

## Optimization of Annealing & Pickling Processes for AISI 304 Stainless Steel Sheet Corrosion Resistance

AISI 304 Paslanmaz Yassı Çelik Üretiminde Korozyon Dayanımı için Tavlama ve Passivasyon İşlemlerinin Optimizasyonu

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### Abstract

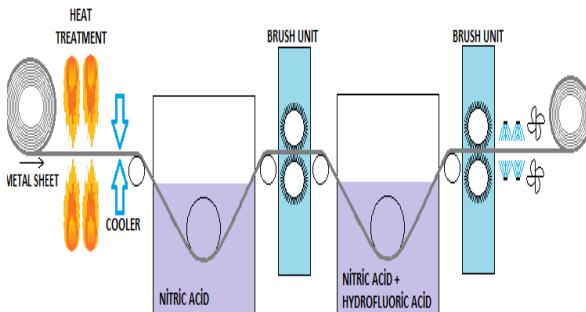
AISI 304 quality stainless steel has become an indispensable material for daily use thanks to its high corrosion resistance, high heat conductivity, formability and visual properties [1-2]. Stainless steel flat materials are produced with hot rolling, annealing and cold rolling after the casting process and then it is prepared for service processes by ensuring annealing and surface passivation. In this study, the effect of annealing temperature, time and the difference of acidification processes on the corrosion resistance of the material is investigated.

### 1. Introduction

#### 1.1. Surface Passivation in Stainless Steel

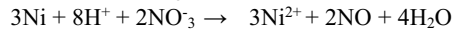
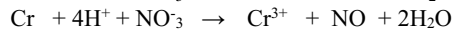
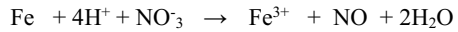
The next stage in stainless steel plate production is surface passivation after cold rolling process. Surface passivation is usually done in 2 phases. In the first stage, the descaling which caused by the annealing process on the surface of the plate with a specific acid solution is resolved.

After that, descaling surface will be passivated with a specific acid solution. Thus, the material will regain its stainless property.

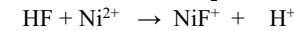
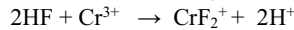
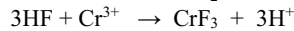
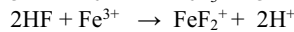
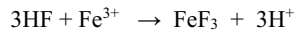
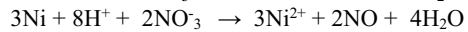
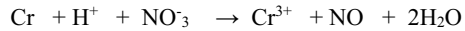
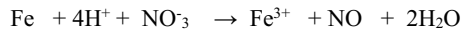


**Figure 1:** Trinox Metal Annealing and Pickling Process Machinery

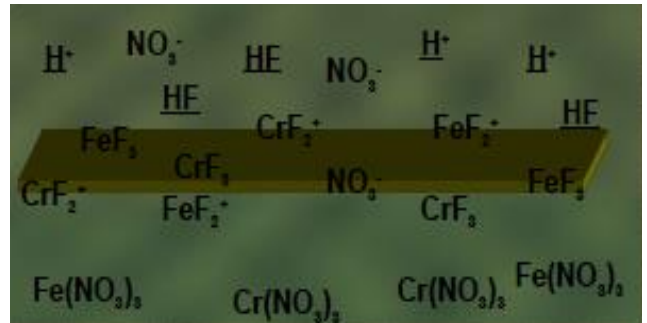
In the passivation process, the material is submerged in nitric acid for firstly descaling operation and surface is prepared to passivation. The following reactions occur here:



The material is submerged in nitric acid and hydrofluoric acid tank for the passivation after the nitric tank operation. In this bath, following reactions occur:



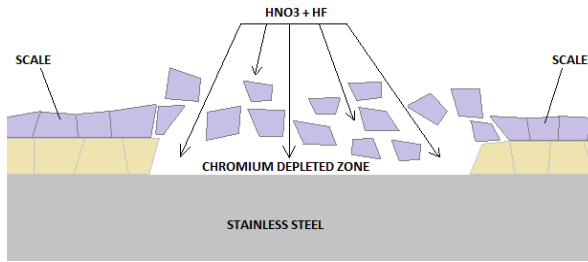
The schematic representation of the reactions is given in figure 2. [3]



**Figure 2:** Chemical reactions in the pickling process

In this point, HNO<sub>3</sub> is used as H<sup>+</sup> Source, oxidizing and shining agent. HF is used as a complex agent for Fe<sup>3+</sup>, Cr<sup>3+</sup>, Ni<sup>2+</sup>, and H<sup>+</sup> Supplier.

