Electrochemical Behavior of Oxide Films of Stainless Steel in 40 kHz Sonicated Sulphate Electrolytes

ZHU Li-qun[a],*, LI Min-wei[a], WANG Hui[b]

[a]School of Materials Science and Engineering, Beijing University of Aeronautics and Astronautics, Beijing 100083, China

[b]Shenyang Liming Aero-Engine Group Corporation, Shenyang 110043, China

Abstract

This paper describes effects of 40 kHz ultrasound on the oxide films of stainless steel in sulphate electrolytes so as to determine the transmitted power and to characterize mass transfer and peak current density on the electrode surface. Emphasis was mainly laid on electrochemical oxidations and peeling mechanism of oxide films in sonicated sulphate solutions (0.5 and 1.0 mol/L). Polarization voltammetry, current response traces and SEM analysis were carried out in order to provide full information as to oxide films surface. Results shows that the rate of electrochemical oxidation, the shape of polarization curves and the surface micrographs in sonicated sulphate electrolytes are different from those obtained without introduction of ultrasound. It is concluded that ultrasound can change the electro-chemical behavior of oxide films by its cavitaion effects, which would produce transient mechanical impulsive force and enhance electrochemical reactions.

Keywords: stainless steel; oxide films; electrolysis; ultrasound; cavitation

1 Introduction

Oxide films are easy to grow on the surface of stainless steel when a machine part is subjected to heat treatments or brought into operation. Half-baked films will usually accelerate the surface electrochemical corrosion of base metal, and thus formed oxides will also promote surface stress corrosion[1]. Therefore, to remove these films from stainless steel appears essential for protecting working parts and ensuring further processing on accessories.

There are mechanical, chemical and electro-chemical methods to remove oxide films[1] in recent published literatures. However, they have many problems inclusive of mass consumption of energy, heavy corrosion and serious environmental pollution waiting to be solved. On the other hand, as a typical and effective method of removal of oxide films, the character of electrolysis is well documented; whereas, few literatures as to combining electrolysis with ultrasound to remove oxide films from stainless steel surface have been made public. With its wave 20 to 100 kHz in length propagating through liquid media and thereby inducing strong mechanical, physical and chemical effects on interface of solid and liquid, the ultrasound is well known for its increasing mass transfer in electrochemical processes[2, 3]. It is also known that both acoustic streaming and cavitational effects make a significant contribution to the increase in observed currents[4-6].

In this paper, preliminary findings are presented on the electrochemical behaviors of oxide

*Corresponding author. Tel.: +86-10-82317113.
E-mail address: zhulq@buaa.edu.cn

films of stainless steel treated in 40 kHz sonicated sulphate electrolytes. It also indicates the effects of ultrasound on electrochemical parameters such as limited currents and polarization curves.

2 Experimental Procedure

All experiments were carried out at the room temperature (20 ± 2 ℃) and atmospheric pressure with a constant ultrasonic frequency of 40 kHz, and in 0.5 mol/L and 1.0 mol/L solutions prepared with pure water. A specially designed case was built to accommodate an ultrasonic source i.e. a generator of ultrasound and a container of ultrasound (shown in Fig.1). Electrochemical experiments were performed using a conventional tri-electrode assembly connected to a potentiostat. The working electrode was situated opposite and parallel to the Luggin capillary horn face. The Hg/HgO reference electrode filled with saturated KCl (E_{eq} = 0.244 4 V) was held in a side arm. The counter electrode was made of stainless steel.

1 − Hg/HgO refererce electrode   4 − Cathode (stainless steal)
2 − Anode (sample)   5 − Generator of ultrasound
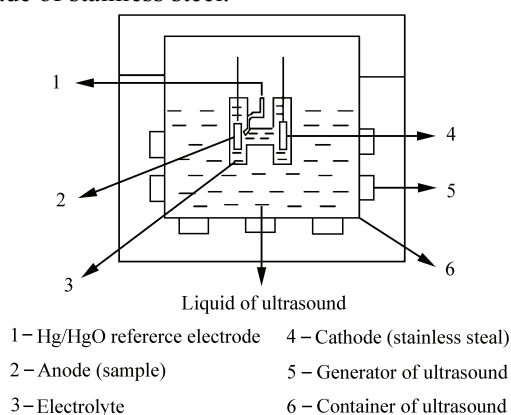3 − Electrolyte   6 − Container of ultrasound

Fig.1   Diagram of the experiment.

Plate-samples, measured 30 mm by 25 mm, were made from 1Cr18Ni9Ti stainless steel. After being treated at over 1 000 ℃, thick and compact oxide films formed on the stainless steel samples mainly consisted of NiO, Cr_2O_3 and un-dissolved $FeO \cdot Cr_2O_3$[7].

