Electrochemical Descaling of Metal Oxides from Stainless Steel Using an Ionic Liquid–Acid Solution

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1. INTRODUCTION

Stainless steel is a very strong metal alloy containing Cr and Ni with highly corrosion-resistant properties and is widely used for components of various hardware and equipment, such as many industrial parts of automobiles and aerospace engineering structures. Among various crystalline structures of stainless steel, austenitic (or 300 series) production is up to ∼70%, which is higher than that of other structures such as ferrite and martensite.1 The formation of a thick oxide layer on a matrix surface is generally inevitable during high-temperature manufacturing processes and, therefore, an acid-pickling process is often required before the product engineering of stainless steel.2,3

The acid-pickling process is generally conducted under highly acidic (or alkaline) conditions, with the use of hydrochloric, sulfuric, and mixed acid (HNO3 + HF) solutions, and/or in highly toxic molten salt environments (NaOH + NaNO3) at high temperatures, and it often generates toxic byproducts.4−7 The generation of a high concentration of NOx gas from the use of HNO3 has caused continuous and serious environmental issues, and many countries have begun to apply stricter consolidated regulations to limit and control its emission standard.8−10 Operation of DeNOx (i.e., NOx removal) facilities often requires satisfying the strict emission standard, and therefore, it obviously caused an overall productivity reduction due to the additional financial burden. While a nitric acid-free acid-pickling condition for descaling was developed using hydrogen peroxide with sulfuric acid and hydrofluoric acid,10−14 it still did not reach the sufficient level of descaling efficiency owing to the autoxidation of hydrogen peroxide.15,16

Recently, the use of ionic liquids for descaling has drawn extensive attention owing to the high solubility of many metal ions under ambient temperature conditions as well as their recycling capability and stability.13,14,17−19 We analyzed the tendency of metal extraction/dissolution capabilities of many ionic liquid6,18,20−23 from the collection of many solid matrices and solutions of metal ions (Fe, Cu, Zn, and Cr)24 According to this preceding study, the chemical and physical states of metals in solution and in the oxide scale, particularly, the ionic or oxidation state, is one of the most critical factors to determine the extraction/dissolution efficiencies.6,18,20,21 For example, it was shown that the dissolution or extraction efficiency of the trivalent Fe reached 20−90% within 30 min,20,22,23 whereas it was only 10% for most iron oxides (e.g., FeO, Fe2O3, or Fe3O4) even after 48 h.18,21 Trihexyltetradecylphosphonium chloride ([P66614][Cl]) is known to be the most efficient ionic liquid for dissolving iron oxide, and the mixed solution of [P66614][Cl] + 12 M HCl dissolved up to 65% of iron oxide within 2 h.18 However, the time scale requirement of the industrial manufacturing process for oxide descaling, which is preferably less than several minutes, is still far from the current descaling efficiency, and therefore, the...
The number of CV cycles was varied to analyze the tendency of the dissolution of scales. Figure 1 shows the results obtained by applying 2, 4, 6, 8, and 10 cycles of CV in the 0.17 M [P66614][Cl] + 1 M HCl solution (pH 0.146). The electrolyte solution was composed of [P66614][Cl] + 1 M HCl, which has a much lower concentration of HCl than the previously reported solution ([P66614][Cl] + 12 M HCl, which showed a descaling efficiency of 65% in 30 min).25

These CV results can be classified into two main features. In the first two cycles, the current increases linearly with the increase in the voltage and then decreases linearly (Figure 1a). This is similar to the case of measuring resistances with constant values in CV. That is, in the first two cycles, a large resistance value (because of the scale) causes the entire electrochemical cell to behave as if a resistor of a certain size is connected. However, different types of results were observed after three cycles (Figure 1b–e). In the forward scan, the same result, as if the electrochemical cell was connected to a resistor, was still observed, whereas in the reverse scan, the current density was drastically reduced at the point where the voltage was switched. This can be interpreted as a typical capacitor current density–voltage result. These two features are the result of removal of scales through the first two cycles of CV, and the rest of the cycles expose the matrix to the solution, which behaves as a metal electrode and generates a capacitance. Therefore, when three or more cycles are applied, the surface of the specimen behaves as a resistor in the forward scan, and it behaves as a capacitor formed by a contact between the electrode and the solution in the reverse scan. This tendency becomes evident with the increase in the number of CV cycles. As the number of cycles was increased to 4, 6, 8, and 10, the current density values were further decreased at the switching point. For the reverse scan in CV, the current (i) follows the formula26

