The Effect of Different Oxide Characteristics and Acid Combinations on Descailing Capability on Aisi 304 Quality Stainless Steel Surface

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Abstract. AISI 304 quality stainless steel is an indispensable material for daily use thanks to its high corrosion resistance, high thermal conductivity, formability and visual properties. Especially in the kitchen, petrochemical, marine industry and in the manufacture of medical equipment, stainless steels are frequently used. Stainless steel flat materials are produced by hot rolling, annealing and cold rolling after casting, and are then prepared for service lines by annealing and surface passivation [1].

INTRODUCTION

Austenitic stainless steels are widely used in industry with their high formability and corrosion resistance. AISI 304 quality austenitic stainless steel is the most preferred alloy in the austenite family. Flat products are used in many areas from kitchen tools to fuel tanks to the manufacture of welded pipes. Cold rolling is also an important process in the production of flat products. Passed through a series of parallel rolls, the stainless steel is rolled to the desired final thickness. The structure, which becomes brittle after rolling, is subject to solution heat treatment. With this annealing, the structure that turns from austenite to martensite is regained to its austenite form, while the carbon that has collapsed to the grain boundaries is also taken back into solution [1-2].

The solution heat treatment takes place at the minimum recrystallization temperature and with sufficient time. Although it varies according to the deformation rate for 304 quality stainless steel, the average is 950 degrees. It is possible to produce materials with desired properties with time optimization at temperatures above 950 degrees. At these temperatures, especially if the heat treatment conditions are not realized in a protective atmosphere, high temperature oxidation occurs on the material. High temperature oxides not only reduce the corrosion resistance of the material, but also eliminate the surface expectation. It can also affect the mechanical properties of the material. In order to eliminate these negative effects, it is necessary to remove the high temperature oxides formed on the surface. For this, a two-stage process is applied. Descaling and pickling. In these processes, which are applied by means of acids, a gradual dissolution process is applied. During the descaling stage, the chromium oxide layer, which is especially diffused to the upper layers, is broken and the surface is made ready for final dissolution. After pickling, the high temperature oxides that are completely removed from the surface are replaced by a regular passive oxide layer consisting of chromium oxide, which provides corrosion resistance in stainless steels [3-5].

304 quality stainless steels generally contain 18% chromium and 8% nickel by mass as the main alloying element. The high affinity of chromium against oxygen creates a passive oxide layer on the surface, as well as forming an important part of the high temperature oxides that grow on the surface by oxidizing during annealing. At the same time, silicon and manganese, which are alloy elements, are also oxidized and added to the structure. Especially silicon and manganese play an important role in the formation of spinel oxides. Since these spinel oxides are complex compounds, they are difficult to dissolve with acids. Temperature and time also have significant effects on the oxide structure and oxide surface morphology. As the temperature and time increase,

oxidation increases and the oxides formed tend to form a porous structure away from forming a regular oxide structure [4,5,8,9,11,13].

It is seen that they have a more regular oxide structure and oxide morphology at low temperatures. The increase in annealing temperature and time also leads to the formation of oxide islands on the oxide surface and then the growth of these islets that show nucleation on the surface. The growth of the oxide islet also helps the porous growth of the structure that will show stratification on the surface. At the same time, since the oxide islands on the surface change the surface morphology, it also increases the surface roughness at the macro scale. The porous and rough surface has an expanded surface network for the acid solution to adhere to and diffuse. In this study, the character of surface oxides formed due to annealing conditions and the ability of different acid combinations to dissolve these oxides are investigated [7,8,9,10,11,13].

EXPERIMENTAL PROSEDURE

Trinox Metal production processes were taken as a reference in the experimental design. The sheets were rolled from 3 mm to 0.8 mm thickness with Sendzimir mill. Small plates of 15x15 cm2 were cut with a laser over these plates. Samples were formed using a single lot number of AISI 304 alloy rolled up to 0.8 mm thickness at a constant deformation rate of 73,333%. In Trinox Metal production processes, after rolling, it is passed through a tunnel-type open-flame furnace, and then it enters acid tanks and descailing and pickling processes are applied in these tanks. The schematic representation of the annealing and pickling process is in Figure 1.
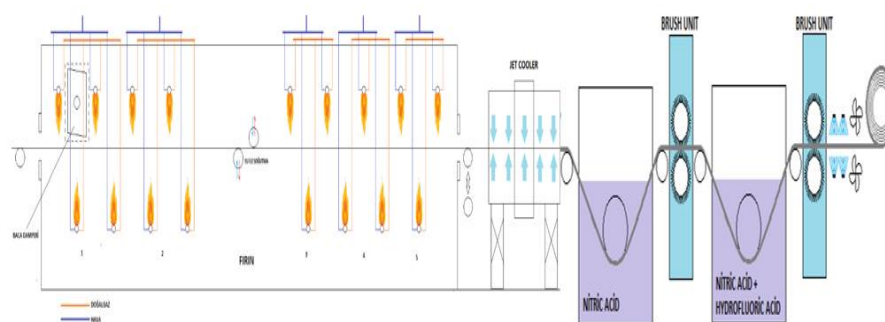