Considering the physical aspect of ultrasound, it is important, with various electrical input powers, to determine the transmitted power as a function of the liquid height. Measurements were based on the calorimetric method[8]. The absorbed acoustic power,

P, was calculated as follows

$$P = mC_p(dT/dt) \qquad (1)$$

where m is the mass of water (kg), C_p the specific heat capacity of water (4 180 J·kg^{-1}·℃$^{-1}$) and (dT/dt) is the temperature rise per second (K·s^{-1}). Supposing that the mass of water equal to 1.0 kg was constant, the temperature was measured at time intervals during sonication through a total length of 8 min.

Mass transfer rate measurements in sonication were performed using the electro-diffusion method[9, 10]. Traditionally, as an utmost important parameter, the limited current is able to give out a direct measurement of the mass transport on electrode surfaces. The simple approach of a planar diffusion layer model employed in several studies is

$$i_{lim} = nFDAc/\delta \qquad (2)$$

where i_{lim} is mass transport-limited current density (A·m^{-2}), F is the Faraday constant (96 500 C·mol^{-1}), n is the number of exchanged electrons, A is the electrode area (m^2), and c is the concentration of electro-active species (mol·m^{-3}). Given the unknown diffusion layer thickness δ, it is possible to quantify the kinetics of chemical process coupled to the electron transfer.

3 Results and Discussion

3.1 Ultrasonic parameters measurements

If the distance between the generator of ultrasound and the liquid surface is set to be $\lambda/4$ multiple values, a steady-state wave system takes place in the reactor, and the distance separating a minimum of pressure from a maximum one is $\lambda/4$[11]. As shown in Fig.2, the transmitted power increases with the height of liquid except that when the distance between the generator and the water surface is set to be a $2\lambda - \lambda/4$ multiple value, transmission yields ranging from 60% to 84% and two maximum transmitted powers will be recorded at electrolyte heights corresponding to $2\lambda - \lambda/2$ and $2\lambda + \lambda/4$, which attests to the height of liquid being able to affect the transmission of ultrasonic waves.
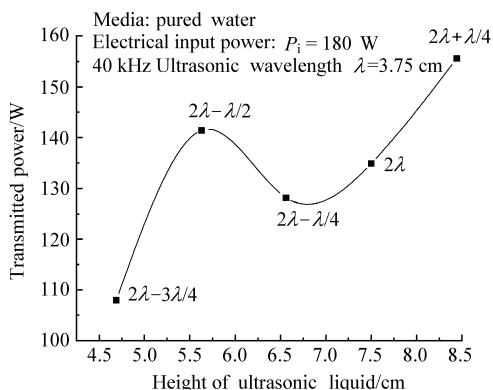
Fig.2   Ultrasonic power as a function of height of liquid in the reactor.

3.2 Mass transfer variations

A mass-transport-controlled current response (limited current) can be detected from the sono-voltammogram[12]. Fig.3 gives out detailed information about the effects of the considerable changes in ultrasonic input power on the limited current.
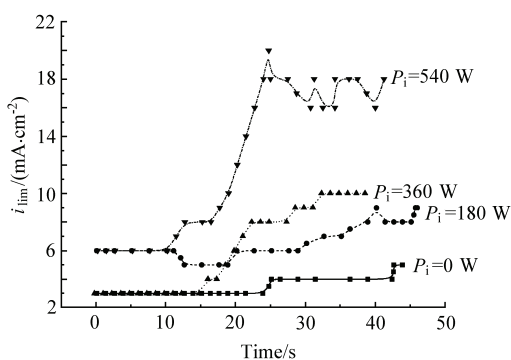

Fig.3   Current response traces for the sonoelectrochemical (8.5 cm electrode-to-generate distance) oxidation in 1.0 mol/L sulphate electrolyte with the potential of E_{app}= 0.9 V vs. SCE.

Fig.3 shows clear discriminations in these current response trace curves. i_{lim} rises dramatically as the ultrasonic power increases when the polarization lasts more than 15 s, and many current peaks will be present during the last polarization period. From Eq.(2), it follows that diffusion layer thickness δ decreases evidently as ultrasonic power increases, and, moreover, the mass transfer will be enhanced by ultrasonic cavitations indicative of substantial cavitational action on the electrode surfaces.

