IATS'21 9th International Advanced Technologies Symposium 27-28 OCT 2021

Investigation of Descailing Conditions and Oxide Characteristics on the Dissolving of High Temperature Oxides Created at Different Temperatures and Times on AISI 430 Stainless Steel Surface

O. Ay[1],[2], H. Ekici[2], B.Güraydin[2], İ. E. Karabulut[2], B. Tatar[1],*

[1] Tekirdağ Namık Kemal University, Süleymanpaşa/Tekirdağ/Turkiye
[2]Trinox Metal San. Ve Tic. A.Ş., Ergene/Tekirdag/Turkey

Abstract

Stainless steels are widely used in industry with their corrosion resistance and high formability. Since ferritic stainless steels do not contain nickel, they rise to a more advantageous position in terms of price compared to austenitic stainless steels. Stainless steel sheets are cast as slabs for hot rolling after the chemical composition and necessary refining processes are completed. Stainless steels, which become flat plates with hot rolling, are subjected to cold rolling processes after heat treatment and surface treatment and are reduced to the thickness desired by the user. After cold rolling, annealing is applied to relieve the stress in the structure. During annealing, the high temperature oxides formed on the surface of the material must be removed from the surface. For this, descaling and pickling operations are applied with acits. In this study, the effects of oxides, descaling acids and their combinations on the material surface under different annealing conditions were investigated. At the same time, the morphology of the surface oxides, the oxide structure and the presence of spinel oxides are effective on the ability of acids to dissolve oxides. Considering the reaction kinetics in the study, the decrease in the density of the complex oxysts formed in the oxide structure accelerated the dissolution kinetics. For this reason, it was observed that a better dissolution was obtained on the samples annealed at 750 degrees and 850 degrees for 65 seconds, especially in the sulfuric acid solution compared to the nitric acid solution.

Keywords: Stainless Steel, AISI 430, Cold Rolling, Annealing, High Temperature Oxidation, Opticprofilometer, Sufnace Morphology

1. INTRODUCTION

Steels with chromium content and non-corrosive properties are called stainless steel. Stainless steels show different properties according to the ratio of alloying elements that stabilize the ferrite phase and stabilize the austenite phase they contain. For example, alloying elements such as nickel and manganese that stabilize the austenite region form the austenitic stainless-steel family and improve the formability and corrosion resistance of the steel. Ferrite-forming alloying elements such as chromium and silicon allow the formation of ferrite phases in the structure and the formation of ferrite phases in steels in the austenitic group, forming the structure of double phase duplex stainless steels. AISI 430 stainless steel, which is in the ferritic stainless-steel family, contains more than 16% chromium by mass, giving the steel a stainless feature. Since they do not contain nickel, they are very advantageous in terms of price compared to austenitic stainless steels such as AISI 304. AISI 430 stainless steels are highly preferred for decorative purposes due to their glossy surface. Thanks to their weldability, they are frequently used in the manufacture of welded pipes and automobile exhausts [1,2].

Production of stainless-steel plate starts with slab casting. After the liquid metal brought to the desired chemical composition is poured as slab, it is subjected to hot rolling process. After the heat treatment and surface treatment of the stainless steel, which is reduced to relatively rough thicknesses by hot rolling, it becomes ready

[1] **Corresponding author. Tel: +90 534 334 78 07*
E-mail adress: onurayiu@gmail.com

for cold rolling to be reduced to thinner thicknesses. With cold rolling, thicknesses of 1 mm and below are achieved with precise thickness tolerances. At the same time, cold rolled products can show a more durable structure than hot rolled products. Cold rolled products show strain hardening with deformation. To remove the stresses in the internal structure and especially in ferritic stainless steels, the grains elongated in the rolling direction are brought back to the coaxial structure by heat treatment. Heat treatment causes the formation of high temperature oxides on the material relative to the application atmosphere. Especially in the rich oxygen atmosphere in natural gas furnaces, oxidation is quite high. High temperature oxides not only affect the corrosion resistance of the material negatively, but also cause the strength values of the material to be adversely affected. At the same time, it also spoils the surface quality of such materials, which have visual expectations [3].

AISI 430 stainless steels contain around 16% chromium, less than 1% silicon and less than 1% manganese as an alloying element. As a result of heat treatment, besides alloying elements such as chromium, silicon and manhan, iron forming the main matrix is oxidized in different oxide compositions and forms oxide structures in different layers. When we look at the general structure, it is seen that the wustite layer shows stratification on the base metal first, magnetite and hemantite layers above it, and finally the chromium oxide layer is dominant on the uppermost layer. Depending on the increasing temperature and time, the oxide layer thicknesses also increase [4].

