Journal of Metals, Materials and Minerals, Vol.20 No.2 pp.1-6, 2010

Pickling Behavior of AISI 304 Stainless Steel in Sulfuric and Hydrochloric Acid Solutions

Wanna HOMJABOK[1*], Siriwan PERMPOON[2] and Gobboon LOTHONGKUM[1*]

[1]*Department of Metallurgical Engineering, Faculty of Engineering, Chulalongkorn University, Patumwan, Bangkok 10330, Thailand*
[2]*Thainox Stainless Public Company Limited, 324 Moo 8, Highway no. 3191 Road, Tambol Mabkha, Nikom Pattana, Rayong 21180, Thailand*

Abstract

Oxide scales as well as a Cr-depleted layer, which grows between the oxide scale and base metal, are formed on AISI 304 stainless steel surface during high temperature processing. Pickling is an important process which includes mechanical and chemical operations to remove oxide scales, Cr-depleted layers, and to recover the surface passivity. The multi-step pickling is commonly used because of its higher efficiency than a single step pickling. In this study, the multi-step pickling of AISI 304 stainless steel in HCl solution was investigated instead of H_2SO_4 solution for the first step of pickling. HF+HNO_3 mixed acid is traditionally used in the second step of pickling. The pickling mechanism of HCl and H_2SO_4 was discussed based on weight loss and the pickled surface qualities. It was found that the first step pickling efficiency directly affected the surface qualities of the final pickled sample. HCl solution showed much lower pickling efficiency than H_2SO_4 solution. This resulted in a high concentration of remaining oxide scales and intergranular attack at the Cr-depleted layer, which cannot be completely removed in the second pickling step. Increasing of HCl concentration and electrolytic current did not improve the pickling efficiency. The addition of a small amount of H_2O_2, which is a strong oxidizing agent, significantly improves the pickling efficiency of HCl. A smooth surface without any oxide scale and free of intergranular attack could be obtained.

Key words: Pickling, Hydrochloric acid, Sulfuric acid, Scale, Stainless steel

Introduction

Acid pickling is an important step for the production of cold rolled stainless steel plates. Its aim is to remove the oxide scale as well as a Cr-depleted layer growing between the oxide scale and the base material. Oxide scale and Cr-depleted layer are formed during high temperature processing. Removing oxide scale processes consists of mechanical descaling and pickling. In mechanical descaling, scale breaker and shot blasting were used to break up the oxide scale. This results in easily penetrating the pickling solution into oxide scales and enhances the pickling efficiency.(1-5) Multi-step pickling is used for the pickling process because it has higher efficiency and better surface quality than single step.(6-7) In the first step, electricity was used in order to increase the pickling efficiency.(8) In this step, the mechanism is that the solution penetrates into metal Cr-depleted layer and the oxide scale is undercut and removed.(6) The acid type and concentration have a strong influence on the surface finish quality. For the second step, HF+HNO_3 has become widely accepted and used for removing the remaining oxide scale and passivation.(8) The sequence at which the pickling steps are used influences the surface finish significantly. H_2SO_4 is a cheap acid and has a good pickling efficiency, which can be improved by being used together with electricity, so that H_2SO_4 with electricity is generally used for the first step. However, H_2SO_4 pickling causes black smut forming. Even though black smut can be removed by HF+HNO_3 in the next step, the surface finish has high roughness and intergranular attack. In this study, the multi-step pickling behavior of AISI 304 austenitic stainless steel in HCl solution was experimented for replacing H_2SO_4 solution in the first step, and the HF+HNO_3 mixed acid solution was used traditionally in the second step. HCl pickling has a uniform dissolution behavior with no intergranular attack.(8-10) Results were discussed

*Corresponding author E-mails: whomjabok@yahoo.com, Gobboon.L@chula.ac.th

based on weight loss and surface finish of the pickled samples.

Materials and Experimental Procedures

Material

AISI 304 austenitic stainless steel strips were hot-rolled down to a thickness of 3 mm. The chemical composition of this material is listed in Table 1. After mechanical descaling process, test samples of 25x50x3 mm were cut. Subsequently, only the unexposed area was painted with EPIGEN XD005 (acid-resistant at high temperature), and cleaned with acetone and ethanol. The test samples were finally dried with air and kept in a desiccator before experiment.