3.3 Effects of ultrasonic power in 1.0 mol/L sulphate electrolyte

Fig.4 shows potential sweep experiments ac-

complished at 10 mV/s under both silent and sonicated conditions. The current potential (*i-E*) curves exhibit typical polarization behaviors. In the case of potentials below 0.6 V vs SCE, the global current is mainly generated by the transformation of O_2 and OH^- to the active radical [O]. With $E > 0.9$ V vs. SCE, the current starts to become positive as the anodic oxidation process becomes predominant. This corresponds to an active oxidation of oxide films. By AAS and ICP-MS analysis, there are Fe and Cr ions found in the electrolyte, where the impossible reactions of anodic oxidations are illustrated as follow

$$2FeOCr_2O_3 + 7O - 14e \rightarrow Fe_2O_3(CrO_3)_4$$
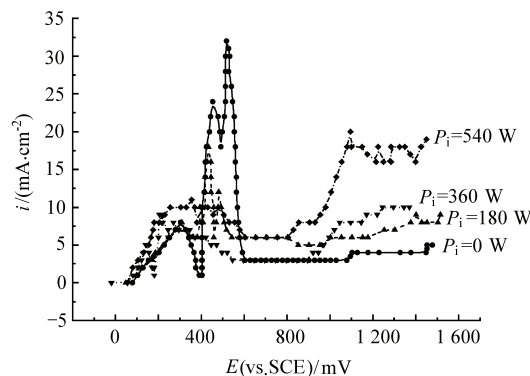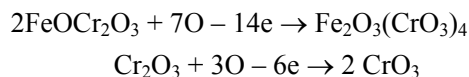$$Cr_2O_3 + 3O - 6e \rightarrow 2\,CrO_3$$

Fig.4   As a function of the ultrasonic power, polarization curves obtained on stainless steel covered with oxide films immersed in 1.0 mol/L sulphate electrolyte.

In the case of oxidation developed under a silent condition, the current will increase slowly approaching an almost constant value; in contrast, current plateau and current oscillations appear under an ultrasonic condition, where the plateau is induced by the local mass transfer change, while strong current oscillations are associated with pressure fluctuations produced by the ultrasound. Besides, the cavitations also produce pressure on loose oxides that results in oxides peeling off and oxidation expanding into the inner oxide films. Evident, the effects of ultrasound on the electrochemical behaviors of oxide films in 1.0 mol/L sulphate electrolyte demonstrates itself in accelerating electrochemical reactions characterized by current enhancements as the ultrasonic power increases.

3.4 Effects of ultrasonic power in 0.5 mol/L sulphate electrolyte

Similar experiments were performed in dilute sulphate solution (0.5 mol/L), where the obtained shape of the polarization curve resembles that mentioned above except in the case of potential below 0.6 V (see Fig.5).
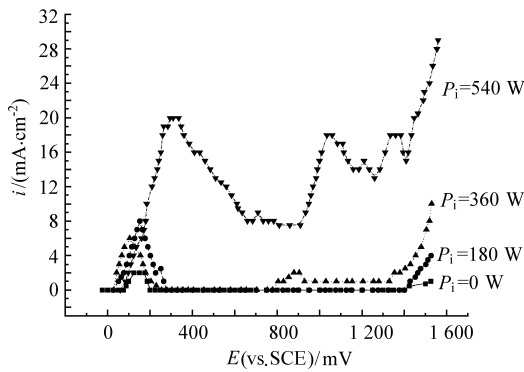

Fig.5 Polarization curve obtained on a stainless steel covered with oxide films immersed in to 0.5 mol/L sulphate electrolyte as a function of the ultrasonic power.

The influences of ultrasound are also similar to that observed in 1.0 mol/L sulphate but to a lower extent except with an input power of 540 W, where ultra-sound will activate anodic surface leading to higher current peaks of transformation of O_2 than under the silent condition below 0.6 V vs. SCE. The range of potential that keeps the polarization current constant is 500 mV higher than 250 mV in 1.0 mol/L sonicated sulphate. It could be deduced that low concentration will prolong the activating time of oxide films and decrease the rate of oxide films' oxidation. The fact that, under the condition of 540 W input power, the current increases visible during the whole polarization process is so strange an electrochemical behavior that would be ascribed to the rise of temperature.

3.5 Effects of ultrasound on sample surface

Stainless steel samples were electrolyzed for 5 min at $i = 2.0$ A·dm^{-2} and in both 1.0 and 0.5 mol/L sulphate solutions. Experiments were carried out under both silent and sonicated conditions ($P_i = 180$ W).

