Influence of Mechanical Surface Treatments on Oxide Films Properties Formed on 304L Stainless Steels in Simulated BWR and PWR Primary Water

	Kathleen Jaffre
	Tohoku University
	11301 20076
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カタリーン　ジャフェ

氏　　　　　　　名	Kathleen Jaffré
研究科，専攻の名称	東北大学大学院工学研究科（博士課程）量子エネルギー工学専攻
学 位 論 文 題 目	Influence of Mechanical Surface Treatments on Oxide Films Properties Formed on 304L Stainless Steels in Simulated BWR and PWR Primary Water （BWR および PWR 一次系冷却水模擬環境での 304L ステンレス鋼 の酸化皮膜特性に及ぼす機械的表面処理の影響)
論 文 審 査 委 員	主査　東北大学教授　渡邉　豊　　東北大学教授　秋山　英二 教授　Bernard Normand　　東北大学准教授　阿部　博志 （INSA Lyon）

論文内容要約

Some mechanical surface treatments can be applied during the lifetime of nuclear components, in post-treatment during production finishing or in case of repair. These surface treatments have an influence on the mechanical properties but also on the corrosion behavior of the components. Many components are made of stainless steels because of their good mechanical properties and their resistance to corrosion. The objective of this work is to determine the influence on the surface condition of stainless steel 304L (SS) and its oxidation behavior during exposures in a simulated BWR and PWR environment.

An austenitic stainless steel 304L was chosen as the test material. This material is the most common austenitic grade used for chemical process equipment, heat exchangers, or nuclear power plants. Several surface treatments were selected in order to compare the results and try to identify the most critical surface properties. The surface treatment by dry grinding was selected as it is used in the industry. The mechanical polishing 2400 SiC and 1 μm then a polishing with colloidal silica were selected. Polished samples are known to induce fewer surface changes than grinding, and, colloidal silica is known to remove surface defects caused by previous polishing. The samples were prepared from the as-received material sheet to distinguish the role of the different parameters related to surface modifications.

One series corresponds to a manually ground surface. The grinder surface finish was first prepared with Green Ace Gold and then with the Mac flat disc. Each grain of abrasion on the wheel's surface cutted small chips from the workpiece via shear deformation. The other three sets of samples were the polished samples of the plate as received. The first series was polished with emery paper down to 2400 SiC (320, 600, 1200, and 2400) while the second was polished with several emery papers and diamond paste, down to 1 μm (320, 600, 1200 and 2400, 3μm and 1μm) and the last one was polished at a superfinishing step with colloidal silica suspension (OPS). Then, the characteristics of these surfaces were compared as well as their behavior in oxidation.

To describe the microstructural modification induced by the different surface treatments, subsurface characterizations were first performed. The characterization techniques used are scanning electron microscopy (SEM) to observe the surface. Transmission electron microscopy (TEM) was used to observe the microstructure in cross section. The 3D optical profilometer was used to characterize the surface roughness (RMS). And, X-ray diffraction (XRD) was used to measure the residual stresses.

Then, the reactivity of the selected surfaces was evaluated in a first step at low temperature. Then, the reactivity of these surfaces was evaluated in simulated REB and REP environment in order to get closer to the real conditions of exposure of the materials. At room temperature, passive films were characterized and at higher temperatures, oxides were characterized.

Only few studies have made a link between the surface properties due to mechanical surface treatment and the electronic properties of passive films and oxides. Therefore, in this PhD work the link between these two aspects will be made. In addition, the relation between the resistance of the passive film and the properties of the film will be made via the electronic properties.

Passive film and oxide layer characterizations were carried out in an electrochemical cell containing an acid boric/borate buffer solution H3BO3 (0.05 M), Na2B4O7 10H2O (0.075 M) (pH=9.2), at room temperature and atmospheric pressure. This solution was selected because the oxides formed on stainless steel exhibit very low

solubility. Then, this solution is perfect for characterizing ex-situ the properties and features of the different grown oxides. The passive films were grown for 24h in this solution at room temperature before the characterization. Oxidation tests were conducted in an autoclave to simulate the industrial conditions of primary water reactor (PWR). The environment was simulated with a solution of boric acid (500 ppm B) and lithium hydroxide (2 ppm Li), and 2.7 ppm H2 in pure water. Specimens were placed in the autoclave chamber. The pressure and temperature are set at 15 MPa and 325°C, respectively, for 120 hours. After the test, the autoclave was cooled to room temperature and purged to extract the oxidized specimens. In parallel, boiling water reactor (BWR) exposure tests were carried out in autoclave. A pure water solution simulates the primary water. Pressure and temperature were set at 10 MPa and 288°C, respectively. In a BWR environment, the pressure is lower than in the simulated PWR environment, resulting in presence of a vapor phase. Besides, the O2 concentration is controlled inside the BWR autoclave.   Artificial air-saturated water was fed to the autoclave. About 8 ppm O2 was included in the feed water under atmospheric pressure. The autoclave is refreshed, with a flow rate 10 mL.min-1, the volume of the vessel is 1.2 L and the outlet conductivity is 0.3 μS.cm-1. As for PWR exposure, the duration for BWR exposure was fixed at 120 h to characterize the first stage of oxidation in this environment.

Since the passive films and oxides are defective, they can be assimilated to semiconductors.   The defects being the dopants (donors and acceptors). It is then possible to characterize the semiconducting properties of passive films and oxides in order to have more information on the corrosion behavior and to be able to link the surface properties to the corrosion behavior. This work focused on the characterization of passive films and oxides using the same methodologies. The methodologies were first implemented for the characterization of passive films and then transposed for the characterization of oxides.