It has been observed that spinel oxides are formed on the base metal, that is, at the interface with the oxide layers, depending on the alloying elements during the heat treatment of AISI 430 stainless steels. At the same time, spinel oxides containing manganese and chromium are also observed in the upper layers. Spinel oxides are complex oxides. They may contain alloying elements such as silicon, manganese, chromium and iron in their structures. In particular, increases in silicon and manganese increase the density of spinel oxides. With their complex structure, spinel oxides are difficult to dissolve in acids. Therefore, the increase in temperature and time under heat treatment conditions increases the density of spinel oxides in the structure and becomes very difficult to dissolve with acids. At the same time, complex oxides that settle at the interface adversely affect the porosity structure of the oxide growing on the surface, as it makes it difficult for the alloying elements such as chromium and iron to participate in oxidation from the base metal. [4,5,6,7,8].

Large-scale pickling studies are carried out to see the effects on different oxide forms and different acid combinations of these oxides, and to design more environmentally friendly and more efficient processes. In this study, the descailing abilities of different acid combinations at two different temperatures and four different times were investigated.

2. EXPERIMENTAL METHOD

Trinox Metal process was taken as reference in the experimental studies. The samples used in the study were rolled samples from 3 mm thickness to 0.8 mm thickness in Sendzimir rolling mill. This thickness difference has a deformation rate of 73.33%. AISI 430 alloy stainless steel used in the study was selected from a single coil and rolled under the same conditions throughout the coil. In Trinox Metal process conditions, the materials that are put into suitable condition in the open flame annealing furnace after cold rolling are then entered into descailing and pickling tanks to obtain the final surface quality. The schematic image describing the process is shown in Fig. 1 The time spent in the furnace and in the acid tanks for the appropriate condition conditions has been moved to the test conditions. Samples cut in 15x15 cm dimensions at the times determined for the lower and upper limit hardness values with reference to the line speeds, after the samples were annealed in a laboratory type electric furnace, after cooling in air. The effects of acid types were investigated by desclinging two groups of experimental sets in 12% H_2SO_4 + 12% HCl +1.5% H_2O_2 solution and two groups of experimental sets in 15% HNO_3 solution from the samples cooled in air. After annealing, the samples were immersed in the solution in the prepared acid baths for the periods calculated depending on the line speed, and after immersion, they were washed with water and brushed. The reaction kinetics were calculated based on the mass loss measurements of these two different acidic solutions. Rolled samples used in the experiment were not cleaned of rolling oil in order to fully reflect the process conditions. The rolled samples were stored under vacuum to prevent oxidation after annealing. The pickling processes of the annealed samples under vacuum were also carried out within one week at the latest. Two different types of descaling operations with different concentrations were carried out. The chemical composition values of AISI 430 quality stainless steel used in the study are shown in Table 1. The table of the experimental design is shown in Table 2. The etchings were carried out in a fume hood in the laboratory using personal protective equipment.

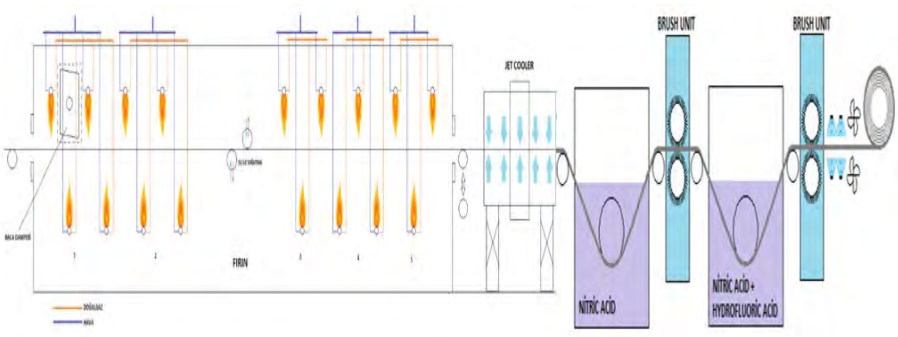


Fig. 1. Annealing and Pickling Line Schematic Illustration

Table 1. Design of Experimental Tabel.