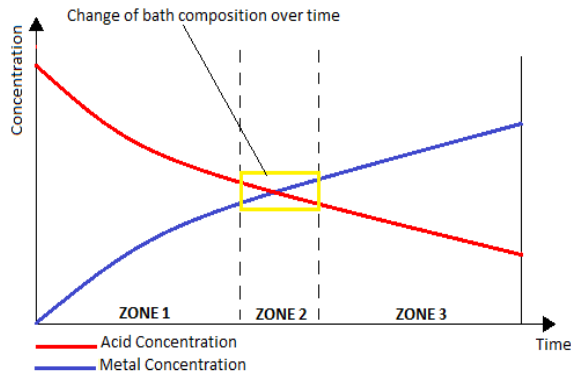
The physical effect of the HNO<sub>3</sub> / HF mixture on the surface of the sheet is like in Figure 3. [3]



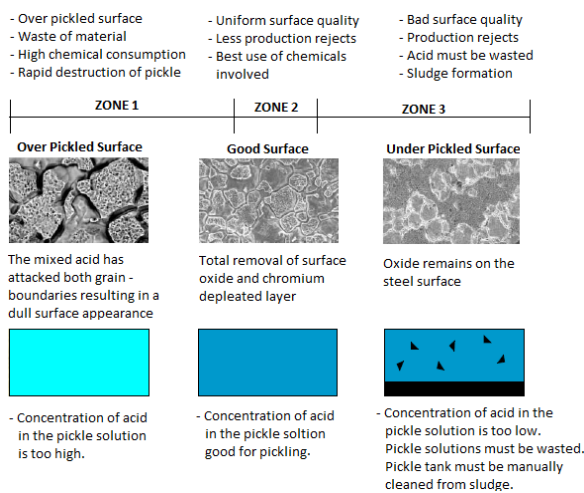
**Figure 3:** Effect of pickling chemicals on material surface

The relationship between the acid concentration and the concentration of metal in the acid baths should be under control to make the passivation process well done. [4]

Figure 4 shows the areas belonging to this relationship, and in Figure 5 shows the surface images of the plate that arise depending on these regions.



**Figure 4:** Connection of metal and acid concentrations



**Figure 5:** Material surface depending on metal amount and acid concentrations [4]

## 1.2. Pitting Corrosion in Stainless Steel

Corrosion is an electrochemical phenomenon that causes various problems depending on the conditions in which the engineering alloys are used. Stainless steels are also alloys produced for conditions where corrosion resistance is required. Although stainless steels have good corrosion resistance alloys, the conditions of use and unsuitable operations on the material surface can cause undesirable consequences.

Corrosion resistance of stainless steel is most fundamentally dependent on alloying elements. Then, the surface layers resulting from process conditions become important for corrosion. [5]

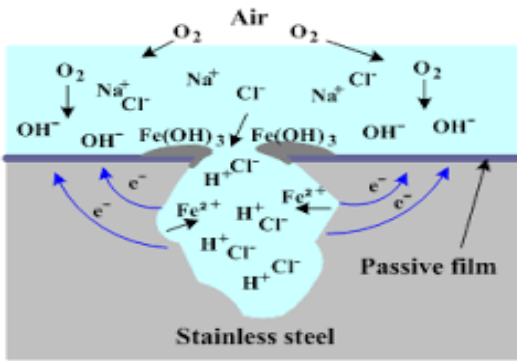
Especially in aggressive conditions or when the surface is subjected to a physical effect along with a chemical effect, the protective passive layer is deteriorated by a localized effect, resulting in a very narrow area of pitting corrosion.

