Effect of KMnO4 on the HCl-based Pickling Process of 430 Stainless Steel

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Abstract—The effect of potassium hypermanganate (KMnO4) as an oxidant on pickling behavior in HCl-based electrolyte and the surface quality of original hot-rolled and blasted 430 stainless steel (430-SS) plate are studied, using weight-loss tests, microstructure analyses (scanning electron microscope and laser scanning microscope), potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) measurements. The results showed significantly accelerated pickling process for 430-SS by adding KMnO4 through enhanced cathodic reaction rate and reduced charge-transfer resistance (Rt). The weight loss rate of 430-SS is 83.6% higher under the condition of 1wt% KMnO4 than that without oxidant, which grows an enormous 2.33 times with KMnO4 content of 2wt%. The 430-SS plate is left as a total clean one without any oxide layers left or any kind of local corrosion, when 1.5wt% KMnO4 is added. KMnO4 can be confirmed as an appropriate oxidant when many factors such as accelerating the pickling process in the process of the pickling, improving the 430-SS' surface quality, solution recycling possibility and environment protection are considered as a whole.

Keywords-Potassium hypermanganate (KMnO4); 430 Stainless steel; HCl-based pickling; Polarization curves; EIS

I. INTRODUCTION

Pickling process in production of stainless steel is the removal of the oxide layer and the chromium depleted layer produced in heat treatment, in order to gain a smooth and clean finish[1,2]. Different pickling methods can influence the state and microstructure in the surface of stainless steel, and these would further influence the mechanical and anti-corrosion characteristics[3,4].

At present time, a mixture of nitric acid (HNO3) and hydrofluoric acid (HF) is the widely used material in pickling stainless steel. HF is highly toxic, while HNO3 may be deoxidized to NOx or nitrite in the pickling process, both of which could lead to environmental pollution. Furthermore, remaining chromium depleted layer and serious local corrosion are often found in the pickled stainless steel plate, which would downgrade the product.

A new pickling method utilizing hydrochloric acid (HCl) is being developed by our research group in order to solve the problems with the mixed acid pickling process. However, results from our previous work showed low pickling efficiency, left over oxide layer, high roughness of pickled surface and the existence of intergranular corrosion by pickling with HCl alone[5,6]. These problems need to be solved before HCl pickling is useful for industrial application.

Adding oxidants to pickling electrolytes would accelerate the removal of oxide layers and increase pickling efficiency[7]. It is necessary to consider not only the oxidants' accelerating effect and surface quality improvement but also the retrieval and recycling of the pickled electrolytes when an oxidant is being selected.

H2O2 is commonly used as an oxidant in pickling with HCl for stainless steel in many countries of Europe and America [8]. The quality of stainless steel plate pickled with HCl is sensitive with concentration of H2O2, while H2O2 tend to decomposing easily in being stocked, transported or utilized [9]. Furthermore, ions of Fe or Cr are produced in the electrolyte after the first period of pickling, which will also accelerate the dissolving of H2O2. KMnO4 is utilized in the pickling of stainless steel taking advantage of its stability, while its influence to the pickling process and quality of pickled plate is studied, and characterized by electrochemical methods. The outcomes of this research will be of theoretical significance for researching and developing of a new HCl-based pickling technology for ferritic stainless steel.

II. MATERIALS AND METHODS

A. Preparation of samples

430-SS plate samples (thickness of approximately 3mm) are supplied by Taiyuan iron and steel company, with the chemical composition listed in Table 1.

TABLE I. CHEMICAL COMPOSITION OF 430-SS

Element	C	Si	Mn	P	S	Cr	Fe
wt.%	0.12	0.75	1.00	0.040	0.030	16.00~18.00	Bal.

Experimental electrolytes for weight loss and electrochemical tests are developed with deionized water, hydrochloric acid (HCl, 36 wt.%, analytic reagent-AR), and potassium hypermanganate (KMnO4, AR). Among the above agents KMnO4, is pickling oxidant.

B. Simulation of pickling

The 430-SS samples with oxide layers after hot rolling and blasting are placed in a beaker for pickling tests. The samples are horizontally rotating during the pickling process with a rotational speed of 60rpm and a radius of 30mm in order to supply an appropriate dynamic condition to simulate the process of pickling in real applications.

C. Tests and analysis

1) Weight loss tests

Weight differences of the 430-SS samples before and after the pickling process are identified and calculated in the weight loss tests.

The weight loss rate is calculated as followed:

$$\text{错误!未找到引用源。} \quad (1)$$

错误!未找到引用源。 is the weight loss rate in percentage; **错误!未找到引用源。** is the weight before pickling and **错误!未找到引用源。** is the weight after pickling，in grams.