FIGURE 1. Annealing and Pickling Line Schematic Illustration

The experimental design is shown in Table 1. Test times were determined in accordance with Trinox Metal furnace and acid tanks by taking the annealing parameters as reference to TS EN ISO 10088-2, which is the stainless-steel plate production standard. Annealing processes were annealed in an electric laboratory type furnace. After the tests performed according to Table 1, weight measurements and surface roughness were measured after annealing and descaling [6]. As shown in Table 1, a single type of alloy was annealed at 2 different temperatures, 1100 degrees and 950 degrees, and in 2 different times for each temperature value. 4 samples were used for each experimental group. 3 of these 4 samples were used for weight and roughness measurements and one of them was reduced to smaller sizes and used as a surface examination sample. The electron microscope images taken are the surface images of the 4th samples in these experiment sets.

The applied processes are shown in Figure 2. The chemical composition of the 304-alloy used in the study is shown in Table 2. In the study, each experimental set was repeated 3 times. In order for the laboratory studies to fully reflect the production process, the rolling oil on the samples was not cleaned. The applied processes are shown in Figure 2. The chemical composition of the 304-alloy used in the study is shown in Table 2. In the study, each experimental set was repeated 3 times. In order for the laboratory studies to fully reflect the production process, the rolling oil on the samples was not cleaned. Weighing after annealing was followed by decailing at 60 degrees celsius. For these processes, two different combinations of acid solutions were used and the effects of acid types and concentrations on the descailing process of sulfuric acid and hydrochloric acid mixture and nitric acid solutions were investigated. Pickling processes were applied to each temperature and time sample grouped as four. After pickling, mass losses and roughness measurements of the samples were made to reach the reaction kinetics. The roughness measurements were carried out on the samples from 3 different regions in such a way as to fully represent the sample surface. After the roughnesses, the samples were examined by scanning electron microscope from the surface and cross-section. In addition, Mahr M300 roughness device and Phenom XL brand desktop electron microscope were used in the study.

TABLE 1. Design of Experimental Tabel

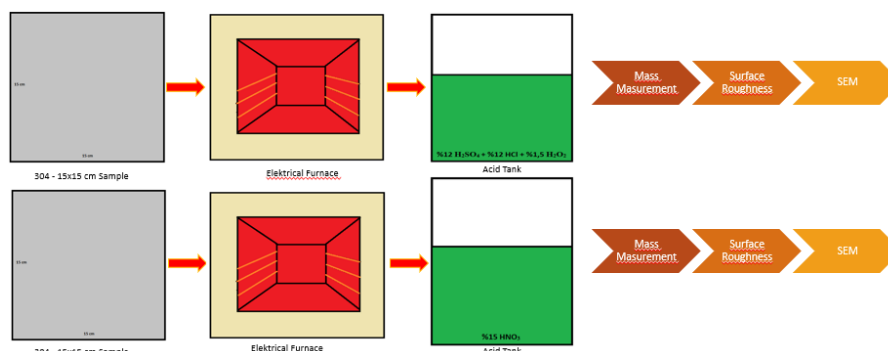| Alloy	Lab. Furnace Temp. (°C)	Time (s)		Concentration	
304		**160**	**60**	**(%12 H₂SO₄ + %12 HCl + %1,5 H2O2)**	**(%15 HNO3)**
1.Group		3+1			
2. Group	**1100**		3+1		
3. Group		3+1			
4. Group			3+1		
Alloy	**Lab. Furnace Temp. (°C)**	**Time (s)**		**Concentration**	
304		**160**	**80**	**(%12 H₂SO₄ + %12 HCl + %1,5 H2O2)**	**(%15 HNO3)**
1.Group		3+1			
2. Group	**950**		3+1		
3. Group		3+1			
4. Group			3+1		

FIGURE 2. Schematic Display of Applied Operations

TABLE 2. Chemical Composition of 304 Alloy

	TS EN ISO 10088-2 Chemical Compositon									
	% C	**% Si**	**% Mn**	**% P**	**% S**	**% Cr**	**% Ni**	**% Cu**	**% Mo**	**% N**
304	0,057	0,39	1,04	0,032	0,003	18,2	8,05	0,06	0,04	0,044

After weighing, the reaction kinetics were found by means of the Equation 1 [7].