The determination of this type of corrosion is difficult and a dangerous situation occurs because it handles the material from very small areas to the inside

On the basis of pitting corrosion which is a type of galvanic corrosion due to the potential difference of electrochemical between the weakened passive layer and the strong passive plate. As corrosion progresses, the weaker passive layer becomes weaker. In this case, the potential difference of the electrochemical between the weak layer and the strong layer will increase more. The corrosion of the pitting will progression rapidly increasing.

This is the direction that makes the çukurcuk corrosion aggressive. Starting from a very small area, it is difficult to detect and quickly processes the material deeper into the material. And there will be no significant weight loss during this time, so the progressive corrosion may not be detected. [1].

The nonmetallic structures contained in the environment are not sufficient to initiate the pitting corrosion alone. Especially the presence of an oxidizing catheter ( $Fe^{3+}$ ,  $Cu^{2+}$ ,  $Hg^{2+}$  etc.) creates a reaction starting point for weak areas in the protective layer. However, especially in the presence of oxygen, all chlorides become dangerous. In the environment where there is an oxygen or an oxyhydrogen component, the corrosion of the pitting becomes much more aggressive.[6]



**Figure 6:** Pitting corrosion appearance [7]

Austenitic stainless steels are the largest and most important group in the stainless steel family. Austenitic stainless steels are alloys with high welding ability, high formability capabilities as well as high corrosion resistance

As the passive chromium oxide layer on the surface provides corrosion resistance. The nickel element in the inner structure stabilises the austenitic phase, preventing carbide precipitating and releasing the chrome. Thus, even if the passive chromium oxide layer on the surface is grazed by a mechanical effect, a passive chromium oxide layer may occur again in the same region.[3]

But over time, this resistance can be broken. In different conditions, the material may become corrosion resistant. This is an acceptable state of engineering for stainless steels; The important thing is to produce the appropriate material in the appropriate process conditions and to find optimum harmony with the environmental conditions [4-5]

There are basically 2 ways to protect the material from corrosion because it is caused by the interaction between the environment and the material.

1. Create appropriate environmental conditions
2. Create a layer of passive film as uniform and deep as possible on the surface of the material [5]

The aim of this study is to create the appropriate material surface as stated in article 2.

## 2. Experimental Procedure

### 2.1. Prepare to sample

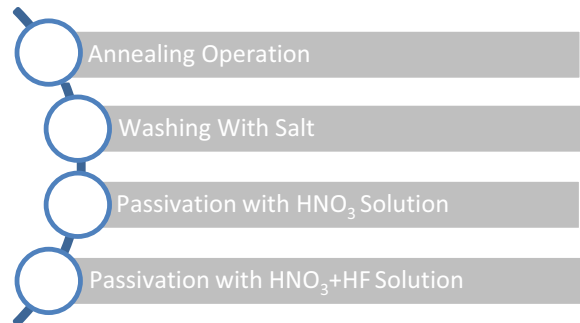
25x10 cm in size 32 pieces of the 304 stainless steel plate samples are processed annealing operation in different temperature and times in the laboratory type of furnace. Then, the samples are cooled in the air environment. (32

pieces: 15 pieces are 0,5 mm thickness; 7 pieces are 1,09 mm)

The work was conducted in the Trinox Metal product and process development laboratory.

A passivation process with HNO<sub>3</sub> and HNO<sub>3</sub>/HF solutions was applied to the annealing specimens at different time and concentrations, respectively.

Samples of 5, 13, 29 were washed with NaNO<sub>3</sub> + NaOH liquid water solution before passivation.



**Figure 7.** Sample processing steps



**Figure 8.** Sample appearance after annealing process

### 2.2. Comparative Corrosion Test

The prepared specimens are insulated to be tested for the surface area of 25 cm<sup>2</sup> for corrosion testing. Isolated specimens weighed.