2) Electrochemical measurements

A semiclosed glass container is used as the electrolytic cell for all electrochemical measurements of the HCl electrolytes, with or without an oxidant. Three electrodes are used, one mechanical polished 430-SS plate, one platimun foil and one saturated calomel electrode (SCE) each as the working electrode (WE), counter electrode (CE) and reference electrode (RE). Condition control and data collection of the experiment are accomplished by using an Autolab PGSTAT by Metrohm. Potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) are analyzed and relevant parameters are gained with an electrochemical software NOVA after the measurements are finished.

The WE is first kept at open circuit potential (OCP) until the potential is relatively stable. After this, a potentiodynamic polarization measurement between 0.5V below and 1.0V above the OCP is acquired, by which a curve between potential and current density is produced.

EIS measurements are taken after the OCP is relatively stable and at OCP, over a frequency range from 10-2 Hz to 106 Hz. The AC voltage amplitude is set to ±5 mV.

D. Microstruture examination

Corrosion effects and microstructures in the surface of the 430-SS plate are observed with scanning electron microscope (SEM) after the pickling tests and local corrosive phenomenons of pitting and intergranular are also searched for.

The “degree of finish” of the 430-SS’surface after pickling are measured by confocal laser scanning microscope (CLSM), 3-dimensional colorr pictures are also obtained for the presentation of, among many characteristics for roughness, altitude difference of the surface and roughness Ra as contour arithmetic mean deviation [10].

III. RESULTS AND DISCUSSION

A. Weight loss rates

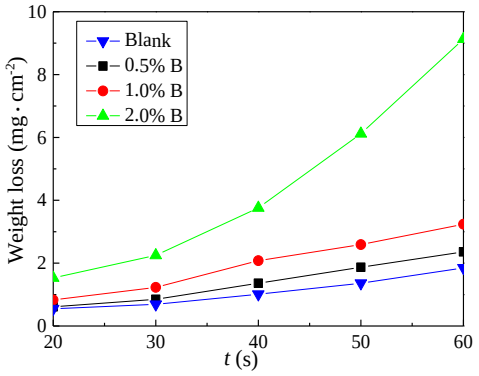

Figure 1. Weight loss rates of 430-SS with various concentration of $KMnO_4$

As is showed in Fig .1, the weight loss rate for 430-SS is magnified with an increasing concentration of KMnO4 and prolonging of pickling. The weight loss rate of 430-SS is 83.6% higher under the condition of 1wt.% KMnO4 after 60s than that without oxidants, which grows an enormous 2.33 times with KMnO4 content of 2wt.%.

B. Microstruture examination

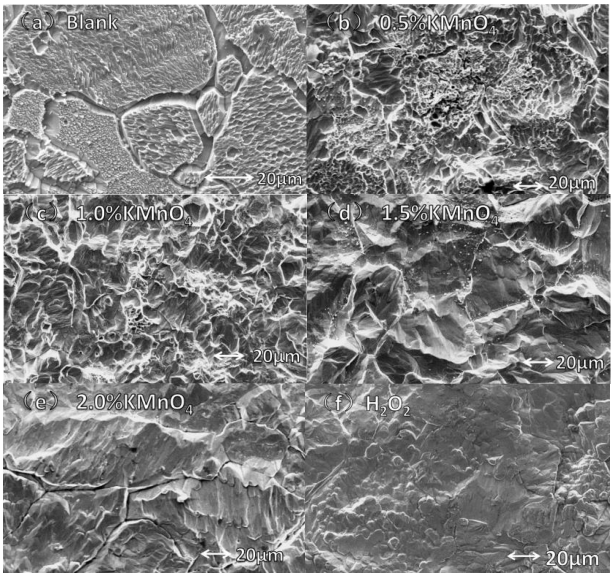

Figure 2. SEM micrographs of pickled 430-SS in HCl electrolytes with (a) no oxidant, (b) 0.5wt.% $KMnO_4$, (c) 1.0wt.% $KMnO_4$, (d) 1.5wt.% $KMnO_4$, (e) 2.0wt.% $KMnO_4$, and (f) H_2O_2.

Fig .2 displays SEM micrographs of pickled 430-SS in HCl electrolytes with (a) no oxidant, (b) 0.5wt.% KMnO4, (c) 1.0wt.% KMnO4, (d) 1.5wt.% KMnO4, (e) 2.0wt.% KMnO4, and (f) H2O2. Intergranular instead of pitting corrosions are found in 430-SS after pickling for 400s in blank HCl solution electrolyte without oxidants (Fig .2a), while remaining oxide layers are found in shorter time. Less oxide layers are found on the stainless steel plate after pickling in the electrolyte with 0.5wt% KMnO4(Fig .2b) than that without oxidant, when the SEM observation is taken after the sample's 50s immersion with any amount of KMnO4 addition; nearly no oxide layers are found in the situation with 1.0wt.%KMnO4(Fig .2c); with more addition of KMnO4(1.5wt.%, Fig .2d), the stainless steel plate is left as a total clean one without any oxide layers left and more smooth; nevertheless, local corrosion, especially intergranular ones are found in the surface of the plate when 2.0wt.% KMnO4 is in the electrolyte for pickling, while the surface quality deteriorating at the same time. Comparing HCl-based pickling containing KMnO4(Fig .2d) with that including H2O2(Fig .2f, pickled in a steel mill) showed similar surface quality and local corrosion of stainless steel plate.