Table 1. Chemical composition (wt%) of AISI 304 stainless steel used in this study, analyzed by Optical Emission Spectrometer (OES).

Element	C	Cr	Ni	Mn	Si	P	S	Fe
Content (wt%)	0.04	18.1	8.03	1.076	0.342	0.029	0.001	Balanced

Pickling

To prepare the HCl, H_2SO_4, HF and HNO_3 electrolytes, analytical grade was used. A purity of 50% of H_2O_2 was used in this study. During pickling, temperature was controlled constantly in a water bath with constant stirring. After pickling, the samples were rinsed with tap water and brushed for removing any reaction products. The first step of pickling conditions was 4.0, 4.5, 5.0, 6.0-M HCl at 85°C or 4.0-M HCl with electricity at 85°C or 4.0-M H_2SO_4 with or without electrolytic at 85°C or 4.0-M HCl + 0, 5, 10, 15 g/L H_2O_2 at 60°C depending on the purposed tests. After the first step of pickling, the 1.0-M HF+1.0-M HNO_3 mixed acid solution at 45°C was traditionally used in the second step.

Characterization

The surface finish was characterized with roughness profiler (Telescan 150) for surface roughness. Optical microscope (OM) at 200X and scanning electron microscopy (SEM) at 3000X were used for analysis of the remaining oxide level. Figure 1 shows the evaluation of the remaining oxide on the sample surface after the in-house standard.

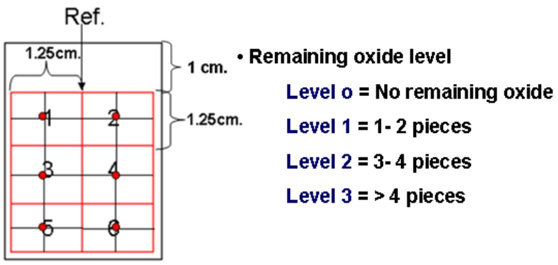


Figure 1. Remaining oxide evaluations, after the in-house standard, on 6-area observations on test sample surface at 200X.

Results and Discussion

HCl solution was investigated instead of H_2SO_4 solution for the first step of pickling. HF+HNO_3 mixed acid solution was still traditionally used in the second step. The traditional and studied conditions for this experiment are shown in Figure 2. The total weight loss resulting from those multi-step pickling conditions is shown in Figure 3. The weight loss of H_2SO_4 condition was high, but some oxide scales remained on the pickled surface in level 2 as shown in Figure 4(a). Pickling by H_2SO_4 solution with electricity followed by HF+HNO_3 solution increased the weight loss and allowed achieving a surface finish free of any oxide scale as shown in Figures 3 and 4(b), respectively.

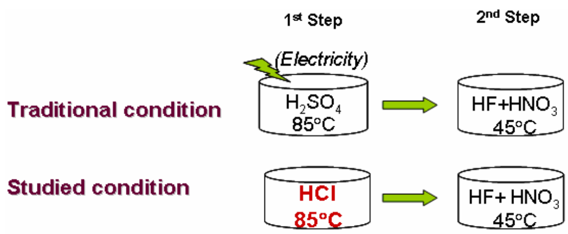


Figure 2. Multi-step pickling of AISI 304 stainless steel between the traditional and studied conditions.

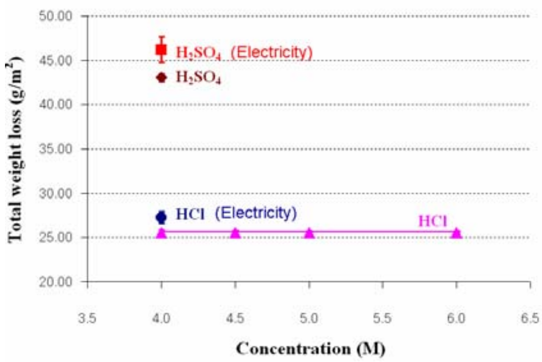
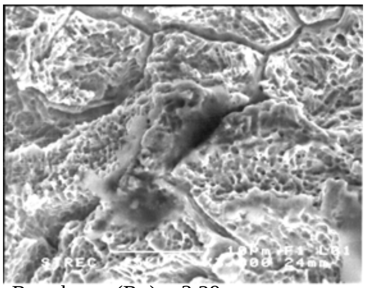


Figure 3. Total weight loss of multi-step pickling of AISI 304 stainless steel in H_2SO_4 at 85°C or HCl at 85°C followed by HF+HNO_3 at 45°C.