Without irradiation, the sample prepared in silent 0.5 mol/L sulphate (Fig.6(b)) has a rough surface with small corrosive points and micro-apertures present in the SEM photographs. As the concentration of sulphate increases, the loosening and roughness become obvious (Fig.6(c)).
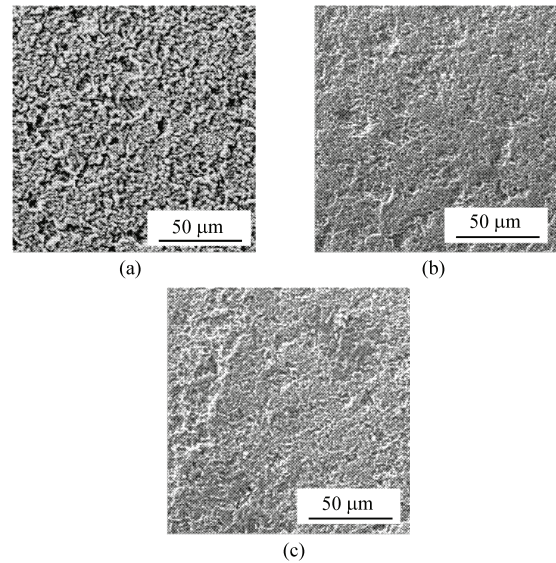

Fig.6 Changes of SEM photograph of stainless steel surfaces after 5 min immersion under silent conditions at $i = 2.0$ A·dm^{-2}. (a) primary surface; (b) in 0.5 mol/L sulphate electrolytes; (c) in 1.0 mol/L sulphate electrolytes.

After irradiation, big changes in micrograph take place under the sonicated condition. Fig.7(c) exhibits that the base metal are featured by a smooth and fresh surface without visible micro ostioles and loose oxides except an existence of few dark oxide films after treatment in 0.5 mol/L sonicated sulphate (Fig.7(b)).
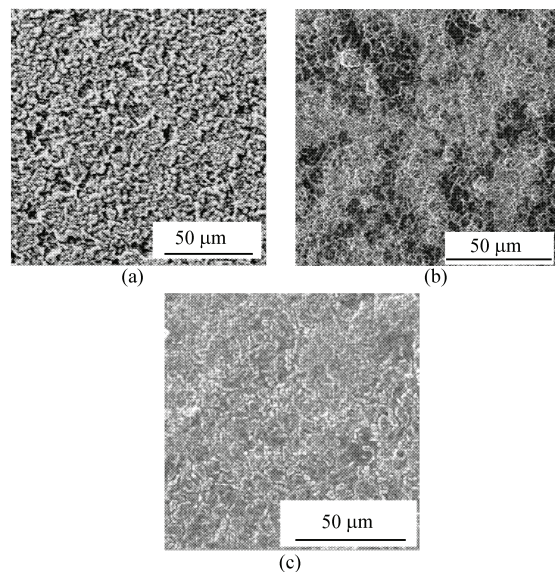

Fig.7 Changes of SEM photograph of stainless steel surfaces after 5 min immersion time with 180 W input power at $i = 2.0$ A·dm^{-2}. (a) primary surface; (b) in 0.5 mol/L sulphate electrolytes; (c) in 1.0 mol/L sulphate electrolytes.

Results illustrate that cavitations release highly energetic micro-streams towards the electrode surfaces, thus producing mechanical impacts and electrochemical changes in the electrolysis process. The shorter treatment time and more uniform current distribution which will improve the surface quality of stainless steel; further, the increased concentration of sulphate will raise the efficiency of electrolysis.

4 Conclusion

Preliminary investigations have been carried out to characterize the power transmission in the reactor and disclose the effects of ultrasound on electrochemical behaviors of oxide films in the electrolysis process. The results of calorimetric measurement show that the distance between the transducer and the liquid surface set to be $2\lambda - \lambda/2$ or $2\lambda + \lambda/4$ will produce the maximum transmitted power and enhance the effects of cavitation. Electrochemical measurements as well as SEM analysis reveal the ability of ultrasound to decrease the active potential and increase the oxidation current when $E > 0.9$ V. The increase of ultrasonic power will reduce the diffusion layer thickness δ and increase the limited current $i_{\lim}$ significantly. The comparison of the shapes of polarization curve shows a falling current peak of transformation of O_2 and a much broader range of the potential to keep the current constant when the concentration of sulphate reduced from 1.0 mol/L to 0.5 mol/L. The surface micrograph of stainless steel after treatment in sonicated sulphate looks smoother than that obtained under the condition without ultrasound. It is concluded that the introduction of ultrasound changes the electrochemical behaviors of oxide films due to the cavitaional effects of producing transient mechanical impulsive force on oxide films and enhancing electrochemical reactions.

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Biography:

ZHU Li-qun   Born in 1955, he received a B.S. degree from Beijing Institute of Aeronautics and Astronautics in 1977, and since then has been working as a teacher in it. He also received a master degree in 1988 and a doctoral degree in 1998. From 1980 up to present, he has joined cooperative research work in the realms of advanced surface technologies, electrochemistry, surface protection and materials corrosion and so on. He has published 6 books and more than 70 scientific papers in various periodicals.

E-mail: zhulq@buaa.edu.cn