Alloy	Lab. Furnace Temp. (°C)	Time (s)		Concentration	
430	850	110	65	(%12 H_2SO_4 + %12 HCl + %1,5 H2O2)	(%15 HNO3)
1.Group		3+1			
2. Group			3+1		
3. Group		3+1			
4. Group			3+1		
Alloy	**Lab. Furnace Temp. (°C)**	**Time (s)**		**Concentration**	
430	750	120	80	(%12 H_2SO_4 + %12 HCl + %1,5 H2O2)	(%15 HNO3)
1.Group		3+1			
2. Group			3+1		
3. Group		3+1			
4. Group			3+1		

Table 2. Chemical Composition Table of AISI 430 Alloy Used in the Experiment [9].

	TS EN ISO 10088-2 Chemical Compositon									
	% C	% Si	% Mn	% P	% S	% Cr	% Ni	% Cu	% Mo	% N
According to TS EN ISO 10088-2 1.4016 (AISI 430)	0,08	1	1	0,040	0,015	16 to 18	-	-	-	-
Measurement Values AISI 430	0,045	0,34	0,43	0,012	0,001	16,13	0,093	0,08	0,002	-

Mahr M300 brand roughness device was used in the study. Besides the surface roughness, Veeco Dektak 8 brand optical profilometer device was used. The penetrating end of the device scans the surface with a 9 µg load. The scanned area is 0.981 mm2. Surface morphology was obtained by scanning from 53 points in this area. Portable USB microscope at 50X magnification was used for macro surface images.

After annealing, the surface roughness of the samples, whose surfaces were coated with high temperature oxides, were measured on precision scales. After the measured values, in order to understand the mass losses of the samples immersed in the acid baths, the surface roughness values were examined again by measuring them on a precision balance. Dissolution kinetics were calculated based on the mass loss values. The effects of acid type and annealing times were investigated over this value.

The reaction kinetics after weighing were calculated according to Equation 1. [10].

$$\eta = \frac{W_0 - W_1}{A * t} \qquad (1)$$

$\boldsymbol{\eta}$ = Reaction Kinetics, $\boldsymbol{W_0}$ = First Tart, $\boldsymbol{W_1}$ = Last Tart, $\boldsymbol{A}$ = Surface Area, $\boldsymbol{t}$ = Descaling Time.

3. RESULTS AND DISCUSSION

The roughness measurements of 32 deformed samples after annealing are as shown in Figures 2 and 3 with reference. The measurements were made from three different regions on the same line and the average values are shown on the graphs. In the examinations in the graph, the roughness values as a result of 4 different annealing conditions were close to each other. Even if the roughness values of the samples that are annealed only at 850 degrees 110 seconds are slightly higher, there is no significant difference. Since high temperature oxides growing on the surface after annealing in austenitic alloys such as 304 show a porous structure, increases in annealing temperature and time significantly affect the roughness values, while the high temperature oxide growing in 430 alloy ferrtic steel is far from a porous structure. This effect is thought to be due to the fact that the silicon alloy element in the stainless-steel settles in the interlayer, making it difficult for the diffusion of chromium to the surface [6,7,8,11,12]. It is thought that the decrease in the alloying element carried to the surface prevents the growth of a porous oxide on the surface.