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

η = Reaction Kinetics, W_0 = First Tart, W_1 = Last Tart, A = Surface Area, t = Descaling Time.

RESULT AND DISCCUSSION

The roughness measurement results taken 32 pieces AISI 304 quality 73,333% rolled and then annealed sample are as shown in the graphs below. The roughness values taken from 8 samples defining each test condition are as indicated in the graphics. In Graphs 1 and 2, the changes in Ra and Rz values depending on temperature and time are examined. As the annealing time and temperature increase, the oxidation on the surface increases. As oxidation increases, more porous oxides and oxide islands grow on the regular oxides formed on the surface.

Thickness of the layers and the formation of islets, obtaining a more porous structure also increase the surface roughness. This prediction is supported by the roughness results [8].
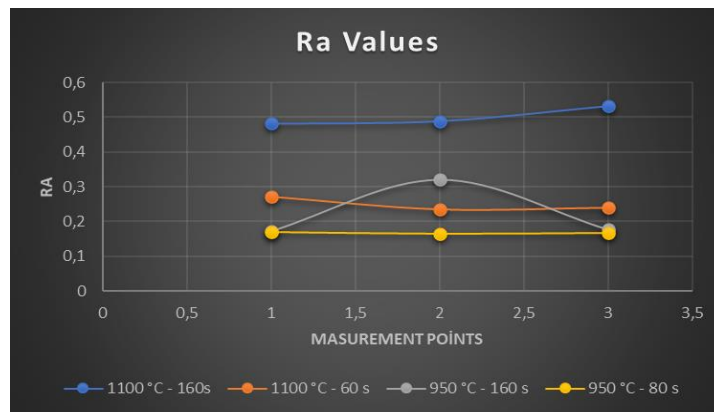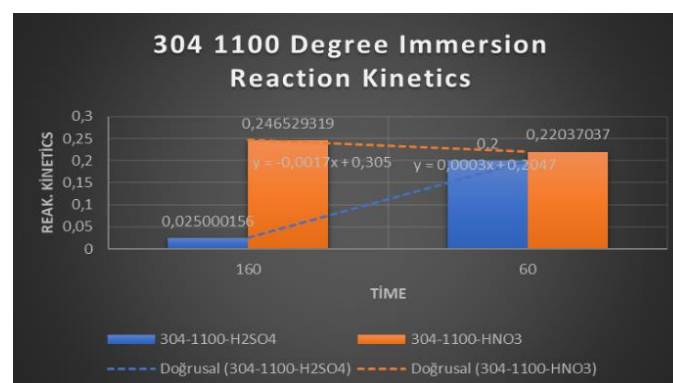

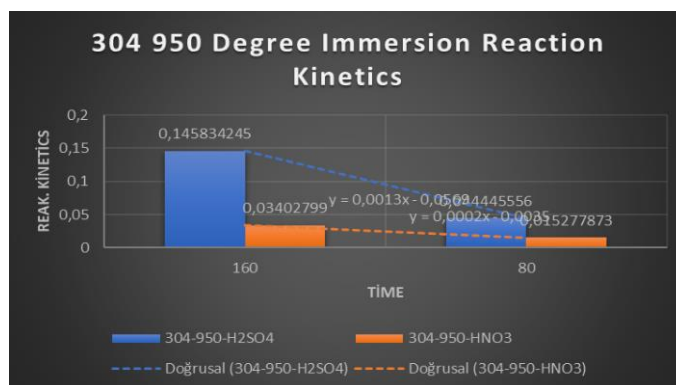**Graph 1.** Graph of R_a Variation with Temperature and Time
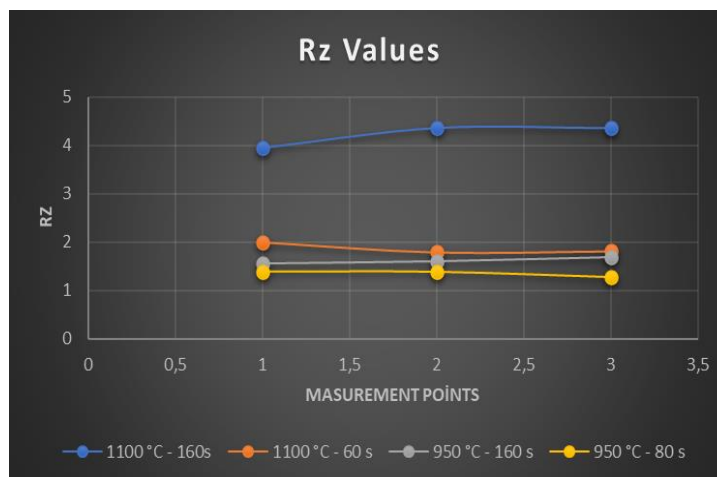
Graph 2. Graph of R_z Variation with Temperature and Time