\[ i = \nu \cdot C_d \]  

where \( C_d \) is the capacitance generated by the electrode and the solution and \( \nu \) is the scan rate. In the reverse scan, \( \nu \) has a negative value, resulting in a decrease in the current. \( C_d \) is a constant that increases in proportion to the electrode area. That is, as the area of scale removal increases, the capacitance increases owing to an increase in the area where the matrix and the solution are in direct contact. Therefore, as the number of cycles of CV increases, the current density also decreases in the reverse scan. The degree of decrease in the current density gradually increases until the sixth cycle and becomes constant from the seventh cycle onward. These results suggest that most simple dissolution in an ionic liquid may not be an effective way of oxide removal to replace the conventional pickling process. In this study, we introduced a novel electrochemical approach, in conjunction with the use of ionic liquids, to remove oxide from the stainless steel surface under ambient and room temperature conditions. It was observed that the application of an anodic potential on a metal oxide surface in an ionic liquid apparently facilitated the oxide removal process and room temperature conditions. It was observed that the application of an anodic potential on a metal oxide surface in an ionic liquid apparently facilitated the oxide removal process and room temperature conditions.

2. RESULTS AND DISCUSSION

2.1. Scale Removal Using CV in a [P66614][Cl] + HCl Aqueous Solution. The number of CV cycles was varied to analyze the tendency of the dissolution of scales. Figure 1 shows the results obtained by applying 2, 4, 6, 8, and 10 cycles of CV in the 0.17 M [P66614][Cl] + 1 M HCl solution (pH 0.146). The electrolyte solution was composed of [P66614][Cl] + 1 M HCl, which has a much lower concentration of HCl than the previously reported solution (([P66614][Cl] + 12 M HCl, which showed a descaling efficiency of 65% in 30 min).25

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of the scales of the specimen were removed in the seventh cycle.

2.2. Surface Analysis Using Scanning Electron Microscopy (SEM), Energy-Dispersive X-Ray Spectroscopy—SEM, and Surface Profiling. By examining the specimen after applying the potential, it could be observed that the color of the surface to which the potential was applied had changed. When the specimens were observed through visual inspection, only the part used as the working electrode (WE) changed to a bright color (Figure 2a). Therefore, it could be concluded that the scale on the surface of the specimen was removed considerably even if only two cycles of CV were performed. The scanning electron microscopy (SEM) results show that the change in the specimen surface can be identified. In Figure 2b, it could be confirmed that a part of the specimen surface was reliably etched, and the edge of the circle was more etched when the observed circle part was divided into the center and the edge. The change in the chemical compositions on the surface of the etched specimens was observed by energy-dispersive X-ray spectroscopy (EDS)—SEM (Figures 2c and S2). In the EDS—SEM results, among the elements present on the scale, the O atom shows the most remarkable change in the content after CV. The O content is 9.51% for the bare specimens; it decreases to 3.78% after 2 cycles and further decreases to 1.74% after 10 cycles (Figure S3). As O forms the metal oxide in the heat treatment process of stainless steel, it is the most abundant element on the surface. Therefore, the reduction in the O content indicates that the scale is effectively removed from the surface of the specimen.

After removing the scale, the surface profiles were measured to determine the depth from the surface (Figure 3). Compared with the bare substrate (Figure 3a), it was confirmed that the oxide layer on the surface was significantly etched even after only two cycles (Figure 3b). The roughness of the surface to which the potential was applied became remarkably harsh, and some parts were observed to be removed to a depth of ∼5 μm. As the number of cycles increased, the measured maximum depth also increased (Figure S1). To etch the oxide layer, the solution (ionic liquid and HCl) must effectively reach the surface of the specimen through the diffusion process; this diffusion process is faster at the edge than at the center of the circle surface. The plot illustrating the slope change with respect to the depth versus the number of CV cycles shows that, as the number of cycles increases from two to six, the slope of the graph gradually becomes gentle but increases again at the eighth cycle (Figure S1). This indicates that the scale on the surface of the specimen was preferentially removed until two to six cycles and that the etch pattern was changed to remove the matrix of the specimen from the eighth cycle onward.