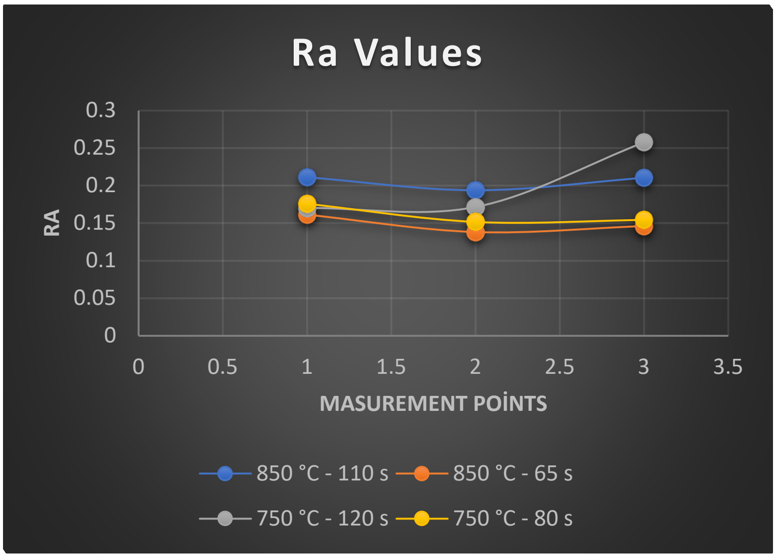


Fig. 2. Graph of Change in Ra Values with Temperature and Time After Annealing

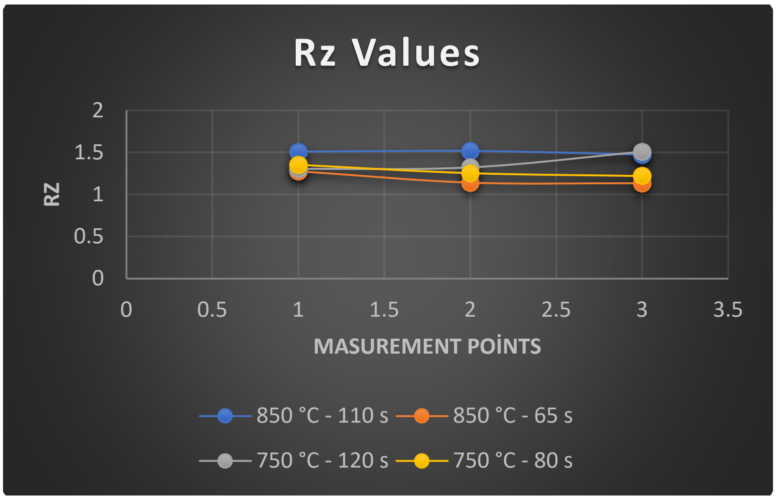


Fig. 3. Graph of Change in Rz Values with Temperature and Time After Annealing

In the reaction kinetics calculated with reference to mass loss measurements after deciling, it is seen that the sulfuric acid solution shows better dissolution for both temperature values of 850 and 750 degrees. It is seen that the dissolution values at 850 degrees 110 seconds, the formation of oxides that are difficult to dissolve by the placement of the silicon alloy elements on the interface and the increase in the density of the spinel oxides formed in the structure also make it difficult to dissolve. The low incidence of spinel oxides at 750 degrees makes it possible to dissolve in acids [6,7,8]. The outputs in the roughness values are also supported by the dissolution kinetics. Dissolution kinetics graphs at 850 and 750 degrees are shown in Figures 4 and 5.

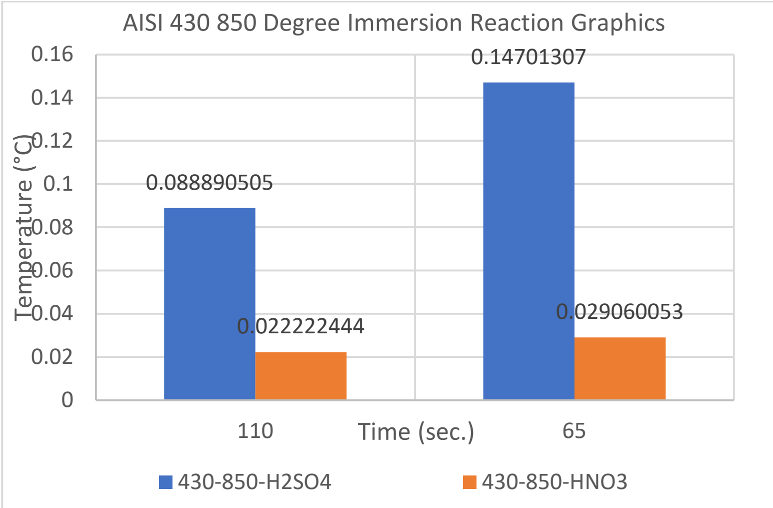


Fig. 4. Graph of Reaction Kinetics Occurring at 850 Degrees Sulfuric Acid and Nitric Acid