Graph 3 shows how the reaction kinetics due to mass loss at 1100 degrees and Graph 4 at 950 degrees change in sulfuric acid and nitric acid.

Graph 3. Graph of Reaction Kinetics Occurring at 1100 Degrees Sulfuric Acid and Nitric Acid

Graph 4. Graph of Reaction Kinetics Occurring at 950 Degrees Sulfuric Acid and Nitric Acid

Increase in structural porosity and roughness with increasing temperature and time facilitates the diffusion of acid to the surface of the samples immersed in acid. This prediction is also supported by the mass losses and the calculated dissolution kinetics. The increase in structure porosity and roughness facilitates the diffusion of acid to the surface of the samples immersed in acid. The mixture of sulfuric and hydrochloric acid caused more mass loss than nitric acid at all temperatures and times except 1100 degrees 160 seconds. It is predicted that the factor causing this situation, together with the rapid onset reaction, causes the reaction to slow down at the hydrogen gas output reaction interface [10,12].

It is understood that the sample images, which were examined after annealing, support the roughness and mass loss measurements and that the results of the measurements carried out are correct. At the same time, EDS analyzes show how alloying elements change the oxide structure with temperature and time.

It is observed that the surface morphology becomes rougher, the diameters and densities of the oxide islands growing on the surface increase, and the traces extending in the rolling direction become stratified at the annealing times of 1100 degrees 60 seconds and 160 seconds. The increase in islets of stratification is also effective in the ratio of roughness and porosity. The cross-sectional view of 1100 degrees 160 seconds also shows how porous the structure has become. Surface images are shown in Figure 3 and Figure 4, and cross-sectional images are shown in Figure 5. Figure 3 shows the sample image of the 2nd group experiment set at 1100 degrees annealing temperature. In Figure 6, the sample image of the 1st group experiment set at an annealing temperature of 1100 degrees is shown. Figure 5 is the cross-sectional view of the sample in the 1st group experimental set [4].
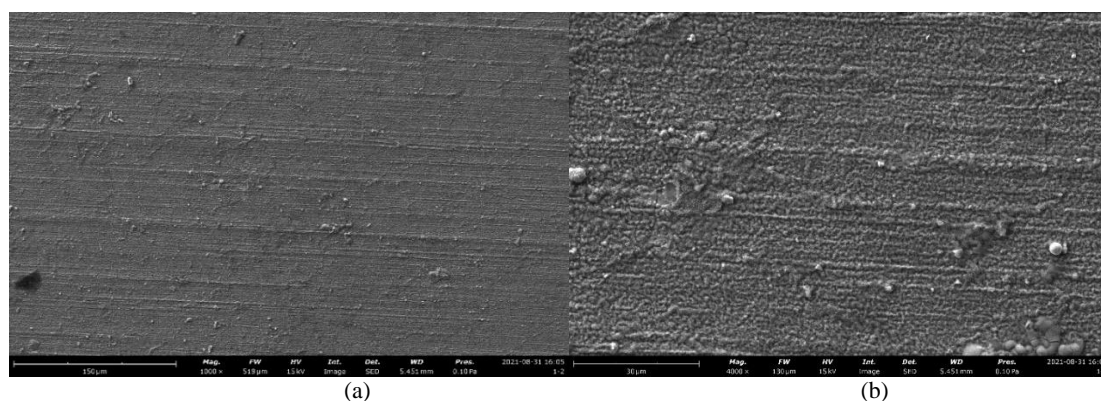

(a)   (b)