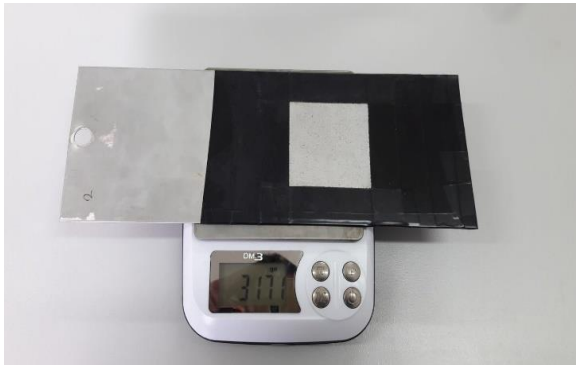


Figure 9: Weighing of prepared material

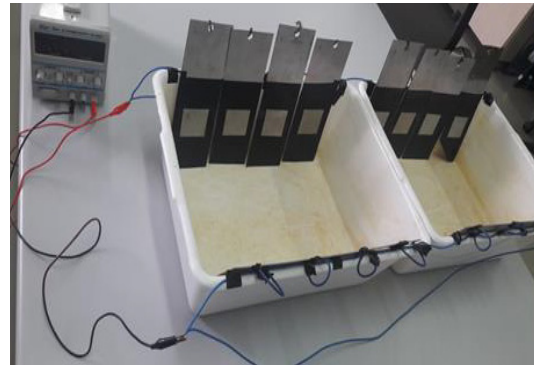


Figure 12. Establishment of an experimental set-up

Samples were placed in pools containing 3.5% NaCl solution. The uninsulated area has been considered to be immersed in the pool.

After making the necessary connection, 4A Current was given and corrosion test was carried out 1 hour.



Figure 10: Placement of samples

### 3. Results and Discussion

#### 3.1. Corrosion Test Result

The table with all the data is as follows.

Table 1. Experimental Data

No	Thick-ness (mm)	Anneal-ing Temp. (°C)	Anneal-ing Time (sec.)	NaNO <sub>3</sub> +NaOH		1. Pickling Unit				2. Pickling Unit				Picklin-g Time (sec.)	Corrosi-on Test Time (sec.)	Weigh Loss (Gn/c m <sup>2</sup> )
				Conc.	Temp.	HNO <sub>3</sub> Conc. (%)	Temp. (°C)	HNO <sub>3</sub> Conc. (%)	HF Conc. (%)	Temp. (°C)						
1	1,1	1050	180			22	65	17	2,9	65	120	60	0			
2	1,1	1050	180			16	60	15,4	2,05	61	140	60	0,16			
3	1,1	1050	180			13,7	60	15,4	0,91	60	140	60	0,16			
4	0,5	1100	180			13,7	59	15,4	0,91	61	70	60	0,2			
5	0,5	1100	60	30	420	12	60	10	2,05	61	70	60	0,24			
6	0,5	1000	120			16	60	15,4	0,91	61	70	60	0,24			
7	1,1	950	180			13	58	12	3,5	61	120	60	0,28			
8	1,1	1050	120			18	60	18	3,69	60	120	60	0,28			
9	0,5	950	120			18	65	17	2,91	68	90	60	0,28			
10	0,5	1000	60			22	65	17	2,9	68	70	60	0,28			
11	1,1	1100	120			13	57	12	0,87	57	100	60	0,32			
12	0,5	1050	180			13,7	60	15,4	0,91	61	70	60	0,32			
13	0,5	1050	120	30	420	11,8	60	10	2,05	60	70	60	0,32			
14	1,1	1000	180			18	60	18	3,69	60	120	60	0,36			
15	0,5	950	60			18	65	17	2,91	68	90	60	0,36			
16	0,5	1000	120			22	65	17	2,9	68	70	60	0,36			
17	0,5	1100	60			22	65	17	2,9	68	70	60	0,36			
18	1,1	1000	180			13,7	59	15,4	0,91	60	140	60	0,36			
19	1,1	1000	120			18	58	18	3,69	61	120	60	0,4			
20	0,5	1050	120			22	65	17	2,9	68	70	60	0,4			
21	1,1	1000	240			13,7	59	15,4	0,91	60	140	60	0,4			
22	0,5	1050	180			18	65	17	2,91	68	90	60	0,44			
23	0,5	1100	120			16	60	15,4	2,05	15,4	70	60	0,44			
24	1,1	1050	120			16	60	15,4	2,05	61	140	60	0,44			
25	1,1	1100	240			13	57	12	0,87	57	100	60	0,56			
26	1,1	1100	60			16	60	15,4	2,05	61	140	60	0,64			
27	1,1	1150	180			13	57	12	0,87	57	120	60	0,72			
28	1,1	1000	180			16	60	15,4	2,05	61	140	60	1,56			
29	0,5	1000	120	30	420	11,8	60	10	2,05	60	140	60	1,76			
30	1,1	1100	120			13,7	59	15,4	0,91	60	140	60	1,8			
31	1,1	1050	120			13,7	59	15,4	0,91	60	140	60	1,8			
32	0,5	1100	180			11,8	60	10	2,05	60	70	60	2,52			