The case of HCl pickling instead of H_2SO_4 pickling showed that HCl had lower pickling efficiency than H_2SO_4 (Figure 3) and many oxide scales remained (Figure 4(c)). Increasing HCl concentration and HCl pickling with electricity did not result in increasing the pickling efficiency to be higher than H_2SO_4 pickling efficiency. The surface finish of HCl pickling had a rougher surface and more intergranular attack than H_2SO_4 pickling as shown in Figure 4(d). The result was not the same as reported by Li et al. (2008) who stated that uniform dissolution and no intergranular attack were observed by HCl pickling.

4.0 M H_2SO_4; 85°C
followed by HF+HNO_3; 45°C

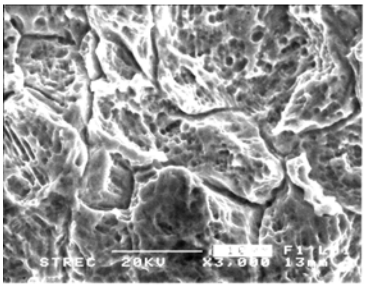
(a)



Roughness (Rq) = 3.29 µm
Remaining oxide level 2

4.0 M H_2SO_4 (Electricity); 85°C
followed by HF+HNO_3; 45°C

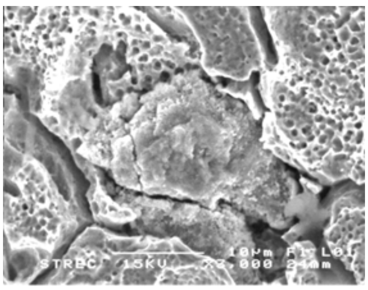
(b)



Roughness (Rq) = 3.30 µm
Remaining oxide level 0

4.0 M HCl; 85°C
followed by HF+HNO_3; 45°C

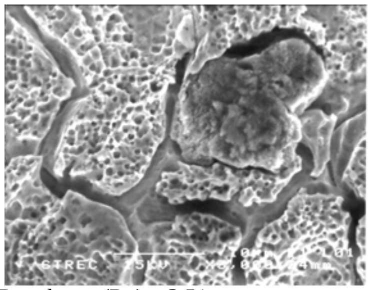
(c)



Roughness (Rq) = 3.34 µm
Remaining oxide level 3

4.0 M HCl (Electricity); 85°C
followed by HF+HNO_3; 45°C

(d)



Roughness (Rq) = 3.51 µm
Remaining oxide level 3

Figure 4. SEM surface characterization of AISI 304 stainless steel after multi-step pickling.

To understand the pickling mechanism by both HCl and H_2SO_4 in the first pickling step, which has a significant effect on the final surface finish after HF+HNO_3 pickling, weight loss was analyzed step by step as shown in Figure 5, and the surface was characterized by SEM as shown in Figure 6. HCl pickling had much lower weight loss than H_2SO_4 pickling, and the surfaces of both samples were covered with oxide scale (Figure 6(a) and 6(b)). HCl pickling had smooth surface compared with H_2SO_4 pickling. After the second pickling step with HF+HNO_3, HCl pickling had higher weight loss than H_2SO_4 pickling and the intergranular attack became more pronounced on surface finish (Figure 6(c) and 6(d)).

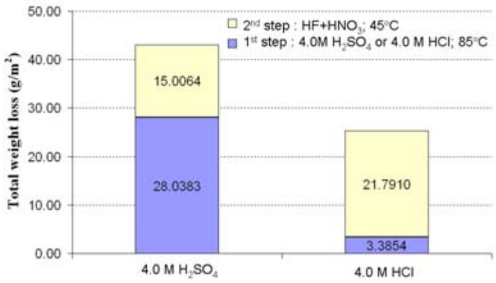
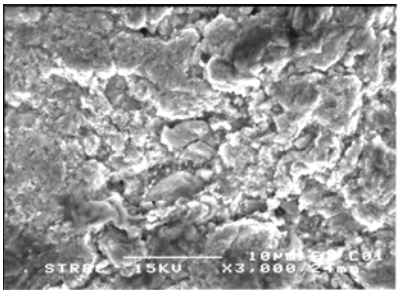


Figure 5. Step by step weight loss of AISI 304 stainless steel after pickling in 4.0 M H_2SO_4 at 85°C or 4.0 M HCl at 85°C followed by HF+HNO_3 at 45°C.