FIGURE 3. 1100 °C 60 s (2. Group Sample) SEM Figures a) 1000X, b) 4000X
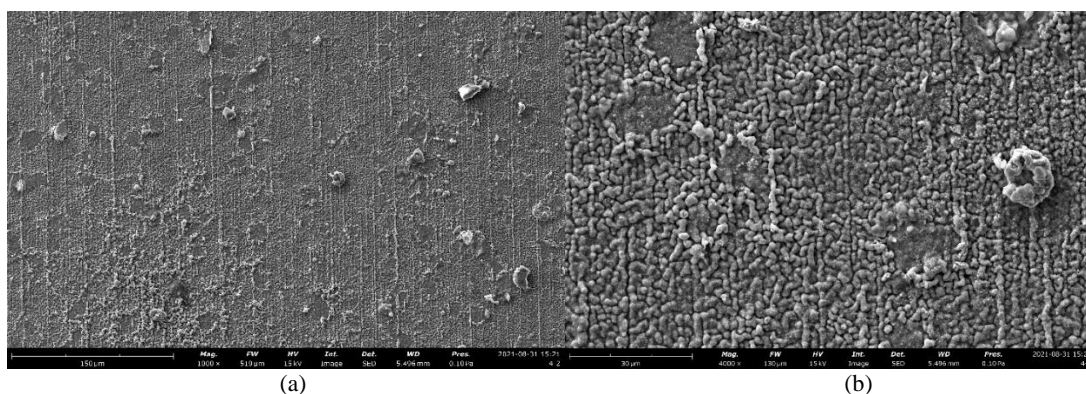
FIGURE 4. 1100 °C 160 s (1. Group Sample) SEM Figures a) 1000X, b) 4000X
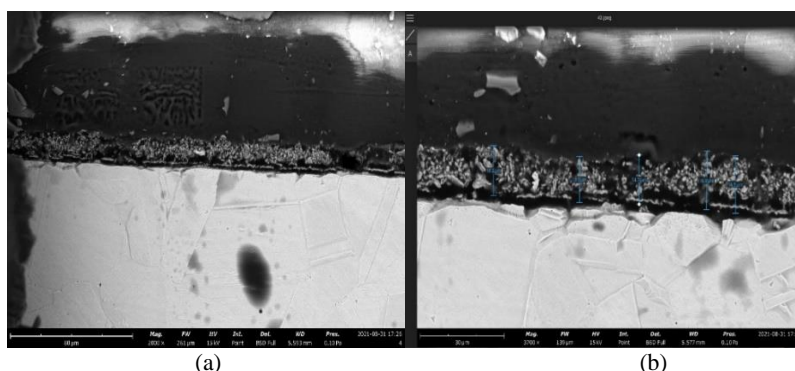

FIGURE 5. 1100 °C 160 s (1. Group Sample) SEM Figures a) 2000X, b) 3700X

The cross-sectional view of 1100 degrees 160 seconds also shows how porous the oxide structure is. At the same time, an average of 15–20-micron oxide layer thickness was measured on the surface. The diffusion of acid molecules into the porous structure is also easy and the dissolution process can be completed in a short time. One of the biggest factors that increase the stratification and layer thickness is due to the diffusion of chromium to the surface due to the increase in temperature and time, and the formation of chromium oxide (Cr_2O_3) structure in the upper layers. At the same time, iron oxides (FeO, Fe_2O_3, Fe_3O_4) in various forms in the substrates continue to be oxidized and the substrate thicknesses increase [4].

EDS results clearly show us that the formation on the surface is an oxidized form. It is seen that the majority of the oxide structure consists of cromium and iron oxides. As the degree of oxidation increases in the cromium oxide structure, it moves more to the surface and takes up more space on the outer layer. It has been observed that alloying elements such as nickel, manganese and silicon also participate in the oxide structure (Figure 6).
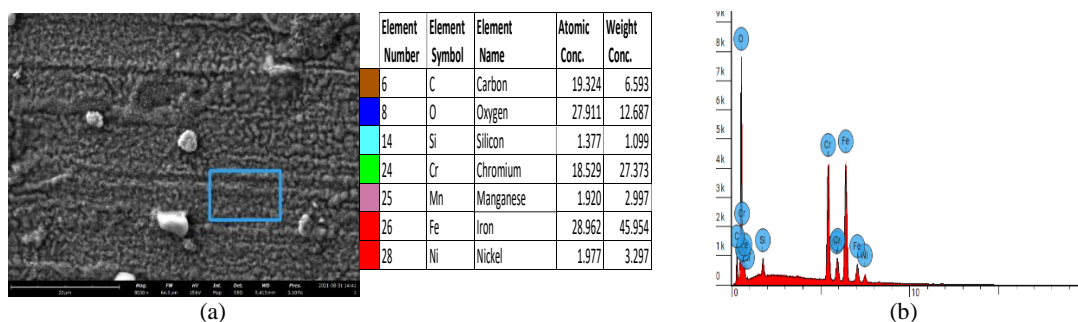

