the sandblasted sample, as received from the steel plant in mass fractions w/%. The areas of the EDS analyses are marked in **Figure 6**.

Tabela 2: Vsebnost elementov na površini peskanih vzorcev iz jeklarne po peskanju v masnih deležih w/%. Analizirana področja so označena na **sliki 6**.

Spectrum	O	Si	Ca	Cr	Mn	Fe	Ni	Mo
Spectrum 1	25.19	0.61	0.94	27.13	2.33	37.45	6.35	
Spectrum 2	25.80	0.76		41.57		28.27	2.11	1.49
Spectrum 3	25.59	0.46	0.42	24.61	1.82	43.45	3.65	
Spectrum 4	19.51	0.57	0.52	46.68	1.27	28.34	2.09	1.02
Spectrum 5	28.60	0.50	0.56	38.68	1.94	26.41	3.31	
Spectrum 6	15.72	0.61	0.57	47.21	1.55	31.76	2.58	

Data in **Table 3** show that the removal rate of the high-temperature scale from the DSS 2205 depends on the pickling solution's composition and temperature. From the data in Table 3 it is concluded that even a slight increase in the pickling temperature shows a large increase in the pickling effect. This is even stronger when the solution is already used and/or the concentration of the acting media is reduced. From **Table 3** it can also be concluded that the acting agent in

Table 3: Effect of the temperature and composition of the pickling solution on the removal rate of the scale of DSS 2205

Tabela 3: Hitrost odstranjevanja oksidne plasti z jekla DSS 2205 pri različnih temperaturah in sestavah kislinskih mešanic

HF / g/L	HNO ₃ / g/L	25 °C /h	40 °C /h	60 °C /h
40	220	2	0.75	0.5
40	200	2	0.75	0.5
40	175	2	0.75	0.5
40	150	2	0.75	0.5
40	125	2	0.75	0.5
30	220	3	1.25	0.75
30	200	3	1.25	0.75
30	175	3	1.25	0.75
30	150	3	1.25	0.75
30	125	3	1.25	0.75
20	220	5.5	2	1
20	200	5.5	2	1
20	175	5.5	2	1
20	150	5.5	2	1
20	125	5.5	2	1
10	220	15	3.5	1.25
10	200	15	3.5	1.25
10	175	15	3.5	1.25
10	150	15	3.5	1.25
10	125	15	3.5	1.25
5	220	32	5	2.5
5	200	32	5	2.5
5	175	32	5	2.5
5	150	32	5	2.5
5	125	32	5	2.5
2	220	>100	8	3.5
2	200	>100	8	3.5
2	175	>100	8	3.5
2	150	>100	8	3.5
2	125	>100	8	3.5

the pickling of stainless steel is HF, while HNO₃ is important in the processes after the oxide scale removal with the role of passivation of the DSS 2205 surface.

4 CONCLUSIONS

The role of hydrofluoric acid in the pickling of scale from the surface of duplex stainless steel is essential, as it bonds excess Fe³⁺, so forming fluoride complexes.

A continuous layer of scale formed by the soaking and rolling of slabs of duplex stainless steel is present at the surface. The scale consists of an outer layer of mainly iron chromium oxide that is easily spalled, and an inner layer of oxide with a higher content of chromium.

It was found that sandblasting removes the upper scale layer and forms cracks that increase the surface for acid mixture action and makes possible the penetration of the acid mixture into the interface metal oxide that accelerates the separation of the layer of scale from the steel surface. The results obtained in the present investigation confirm the importance of sandblasting and the

proper selection of the pickling solution composition and temperature for steel plants using pickling for high-temperature oxide scale removal.

Acknowledgements

This work has been supported by the company Acroni Jesenice with the data and the material used for the presented work. The authors also acknowledge Mrs A. Kosmač, Mr J. Triplat and Mrs E. Bricelj for providing the DSS 2205 specimens and data on the pickling solutions. The views expressed in this publication reflect only the views of the authors and Acroni Jesenice is not liable for any use that may be made of the information contained therein.