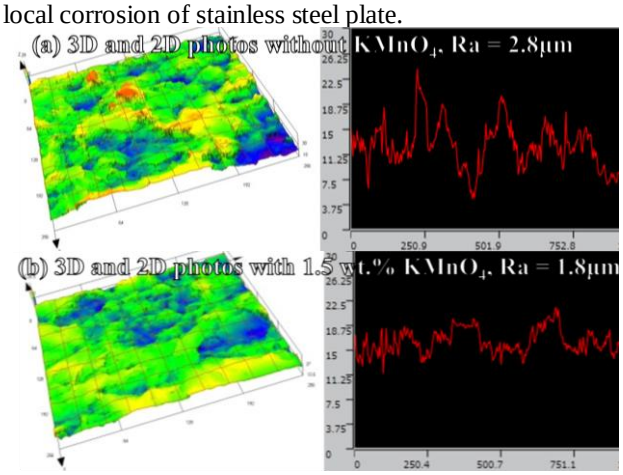

Figure 3. CLSM measurements of pickled 430-SS in HCl electrolytes (a)without $KMnO_4$, (b)with 1.5wt.% $KMnO_4$.

The smoothness of the pickled plate's surface can be directly expressed by roughness. After 100s in HCl electrolytes of 50℃, it can be told from the three dimensional (3D) photos and Ra that 1.5wt.% KMnO4 apparently flattened the plate pickled without KMnO4.

C. Potentiodynamic polarization curves

The basic motivity of a certain polarization process is from the potential difference between the anodic and the cathodic reactions that constituing the process. In the system of electrolyte with only HCl and 430-SS, the motivity is derived from the potential difference between the anodic reaction of metal ion generating and the cathodic reaction of hydrogen absorption.

The specific cathodic reaction happens in the surface of 430-SS in the electrolyte with only HCl is:

$$2H^{+}+2e=H_2\uparrow. \quad (2)$$

Loosing electrons from metals in the surface of the 430-SS to the electrolyte is the anodic reaction of the system, which ends up to corresponding metal ions in the electrolyte:

$$Cr=Cr^{3+}+3e. \quad (3)$$

$$Fe=Fe^{2+}+2e. \quad (4)$$

When KMnO4 is added to the system, for example, the innitial ions reacted from the above such as Fe2+ would be oxidized to Fe3+, a new cathodic reaction is added:

$$Fe^{3+}+e=Fe^{2+}. \quad (5)$$

The polarization process, thus the pickling, could speed up by the way of adding the new cathodic reaction.

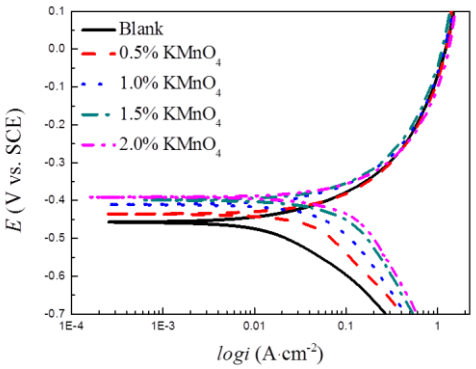

Figure 4. Polarization curves of 430-SS in HCl electrolytes with varying concentration of KMnO4 at the temperature of 50℃

As is shown in Fig.4, cathodic polarization curves shifted right as concentration of KMnO4 increased, while anodic polarization curves are almost still the same. This indicated that the addition of KMnO4 intensified cathodic reactions and increased cathodic current density by adding a new cathodic reaction, meanwhile, surface state of 430-SS in polarizations and the anodic reaction did not change observably.

Parameter values obtained by modeling of the polarization curves in Fig .4 are presented in Table Ⅱ. Ecorr: corrosion potential, icorr: corrosion current density, βa and βc: ethe anodic and cathodic Tafel slopes, and βa/βc ratio of βa and βc. The value of Ecorr shifting positively and the value of Icorr increased gradually upon the concentration of KMnO4 increased, showing an accelerating effect of oxidant on corrosion.