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	19.324	6.593
8	O	Oxygen	27.911	12.687
14	Si	Silicon	1.377	1.099
24	Cr	Chromium	18.529	27.373
25	Mn	Manganese	1.920	2.997
26	Fe	Iron	28.962	45.954
28	Ni	Nickel	1.977	3.297

FIGURE 6. 1100 °C 60 s (2. Group Sample) EDS Results a) Analys Area, b) Results

When we look at the EDS results of 1100 degrees 160 seconds, it is seen that the chromium content increased compared to 60 seconds, and there was a decrease in the nickel content at the same time. This reduction remains in the lower layers before the nickel oxides can diffuse to the upper layers. It is seen that the manganese content increases again, but the silicon behaves like nickel (Figure 7).
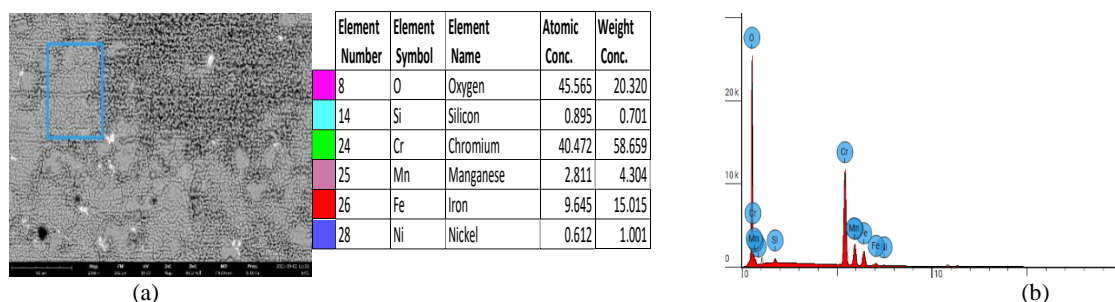
Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
8	O	Oxygen	45.565	20.320
14	Si	Silicon	0.895	0.701
24	Cr	Chromium	40.472	58.659
25	Mn	Manganese	2.811	4.304
26	Fe	Iron	9.645	15.015
28	Ni	Nickel	0.612	1.001

(a) (b)

FIGURE 7. 1100 °C 160 s (1. Group Sample) EDS Results a) Analys Area, b) Results

Looking at 950 degrees 160 seconds, it is seen that oxide islands and layered structures have just begun to form. Although the structure is similar to the oxide form of 1100 degrees 60 seconds, it is understood from the EDS results that it does not show as much oxidation at 1100 degrees (Figure 8).
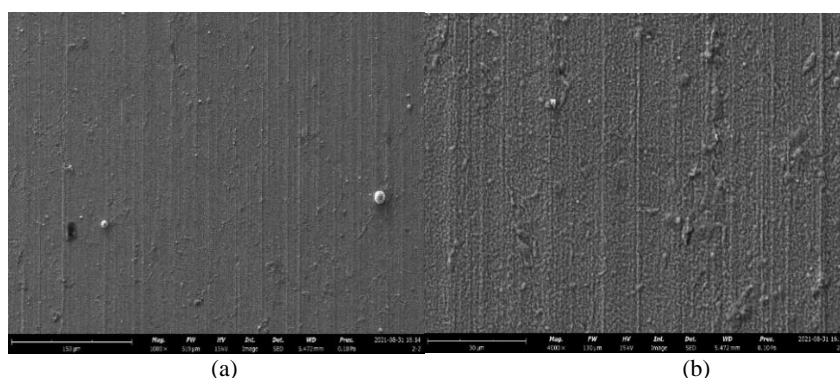

(a) (b)