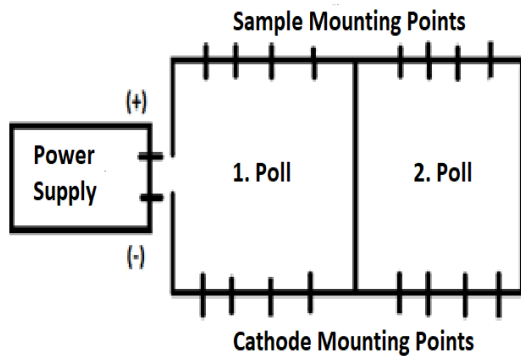
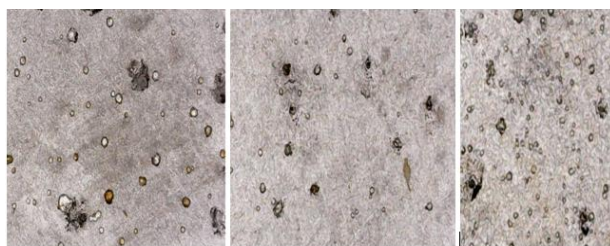


Figure 11: Circuit connection type

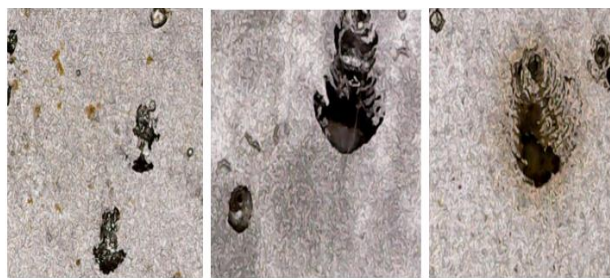


**Figure 13.** Visual appearance of sample after corrosion test

After corrosion testing, all surfaces were made to visual examination. In addition, some samples were examined with help of microscope. During the investigations, the pitting corrosion was seen very clearly.



**Figure 14.** Respectively 2,5,10 Sample Microscope Appearance (500X)



**Figure 15.** Respectively 27,28,32 Sample Microscope Appearance (500X)

Weight loss and sample visuals confirm each other.

#### 4. Conclusion

Pitting corrosion is a variety of corrosive, manifested in the presence of halogens in the surface of metals and alloys. In a very common corrosion type, the material can become unusable in a short time by drilling in the region or by

decreasing mechanical strength. In our study, corrosion impacts appear in microscope images.

In our study, annealing temperature, annealing time and passivation process are taken into consideration. The findings of the study are as follows.

At the same temperature in 1100 °C and the amount of the material annealed at the same time, the HF concentration rate of 1% is increased by 12 times the loss of quantity after corrosion.

At all temperatures, the HNO<sub>3</sub> ratio has no effect on corrosion resistance in annealing periods.

As a result of the annealing operation under the temperature of 1100 °C, the difference in HF concentration has not been influenced by material loss after corrosion. HF concentration is especially the effect of 1100 °C.

In thick materials, annealing temperatures and acid grouts in the same materials, the duration of 10 seconds increase in the 0.037 gr weight loss causes.

It will be useful to continue the study with different sample sets. The study will be enriched by increasing the number of experiments in the coming period.

#### References

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