TABLE II. PARAMETER VALUES OBTAINED BY MODELING OF THE POLARIZATION CURVES IN FIG. 4

KMnO4(wt.%)	E_{corr}(V)	i_{corr}(A/cm^{-2})	β_a(V/dec)	β_c(V/dec)	β_a/β_c
0	-0.457	0.019	0.224	0.093	2.409
0.5	-0.437	0.089	0.105	0.070	1.499
1.0	-0.419	0.111	0.315	0.187	1.684
1.5	-0.414	0.141	0.051	0.151	0.330
2.0	-0.413	0.157	0.475	0.254	1.870

The values of βa and βc both increased and βa/βc are bigger than 1 all the time when the three oxidants are added, indicating that the anodic and cathodic polarizations are all strenthend and the control by anodic polarization as behaved in blank HCl electrolyte isn't altered.

The value of icorr for 430-SS in blank HCl electrolyte is only 0.019 A cm-2. It is enhanced to 0.111 A cm-2 by adding 1wt.% KMnO4 and 0.157 A cm-2 by adding 2wt.% KMnO4.

D. EIS measurements

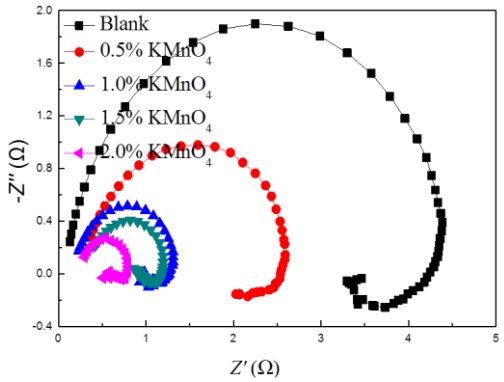

Figure 5. Nyquist plots of 430-SS in HCl-based electrolytes with varying concentration of $KMnO_4$

Fig .5 shows Nyquist plots of 430-SS in HCl-based electrolytes with varying concentration of KMnO4, and Fig .6 is the equivalent electrical circuit for the analysis. All the EIS spectra comprise of a capacitive curve in high frequency with the radius decreased as the concentration of KMnO4 increased; and an inductive curve in low frequency. The shapes of the curves did not change with the addition of KMnO4. Rt is the charge transfer resistance, Rs is the solution resistance and CPE is the constant phase element.

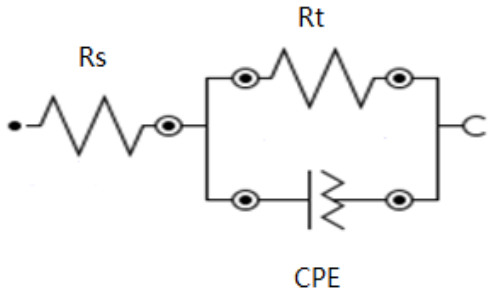

Figure 6. Equivalent electrical circuit for the analysis of the impedance spectra.

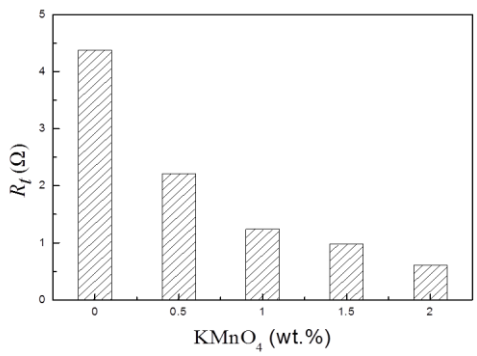

Figure 7. R_t with varying concentration of KMnO4

Fig .7 presents Rt obtained by fitting the experiment results of EIS. Rt declined when KMnO4 is added into the blank HCl electrolyte. An explanation for the phenomena can be that the added KMnO4 enhanced concentrations of adsorbed reactant for cathodic reaction, which lead to a smaller Rt and a faster resolving rate for the 430-SS substrate. Such a theory is also congruent with the enhancement of macroscopic weight loss rate and a greater Icorr obtained in polarization curves.

IV. CONCLUSIONS

The effect of KMnO4 has been studied as an oxidant in the pickling behavior and the surface quality of HCl-based electrolyte on original hot-rolled and blasted 430-SS by weight loss tests, microstructure analyses, potentiodynamic polarization curves and EIS measurements.

The results demonstrated that:

(1). The pickling process for 430-SS can be accelerated significantly with KMnO4 through enhancing cathodic reaction rate and reducing Rt. The weight loss rate of 430-SS is 83.6% higher under the condition of 1wt.% KMnO4 than that without oxidant, which grows an enormous 2.33 times with KMnO4 content of 2wt.%.

(2) The surface quality of pickled 430-SS is altered by varied concentration of KMnO4. The stainless steel plate is left as a total clean one without any oxide layers left or any kind of local corrosion, when 1.5wt% KMnO4 is added to the electrolyte. The surface quality and smoothness of the plate with KMnO4 are almost as good as those with H2O2.

(3) When the pickling process, the pickled surface quality, the factors of recycling of pickled solution and eviroment protection are considered as a whole, KMnO4 is a suitable oxidant for pickling in HCl-based electrolyte of 430-SS.

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