FIGURE 8. 950 °C 160 s (1. Group Sample) SEM Figures a) 1000X, b) 4000X

It can be seen from the image that it has a regular oxide structure. Since this oxide form has not yet formed a sufficiently porous structure, it is not soluble in acids. It appears as a thin oxide layer on the surface where iron oxides are predominantly present. The lack of porosity of the structure prevents the diffusion of acid molecules among the oxides. It prevents the formation of sufficient reaction rate for the test and process conditions. The visuals support the comments made after the roughness and mass loss measurements (Figure 9) [4].
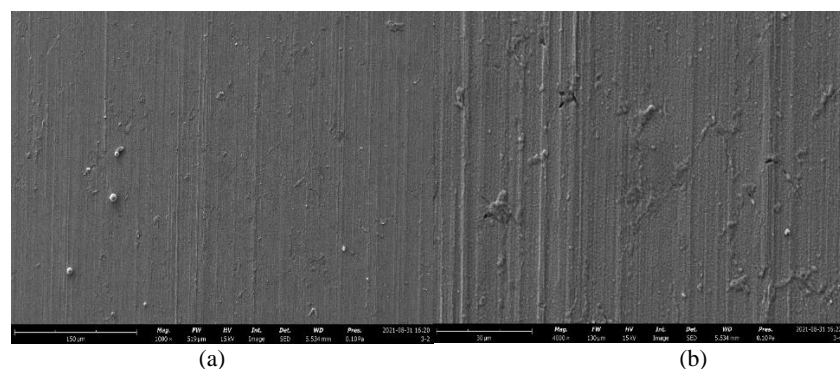

(a) (b)

FIGURE 9. 950 °C 80 s (2. Group Sample) SEM Figures a) 1000X, b) 4000X

In the EDS results, it is seen that the chromium layer does not spread sufficiently to the upper layers and the oxide content in the structure consists of iron oxides. Again, the nickel and silicon content shows that the oxide layer thickness is not as much as in those conditions, as it has more content than the oxide structure at 1100 degrees 160 seconds. EDS results are shown in Figure 10 [4].
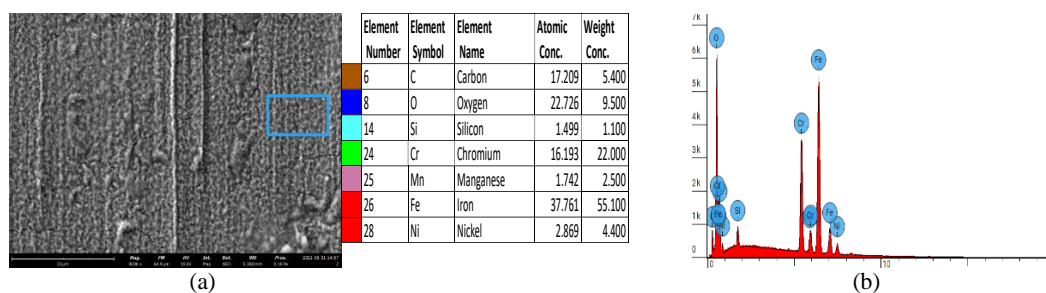
Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	17.209	5.400
8	O	Oxygen	22.726	9.500
14	Si	Silicon	1.499	1.100
24	Cr	Chromium	16.193	22.000
25	Mn	Manganese	1.742	2.500
26	Fe	Iron	37.761	55.100
28	Ni	Nickel	2.869	4.400

(a)   (b)

FIGURE 10. 950 °C 160 s (1. Group Sample) EDS Results a) Analys Area, b) Results

As a result of the test conditions, the oxide obtained as a result of the annealing conditions of 950 degrees 80 seconds, which has the highest nickel content, is the thinnest oxide structure (Figure 11).
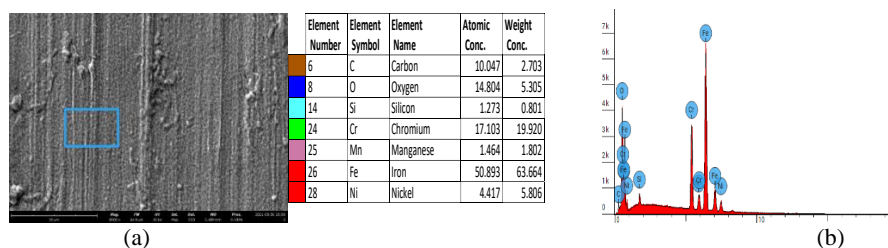

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	10.047	2.703
8	O	Oxygen	14.804	5.305
14	Si	Silicon	1.273	0.801
24	Cr	Chromium	17.103	19.920
25	Mn	Manganese	1.464	1.802
26	Fe	Iron	50.893	63.664
28	Ni	Nickel	4.417	5.806