4.0 M H_2SO_4; 85°C

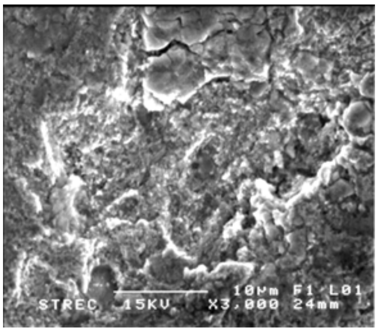
(a)



Roughness (Rq) = 3.81 µm
Remaining oxide level 3

4.0 M HCl; 85°C

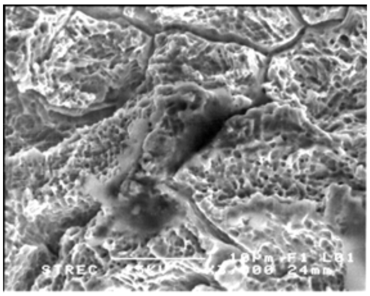
(b)



Roughness (Rq) = 3.15 µm
Remaining oxide level 3

4.0 M H_2SO_4; 85°C
followed by $HF+HNO_3$; 45°C

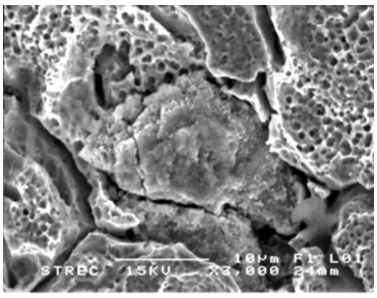
(c)



Roughness (Rq) = 3.29 µm
Remaining oxide level 3

4.0 M HCl; 85°C
followed by $HF+HNO_3$; 45°C

(d)



Roughness (Rq) = 3.34 µm
Remaining oxide level 3

Figure 6. SEM surface characterization of AISI 304 stainless steel after multi-step pickling under the same conditions as in Figure 5.

According to the previous results (Figures 5 and 6) and discussion, the evolution of surface during multi-step pickling in H_2SO_4 and HCl solutions followed by $HF+HNO_3$ can be described as in Figure 7(a) and 7(b), respectively. The original metal surface consists of oxide scale, Cr-depleted layer and base metal. On H_2SO_4 pickling in the first step, H_2SO_4 transports into oxide scale. Then, the Cr-depleted layer is attacked or dissolved. Finally, the oxide scale is removed by undercutting. Most oxide scales, but only some Cr-depleted layers, are removed. The surface is rough because H_2SO_4 pickling behavior is non-uniform dissolution. In the next step of the pickling process by the selective dissolution of $HF+HNO_3$, an intergranular attack appears. The remaining oxide scale and Cr-depleted layer are almost removed. The final surface finish is completely free of oxide scales. The evolution of the surface finish after pickling in HCl followed by a pickling in $HF+HNO_3$ is shown in Figure 7(b). The same mechanism as H_2SO_4 is obtained. However, HCl has lower pickling efficiency than H_2SO_4. Most of the oxide scales and Cr-depleted layers still remain. The observed surface is smooth because HCl pickling behavior is uniform dissolution. By $HF+HNO_3$ pickling in the second step, intergranular attack appears because of a selective dissolution on the remaining Cr-depleted layer.