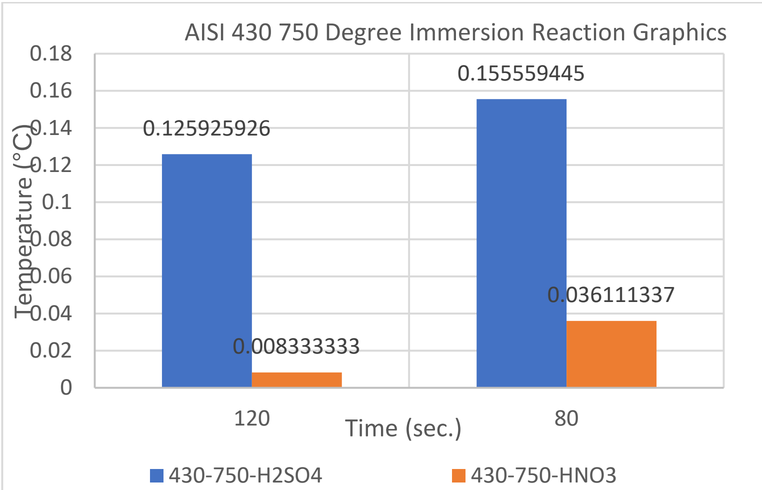
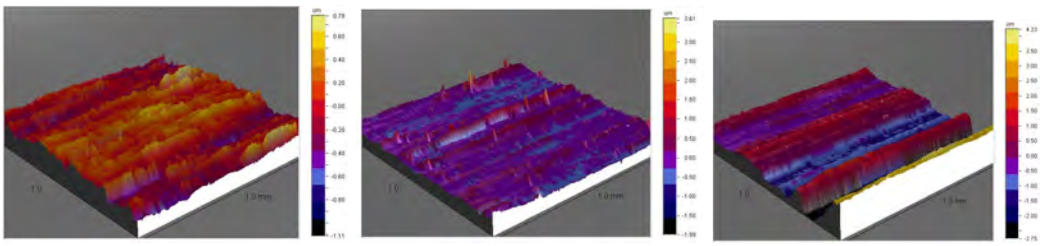


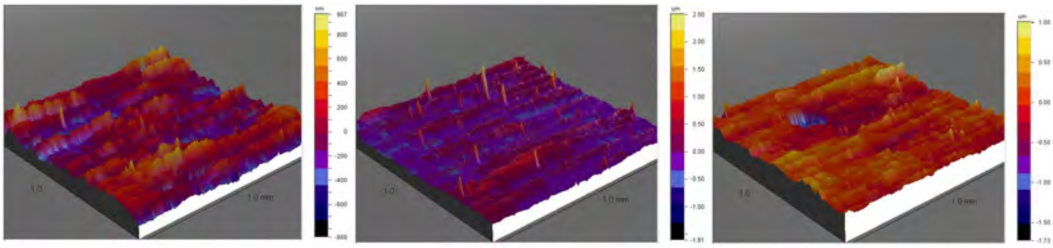
Fig. 5. Graph of Reaction Kinetics Occurring at 750 Degrees Sulfuric Acid and Nitric Acid

When the surface morphologies obtained as a result of the optical profilometer measurements are examined, it is observed that there are more significant changes in the morphology after the annealing, especially after the sulfuric acid solution. When the morphology of the samples annealed at 750°C for 80 seconds is examined (from left to right), the surface structure obtained after the annealing has the smoothest morphology after the sulfuric acid solution, and the dissolution after nitric acid is more limited (Figure 6). surface morphology is close to the appearance after annealing. In Figure 7, the surface after annealing at 850 degrees 110 seconds and the descaling surfaces with very limited dissolution are examined. When these surfaces are examined, it is seen that the surfaces close to the surface morphology after annealing maintain their existence.



(a) **(b)** **(c)**

Fig.6. After Annealing View at 750 Degrees 80 seconds (a), Sulfuric Acid Descaling Group 2 (b), Nitric Acid Descaling Group 4 (c)



(a) **(b)** **(c)**

Fig.7. After Annealing View at 850 Degrees 110 seconds (a), Sulfuric Acid Descaling Group 2 (b), Nitric Acid Descaling Group 4 (c)

Sample macro images from two different sets of experiments immersed separately in acid solutions are shown in Figures 8 and 9. When we look at the macro examinations, it is seen that the samples in the test hardness annealed at 750 degrees dissolve very well, especially in the sulfuric acid solution. It is seen that the solubility in the oxide, which is annealed at 850 degrees 110 seconds as expected in the sulfuric acid solution, that contains more complex oxides in its composition, is very limited. Oxide residues can be easily seen on the sample surfaces during the pickling processes in nitric acid solution. In this case, it is seen that the pickling time is not sufficient for the nitric acid solution. In order to improve the solubility in nitric acid solution, it is necessary to either increase the acid concentration or increase the pickling time.