2.3. Cross-Sectional Analysis Using Transmission Electron Microscopy (TEM) and EDS—TEM. The cross sections of the etched specimens were analyzed by transmission electron microscopy (TEM) (Figure 4). In the bare state sample, the metal oxide was observed on all parts of the surface (Figure 4a). The scale mainly consists of metal oxides including Cr, Mn, Fe, and Si. The scale thicknesses were generally observed to range from 200 to 300 nm and even from 400 to 600 nm in some areas. When the CV was applied twice (two cycles), scales were removed from various parts of the surface, but they remained in many parts of the surface (Figure 4b). However, it was difficult to observe scales in the TEM results when CV was performed for more than four to six cycles (Figure 4c–f). These results indicate that most scales were removed from the surface of the specimen after four to six cycles. Considering the results of CV and surface profiling, it is expected that when CV is applied for more than six cycles, scales can be reliably removed from most surfaces. The constituents of the scale covering the surface of the specimen

![Figure 2](image2.png)

![Figure 3](image3.png)
were analyzed by EDS−TEM (Figure S4). At the top of the scale, chromium and manganese oxide form a thin film, whereas the lower layer shows the formation of a thin film of iron and chromium oxide. The EDS−TEM data show that silicon oxide forms an island or a pillar under the layers. Although the scales of the specimen are composed of various metal oxides, the proposed method can successfully remove most of them.

2.4. Solution Analysis after Applying CV. As the scales removed through CV were contained in the solution, the concentrations of dissolved components were analyzed using an inductively coupled plasma mass spectrometer. Fe, Cr, Mn, and Ni, which are the main components of the scale, were analyzed, and the results showed a similar tendency as the previous surface profiler data, where the concentration in the solution increases as the number of cycles increases (Table 1). This result shows that the suggested descaling method is effective for removing scales on the surface by dissolving the metal oxide.

The concentration of Fe shows a distinct change in the inductively coupled plasma mass spectrometry (ICP−MS) data (Figure S5). The Fe content was significantly higher than that of other elements in all cycles, and the rate of concentration increase in the solution was also higher than that of the other components. This is because iron oxide occupies the largest portion in the scale. In addition, the contents of Cr, Ni, and Mn, which are also the main components of the scale, increase as the number of CV cycles increases. Consequently, the component analysis results of the solution showed the same tendency as the data presented in the previous specimen analysis. It is confirmed that the oxide layer is effectively removed through the electrochemical descaling process in the 0.17 M [P66614][Cl] + 1 M HCl solution.

Table 1. Concentrations of Dissolved Components Measured Using ICP−MS

|          | Fe concentration [mg/L] | Cr concentration [mg/L] | Ni concentration [mg/L] | Mn concentration [mg/L] |
|----------|-------------------------|-------------------------|-------------------------|-------------------------|
| 2 cycles | 15.072                  | 1.766                   | 0.373                   | 0.129                   |
| 4 cycles | 20.898                  | 2.538                   | 0.461                   | 0.156                   |
| 6 cycles | 40.095                  | 4.232                   | 0.815                   | 0.284                   |
| 8 cycles | 69.617                  | 7.206                   | 1.549                   | 0.505                   |
| 10 cycles| 74.930                  | 6.815                   | 1.272                   | 0.477                   |

3. CONCLUSIONS

We proposed a novel electrochemical descaling method of metal oxides using an ionic liquid under ambient temperature conditions instead of the conventional strongly oxidizing conditions using a harsh and hazardous mixed acid (HNO₃ + HF) solution at high temperatures or a strong and hazardous molten salt (NaOH + NaNO₃). It was previously reported that the ionic liquid [P66614][Cl] could dissolve iron oxide up to 65% within 30 min at an ambient temperature when mixed with highly concentrated HCl (0.17 M [P66614][Cl] + 12 M HCl). The descaling efficiency could be significantly improved to eliminate the oxide layer completely within 24−36 s upon application of the electrochemical anodic treatment under even much less acidic conditions (four to six potential sweeps of CV over 0−1.5 V in 0.17 M [P66614][Cl] + 1 M HCl). The descaling efficiency could be significantly improved to eliminate the oxide layer completely within 24−36 s upon application of the electrochemical anodic treatment under even much less acidic conditions (four to six potential sweeps of CV over 0−1.5 V in 0.17 M [P66614][Cl] + 1 M HCl). This result indicated that the optimized electrochemical anodization treatment in an ionic liquid environment could significantly improve the descaling efficiency up to 50−75 times faster than the simple passive and slow dissolution in an ionic liquid and a concentrated acid. The electrochemical extraction mechanism of metals from various oxides in ionic liquid environments is not yet clear, , and it is of interest to elucidate the plausible descaling mechanism in ionic liquids with acid. This is promising for many industrial and commercial manufacturing applications to replace the conventional acid-pickling process.
4. EXPERIMENTAL SECTION