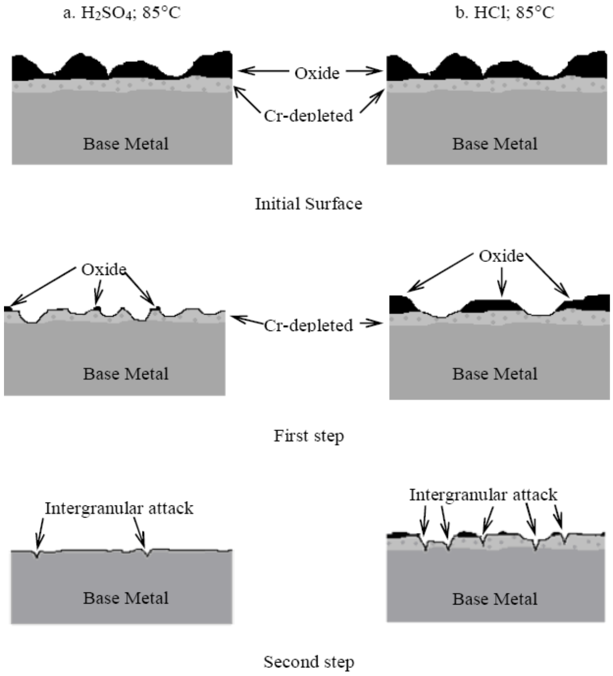


Figure 7. The multi-step pickling mechanism models of intergranular attack.

According to the mechanism, the most important finding is that the surface finish obtained from multi-step pickling is greatly affected by the pickling efficiency of the first step. Multi-step pickling will successively allow achieving a smooth surface finish free of any oxide scale when a high enough pickling efficiency with uniform dissolution in the first step is available. The result illustrates that increasing of HCl concentration and electrolytic currents were not enough to improve its pickling efficiency to be more than the H_2SO_4 efficiency. The addition of H_2O_2, which is a strong oxidizing agent, possibly improved the pickling efficiency of HCl. The temperature for this study must be fixed at 60°C because H_2O_2 decomposes at temperatures higher than 60°C.

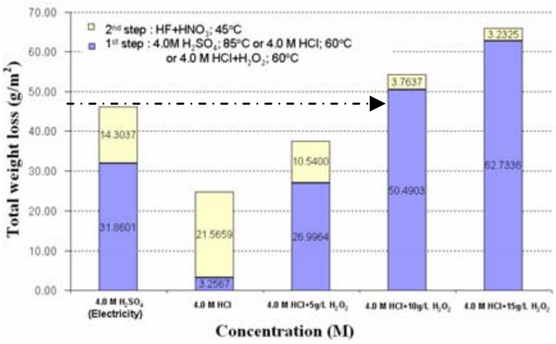
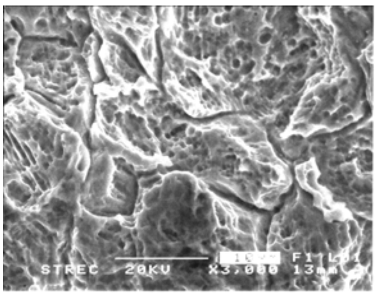


Figure 8. Step by step weight loss of AISI 304 stainless steel by pickling with H_2SO_4 (Electricity) at 85°C or HCl at 60°C or HCl+H_2O_2 at 60°C followed by HF+HNO_3 at 45°C.

Addition of H_2O_2 to improve the pickling efficiency of HCl in the first step resulted in increasing weight loss and effected on the second step pickling by HF+HNO_3 by decreasing weight loss, as shown in Figure 8. It also reduced intergranular attack and delivered a smooth surface finish as shown in Figure 9(c) and 9(d). Multi-step pickling was successive at 10g/L H_2O_2 added to HCl solution. It allowed achieving a higher pickling efficiency than H_2SO_4 efficiency, a smooth surface finish free of oxide scales, and no intergranular attack.

4.0 M H_2SO_4 (Electricity); 85°C
followed by HF+HNO_3; 45°C

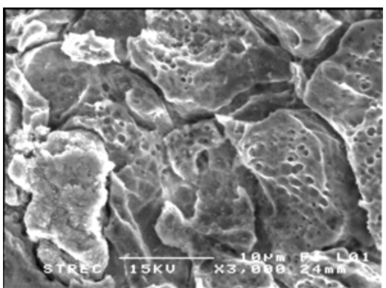
(a)