(a) **(b)** **(c)** **(d)**

Fig.8. Macro Surface Images of Samples Descaling with 12% H_2SO_4 + 12% HCl +1.5% H_2O_2 (a) 750 °C 80 s., (b) 750 °C 120 s., (c) 850 °C 65 s., (d) 850 °C 110 s. Annealed Experiment Sets

(a) **(b)** **(c)** **(d)**

Fig.9. Macro Surface Images of Samples Descaling with Nitric Acid (a) 750 °C 80 s., (b) 750 °C 120 s., (c) 850 °C 65 s., (d) 850 °C 110 s. Annealed Experiment Sets

4. CONCLUSIONS

The high temperature oxides formed on the surfaces of 430 stainless steels after annealing are directly related to their chemical composition. The formation of stable compounds in the oxide structure of silicon and manganese affects the oxidation kinetics as well as the dissolution kinetics after oxidation. While the increase in annealing temperature and time increases the density of stable compounds in the oxide structure, it also prevents the porous growth of the general structure. This makes the diffusion of acid solutions into the oxide structure difficult.

In annealing at 750 degrees and annealing at 850 degrees in 65 seconds, it is possible for the oxides on the surface to dissolve, especially since the stable oxides that have not fully grown at the interface provide a more favorable environment for acid diffusion. The obtained dissolution kinetic values also support the visual findings.

In pickling processes, it is seen that the sulfuric acid solution allows dissolution in much shorter times than the nitric acid solution. Obtained findings show that ferritic stainless steels such as AISI 430 need annealing at as low temperature and short times as possible, that is, without allowing the formation of complex oxides, especially in the interface and upper layers.

Despite the increases in alloying elements that participate in the complex structure such as manganese and silicon in the structure, it is beneficial to choose low times in annealing conditions.

ACKNOWLEDGEMENT

Thanks to İrfan Can DİNÇER, İlknur KUYU and Ahmet DÖNMEZ for their valuable contributions.

REFERENCES

[1] European Steel Technology Platform (ESTEP). Strategic Research Agenda. A Vision for the Future of the Steel Sector; European Commission: Brussels, Belgium, 2005.

[2] Andersson, R.; Schedin, E.; Magnusson, C.; Ocklund, J.; Persson, A. Stainless steel components in automotive Vehicles. In Proceedings of the 4th European Stainless-Steel Science and Market Congress, Paris, France, 10–13 June 2002; p. 57.

[3] Aran, A. ve Temel M.A. (2003) Paslanmaz Çelik Yası 8amuller, Sarıtaş Çelik Sanayi ve Ticaret A.Ş., İstanbul, 165 s.

[4] Y. Y. Yue, C. J. Liu, P. Y. Shi & M. F. Jiang, "Corrosion of Hot-Rolled 430 Stainless Steel in Hcl-Based Solution", Corrosion Engineering, Science and Technology, 1478-422X, 19.05.2016.

[5] S. Chandra-ambhorn, T. Thublahor, P. Wiman, "High Temperature Oxidation of AISI 430 Stainless Steel in Ar-H_2O at 800 °C", Corrosion Science, 2020.

[6] S. Chandra-ambhorn, S. Hayashi, L. Latu-Romain, P. Wongpromrat, "High Temperature Oxidation of Stainless Steels", 1662-9779, Vol. 300, pp 81-106, 2020.

[7] J. Mougin, M. Dupeux, L. Antoni, A. Galerie, "Adhesion of Thermal Oxide Scales Grown on Ferritic Stainless Steels Measured Using the Inverted Blister Test", Mater. Sci. Eng., A 359 (2003) 44–51.

[8] G. Bamba, Y. Wouters, A. Galerie, F. Charlot, A. Dellali, "Thermal Oxidation Kinetics and Oxide Scale Adhesion of Fe-15Cr Alloys as a Function of Their Silicon Content", Acta Mater. 54 (2006) 3917–3922.

[9] Turkish Standard. (2014). Stainless Steels - Part 2: Technical Delivery Conditions For Sheet/Plate And Strip of Corrosion Resisting Steels For General Purposes (TS EN 10088-2).

[10] P. Shi, H. Shi, C. Liu & M. Jiang, "Effect of Pickling Process on Removal of Oxide Layer on The Surface of Ferritic Stainless Steel", Canadian Metallurgical Quarterly, ISSN: 0008-4433 (Print) 1879-1395.

[11] N. Zacchetti, S. Bellini, A. Adrover & M. Giona, "Early Stage Oxidation Of AISI 304 Stainless Steel: Role of Temperature and Oxygen Pressure", Materials at High Temperatures, 26:1, 31-38.

[12] Chu-Hsuan Sha and Chin C. Lee, "Low-Temperature Bonding to 304 Stainless Steel for High-Temperature Electronic Packaging", IEEE Transactions on Components, Packaging and Manufacturing Technology, Vol. 1, No. 4, April 2011.