(a)   (b)

FIGURE 11. 950 °C 80 s (2. Group Sample) EDS Results a) Analys Area, b) Results

The line on the cross-section view of 1100 degrees 160 seconds EDS has an orientation from the base metal to the oxide (Figure 12). It is seen that there is a rapid increase in the chromium content with the transition from the base metal to the oxide, and the chromium peaks and oxygen peaks are also congruent. The increase in carbon peaks seen afterward is due to bakelite.
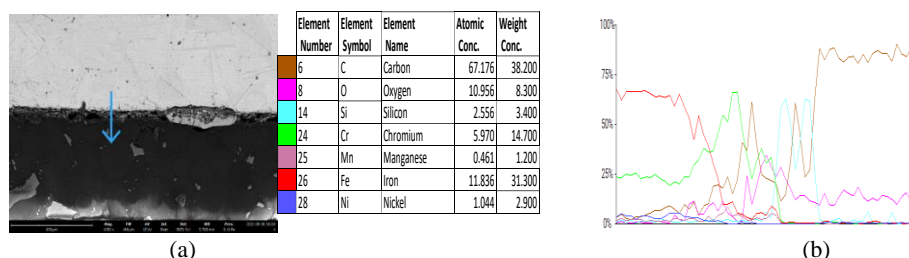

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	67.176	38.200
8	O	Oxygen	10.956	8.300
14	Si	Silicon	2.556	3.400
24	Cr	Chromium	5.970	14.700
25	Mn	Manganese	0.461	1.200
26	Fe	Iron	11.836	31.300
28	Ni	Nickel	1.044	2.900

(a)   (b)

FIGURE 12. 110 °C 160 s (1. Group Sample) EDS Results a) Line Analys, b) Results

It is seen that the undescaled surface after 1100 degrees 160 seconds of sulfuric acid (left) and the high temperature oxides completely cleaned from the surface after nitric acid on the right are replaced by chromium oxide forms. Partial dissolutions were observed on the surface of the material treated with sulfuric acid (Figure 13). In these partial dissolutions in sulfuric acid, the reaction that started to take place rapidly and the hydrogen gas released as a result of the reaction on the base metal surface caused the reaction to slow down without allowing the reaction to progress, and the surface cleaning could not be done properly.
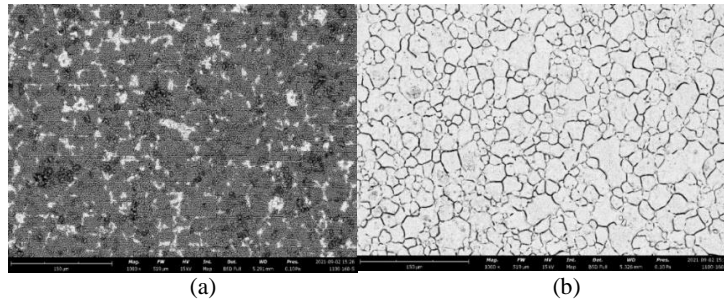
(a)   (b)

FIGURE 13. 1100 °C 160 s After Descaling Surface SEM Figures a) 1100 °C – 160 sn - H_2SO_4 + HCl, (1. Group Sample)
b) 1100 °C – 160 sn - HNO3 (3. Group Sample)

CONCLUSION

- As the annealing temperature and annealing time increase, the high temperature oxide thickness and oxide porosity formed on the surface increase. This increase also increases the surface roughness [8].
- As the annealing temperature and annealing time increase, chromium diffuses into the structure and takes place more in the upper layers of the oxide. Contrary to chromium, it is seen in oxide layers close to the base metal, where nickel has difficulty in being carried to the upper layers as the temperature and time increase.
- Generally speaking, the solubility ability increases depending on the increase in oxide thickness and porosity.
- It is seen from the reaction kinetics that the sulfuric acid and hydrochloric acid solution is a better descaling solution than the nitric acid solution. As such, it is seen that it supports the increase in line speeds (efficiency) and increases the amount of product produced per unit time. At the same time, the study also creates dissolution kinetic data in the literature for the immersion method in these acid and annealing conditions.
- The line can be optimized at current acids between 1100 degrees and 950 degrees, where long times are required for the formation of soluble oxides at 950 degrees, which is the lower limit for the annealing temperature.

ACKNOWLEDGMENTS

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