5 REFERENCES

- ¹ J. R. Davis, ASM specialty handbook: Stainless Steels, ASM, 1996
- ² P. Sevc, D. Mandrino, J. Blach, M. Jenko, J. Janovec, *Kovove Materialy-Metallic Materials*, 40 (2002), 35–44
- ³ M. Godec, A. Kocijan, D. Dolinar, D. Mandrino, M. Jenko, V. Antolic, *Biomedical Materials*, 5 (2010), Sp. iss., doi: 10.1088/1748-6041/5/4/045012
- ⁴ D. Mandrino, M. Lamut, M. Godec, M. Torkar, M. Jenko, *Surface and Interface Analysis* 39 (2007), 438–444
- ⁵ D. Mandrino, M. Godec, A. Kocijan, M. Lamut, M. Torkar, M. Jenko, *Metalurgija*, 47 (2008), 119–123
- ⁶ M. Torkar, D. Mandrino, M. Lamut, *Materiali in Tehnologije*, 42 (2008), 39–43
- ⁷ A. Kocijan, I. Milosev, B. Pihlar, *Journal of Materials Science-Materials in Medicine*, 14 (2003), 69–77
- ⁸ A. Kocijan, M. Conradi, *Materiali in Tehnologije*, 44 (2010), 21–24
- ⁹ A. Kocijan, D. K. Merl, M. Jenko, *Corrosion Science*, 53 (2011), 776–783
- ¹⁰ G. D. S. A. Cigada, A. M. Gatti, A. Roos, D. Zaffe, *Journal of Applied Biomaterials*, 4 (1993), 39–46
- ¹¹ M. Gojic, D. Marijan, L. Kosec, *Corrosion*, 56 (2000), 839–848
- ¹² A. Kocijan, I. Milosev, D. K. Merl, B. Pihlar, *Journal of Applied Electrochemistry*, 34 (2004), 517–524
- ¹³ A. Kocijan, I. Milosev, B. Pihlar, *Journal of Materials Science-Materials in Medicine*, 15 (2004), 643–650
- ¹⁴ L. Milosev, V. Antolic, A. Minovic, A. Cor, S. Herman, V. Pavlovic, P. Campbell, *Journal of Bone and Joint Surgery-British Volume*, 82B (2000), 352–357
- ¹⁵ P. Jian, L. Jian, H. Bing, G. Y. Xie, *Journal of Power Sources*, 158 (2006), 354–360
- ¹⁶ L. F. Li, J. P. Celis, *Canadian Metallurgical Quarterly*, 42 (2003), 365–376
- ¹⁷ L. F. Li, Z. H. Jiang, Y. Riquier, *Corrosion Science*, 47 (2005), 57–68
- ¹⁸ D. Mandrino, M. Jenko, *Vacuum*, 61 (2001), 157–161
- ¹⁹ C. M. Abreu, M. J. Cristóbal, R. Losada, X. R. Nóvoa, G. Pena, M. C. Pérez, *Electrochimica Acta*, 49 (2004), 3049–3056
- ²⁰ C. M. Abreu, M. J. Cristóbal, X. R. Nóvoa, G. Pena, M. C. Pérez, *Surface and Interface Analysis*, 40 (2008), 294–298
- ²¹ M. Jenko, D. Mandrino, M. Milun, *Metalurgija*, 41 (2002), 191–197
- ²² M. Jenko, D. Mandrino, M. Godec, J. T. Grant, V. Leskovsek, *Materiali in Tehnologije*, 42 (2008), 251–255
- ²³ M. Ristic, S. Music, M. Godec, *Journal of Alloys and Compounds*, 417 (2006), 292–299
- ²⁴ A. Minovic, I. Milosev, V. Pisot, A. Cor, V. Antolic, *Journal of Bone and Joint Surgery-British Volume*, 83B (2001), 1182–1190
- ²⁵ J. L. Galvez, J. Dufour, C. Negro, F. Lopez-Mateos, *Isij International*, 46 (2006), 281–286
- ²⁶ B. S. Covino, T. J. Driscoll, J. P. Carter, P. M. Fabis, *Journal of Metals*, 37 (1985), A50–A50
- ²⁷ L. A. Fernando, D. R. Zaremski, *Metallurgical Transactions a-Physical Metallurgy and Materials Science*, 19 (1988), 1083–1100
- ²⁸ G. Hubmer, K. Rendl, A. Osterkorn, R. Puntigam, R. Sestak, W. R. Thiele, *Stahl Und Eisen*, 122 (2002), 59–65
- ²⁹ N. Ipek, B. Holm, R. Pettersson, G. Runnsjo, M. Karlsson, *Materials and Corrosion-Werkstoffe Und Korrosion*, 56 (2005), 521–532
- ³⁰ W. F. Kladnig, *International Journal of Materials & Product Technology*, 19 (2003), 550–561
- ³¹ L. F. Li, C. Peter, J. P. Celis, *Corrosion Science*, 50 (2008), 804–810
- ³² L. Narvaez, E. Cano, D. M. Bastidas, P. P. Gomez, *Revista de Metalurgija* (2005), 417–422
- ³³ J. L. Galvez, J. Dufour, C. Negro, F. Lopez-Mateos, *Journal of Hazardous Materials*, 154 (2008), 135–145
- ³⁴ Č. Donik, A. Kocijan, J. T. Grant, M. Jenko, A. Drenik, B. Pihlar, *Corrosion Science*, 51 (2009), 827–832
- ³⁵ Č. Donik, A. Kocijan, D. Mandrino, I. Paulin, M. Jenko, B. Pihlar, *Applied Surface Science*, 255 (2009), 7056–7061
- ³⁶ Č. Donik, A. Kocijan, I. Paulin, M. Jenko, *Materiali in Tehnologije*, 43 (2009), 137–142
- ³⁷ Č. Donik, D. Mandrino, M. Jenko, *Vacuum*, 84 (2010), 1266–1269
- ³⁸ Y. Riquier, H. Zhang, *Revue De Metallurgie-Cahiers D Informations Techniques*, 101 (2004), 855–865