Roughness (Rq) = 3.30 μm
Remaining oxide level 0

4.0 M HCl; 60°C
followed by HF+HNO_3; 45°C

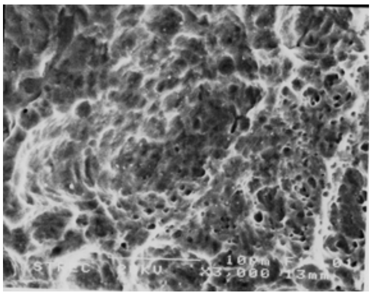
(b)



Roughness (Rq) = 3.24 μm
Remaining oxide level 3

4.0 M HCl+10g/L H_2O_2; 60°C
followed by HF+HNO_3; 45°C

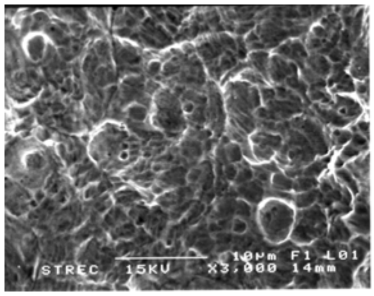
(c)



Roughness (Rq) = 2.92 μm
Remaining oxide level 0

4.0 M HCl+15g/L H_2O_2; 60°C
followed by HF+HNO_3; 45°C

(d)



Roughness (Rq) = 2.95 μm
Remaining oxide level 0

Figure 9. SEM surface characterization of AISI 304 stainless steel after pickling in H_2SO_4, HCl, HCl + H_2O_2 solutions followed by HF+HNO_3 at 45°C.

Conclusions

The multi-step pickling of AISI 304 stainless steel in HCl solution as the first step followed by HF+HNO_3 as the second step was investigated. Mechanism models of pickling by HCl or H_2SO_4 in the first step were proposed. The following conclusions can be drawn from this study:

1. HCl solution has lower pickling efficiency than H_2SO_4 solution.

2. HCl solution can not completely remove Cr-depleted layer and oxide scale.

3. H_2O_2 addition can improve pickling efficiency of the HCl solution. The addition of 10g/L H_2O_2 is enough to deliver a smooth surface without any oxide scales and free of intergranular attack after HF+HNO_3 pickling.

Acknowledgements

The authors would like to thank the Research and Development Center of Thainox Stainless Public Company Limited for test samples, discussion and analysis equipment. We would also like to express our gratitude to the Thailand Research Fund (TRF) and the Office of Small and Medium Enterprises Promotion (OSMEP) for the research fund, content number MRG-OSMET 505034.

References

1. Lacombe, P., Baroux, B. & Beranger, G. (1993). *Stainless steel* (1st ed.). Les Editions de Physique Les Ulis, France.

2. Davis, J.R. (Ed.). (1996). *Stainless steel*; ASM specialty handbook. Ohio, OH: ASM International.

3. Fontana, M.G. (1987). *Corrosion engineering* (3rd ed.); Materials science and engineering series. Singapore : McGraw-Hill.

4. Jones, D.A. (1997). *Principles and prevention of corrosion* (2nd ed.). Singapore : Prentice Hall.

5. Ratanamongkolthaworn, S. (2007). *Effects of sulfuric acid concentration, temperature, ferrous and ferric ion contents on pickling behavior of AISI 304 stainless steel*. Master Thesis in Metallurgical Engineering. Chulalongkorn University.

6. Li, L.F., Caenen, P., Daerden, M., Vaes, D., Meers, G., Dhondt, C. & Celis, J.P. (2005). Mechanism of single and multiple step pickling of 304 stainless steel in acid electrolytes. *Corros. Sci.* **47(5)** : 1307-1324.

7. Li, L.F. & Celis, J.P. (2004). Intergranular corrosion of 304 stainless steel pickled in acidic electrolytes. *Scripta Mater*. **51(10)** : 949-953

.

8. Li, L.F. (2002). Pickling of austenitic stainless Steels. *Internal review report Alz-Arcelor France.*

9. Li, L.F., Caenen, P. & Celis, J.P. (2008). Effect of hydrochloric acid on pickling of hot-rolled 304 stainless steel in iron chloride-based electrolytes. *Corros. Sci*. **50(3)** : 804-810.

10. Li, L.F. (2002). Pickling and re-pickling of stainless steel with UGCO and UG3P $+H_2SO_4$ electrolytes. *Internal review report Alz-Arcelor France.*