4.1. Reagents. Trihexyltetradecylphosphonium chloride ([P66614][Cl]), hydrochloric acid (HCl, 37%), acetone (99.9%), and ethanol (99.8%) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification. 304 stainless steel was obtained from POSCO (Pohang, Republic of Korea). Masking tape (polyimide film tape 5413 Amber) was obtained from 3M (St. Paul, MN, USA). Millipore water (>18 MΩ·cm) was used in all the experiments.

4.2. Sample Preparation. The specimen used in this experiment is 304 stainless steel. The chemical composition (wt %) of the specimen is 62.5% Fe, 18% Cr, 8% Ni, 11.1% Mn, and 0.4% Si. As shown in Figure 5a, the 304 stainless steel (~2 cm × 1 cm × 0.1 cm) specimen was cleaned with ethanol and acetone for 2 min, and the surface was completely wiped with nitrogen gas to remove dust. The washed specimen was sealed with a masking tape, which had insulation and chemical resistance.27

4.3. Sample Analysis. The surface morphology of the specimen was observed using an optical microscope (Nikon Eclipse LV100ND, Nikon Imaging Korea, Seoul, Korea) and a field emission scanning electron microscope (JEOL JSM-7600F, JEOL Ltd., Tokyo, Japan). The elemental analysis of the surface of the specimen was performed using an energy-dispersive X-ray spectroscopy (EDS) system (Oxford Instruments X-Max, Oxford Instruments, Oxford, UK). In field emission SEM (FE-SEM) measurements, an EDS system was used to analyze the changes in the specific chemical composition in the reaction area. A 2D Surfcoorder (SE3500, Kosaka Laboratory Ltd., Tokyo, Japan) was employed to examine the surface profile. A length of 3 mm was measured centering on the etched specimen. A measuring force of 0.75 mN and a drive speed of 0.2 mm/s were applied using a diamond tip. The pH of the solution was measured using a Benchtop pH meter (LAQUA F-71, Horiba, Fukuoka, Japan). A transmission electron microscope (JEOL JEM-2100F, JEOL Ltd., Tokyo, Japan) was used to observe the surface of the specimen. Elemental analysis of the cross section was performed using an EDS system (Oxford Instruments, Oxford, UK) attached to the transmission electron microscope. After the electrochemical experiments, an ICP−MS instrument (NexION 300 ICP−MS, PerkinElmer, Inc., Waltham, USA) was used to analyze the components of the metal and metal oxides dissolved in the solutions. In ICP−MS analysis, the main constituents of scale were analyzed in parts per million units.

4.4. Electrochemical Measurements for Metal Oxide Descaling. The electrochemical experiments were performed using a CHI721E potentiostat (CH Instruments, Inc., Austin, TX). The three-electrode electrochemical cell had a custom-designed Teflon cell. The metal oxide sample was used as a WE, whereas silver/silver chloride (3 M KCl) and platinum wire were used as the reference electrode and the counter electrode, respectively (Figure 5b). When a metal specimen is connected to a potentiostat as a WE, the scale on the surface of the specimen acts as an insulator and hinders the voltage application. Therefore, the surface of the specimen in contact with the potentiostat was polished with sandpaper to reveal the conductive part. The reaction area of the WE was fixed in a circle of 2 mm diameter using a masking tape. The final area of the WE was 0.031 cm². CV was performed by applying a potential of 0−1.5 V and the scan rate was 500 mV/s. The composition of the solution was 0.17 M [P66614][Cl] + 1 M HCl aqueous solution. When the potential was applied to this system, the interface of the working area with the solution was descaled (Figure 5c).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02163.

- Plot of depth as a function of the number of CV cycles;
- EDS−SEM mapping and spectra of the components;
- Plot of weight percent of O mass fraction;
- EDS−SEM mapping and spectra of the components;
- Plot of cross-sectional image obtained from TEM; and
- Plot of the concentration of each component in the solution (PDF)

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Notes

The authors declare no competing financial interest.

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