The topology of the oxidized surfaces was characterized by SEM. The morphology of oxides was characterized by TEM. The elemental maps of the oxides were obtained by TEM - EDX coupling. XPS was used to determine the composition of passive films and oxides. The electrochemical properties of the passive films and oxides were characterized by measurements at the open circuit potential, polarization curve and impedance measurements. The semiconducting properties were determined using an electrochemical protocol, based on electrochemical impedance spectroscopy coupled with Mott-Schottky analysis. This protocol was first set up to study the properties of passive films formed on stainless steel in a boric acid/borate buffer solution at room temperature as a function of the surface treatment. Then, it was transposed to determine the properties of oxides formed on the different surfaces in autoclave. However, this was done ex-situ in the borate acid solution. This protocol worked well on the oxides formed at higher temperatures after 120 h of exposure. The characterization methodology developed for passive films is robust and transposable to thicker oxides (oxidation in simulated REB and REP medium). Moreover, pitting resistance of the passive films formed after 24 hours in the borate buffer solution at ambient temperature were tested in a saline solution (2.5 M NaCl) at pH 6.5.

The first part of the study, on the influence of mechanical surface treatment on the surface state of the material shows, that the ground surface (Figure 1: Grinding) is characterized by intense and deep scratches related to abrasion mechanism degradation resulting in high roughness. The top surface of the ground specimens has an ultrafine grain layer and high plastic deformation so there is a high density of dislocations, removal of material in certain areas, high residual compressive stresses and high roughness. Whereas, the two polished surfaces (Figure 1: 2400 SiC, 1 μm (Diamond paste)) have only an ultra-fine grain layer, scratches and roughness but less than for the ground surface. The compressive stresses of the polished surfaces are also less than for the ground surface. The polished surface with CS does not have this ultrafine grain layer nor any residual stress. Consequently, the polished sample with CS can be considered free of surface defects (Figure 1: Colloidal Silica), microstructure change, and residual compressive stress. Indeed, this last polishing step allows to eliminate all the surface modifications generated by the previous polishings.

Thus, each surface treatment affects the surface state differently. This confirms that the experimental conditions were well selected. Mechanical surface treatment influences the surface condition of stainless steel. However, it has been difficult to dissociate the effects of the ultrafine grain layer, compressive stresses and roughness on the oxidation behavior. Indeed, the mechanical surface treatments generate these modifications which are difficult to generate in an isolated way. It would be necessary to think of carrying out the tests with other methods in order to see the influence of each parameter without the other parameters.
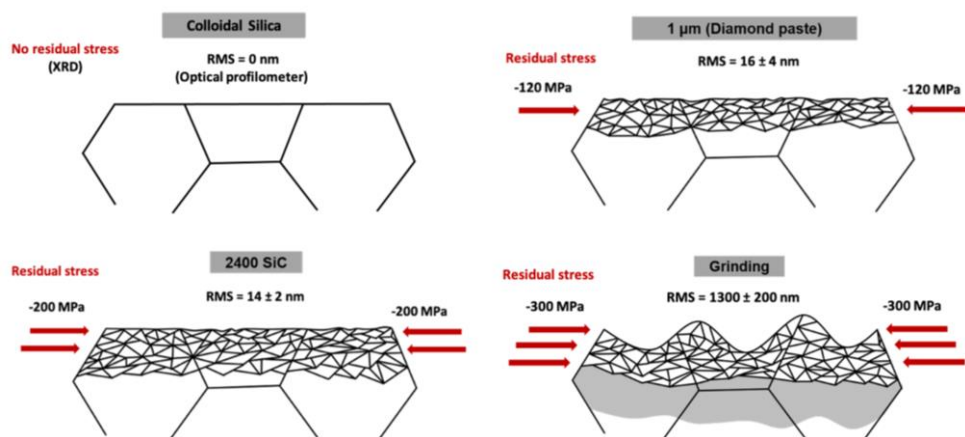
Figure 1. Schematics of surface modifications after mechanical surface treatment on 304L specimens, CS, polished samples down to 1 µm with diamond paste, polished samples down to 2400 with SiC and grinding process.

The second part of the study, on the passive behavior shows that the passive films formed (Figure 2) have a duplex structure composed of outer iron-enriched oxide/hydroxide layer and an inner chromium-enriched oxide layer. The overall passive behavior in the borate buffer solution is similar for all samples. This means that the composition is approximately the same, except for the grinding condition, but the difference is not huge. Thus, the electrochemical behavior is also approximately the same because it depends on the composition. There is a slight difference for the grinding condition. Whereas, results reveal that the number of doping species, the capacitance value, and the passive film's thickness are influenced by the roughness, the defects on the surface, and the residual compressive stresses. Consequently, the passive film formed on the more disordered and reactive surface is the thinnest and the less stable. The ongoing study corroborates this conclusion by evidencing an enhanced reactivity when the sample is immersed in a chloride environment.

The last parts of the study, show that for samples exposed to the simulated PWR and BWR environment, the oxide formed (Figure 2) has a duplex structure composed of outer precipitates iron-enriched oxide/hydroxide and an inner chromium-enriched oxide layer. The oxides formed in the simulated PWR, are rich in Cr and Fe, while, the ones formed in the simulated BWR are richer in Ni and poorer in Cr. For PWR, the outer oxide precipitates are larger, denser, and the Ecorr is more anodic than for the BWR environment. Thus, simulated BWR environment is more oxidizing than the PWR one. Indeed, dissolved oxygen is oxidizing and dissolved hydrogen is reducing. Both have an effect on the thermodynamics and kinetics of the oxidation.

For both environments, the density of the outer oxide crystallites is higher for G sample than for the polished sample down to 2400 SiC. It is worth noticing that the ground surface's outer oxide precipitates' size is the largest. So, the ground surface immersed in the solution oxidizes more rapidly than a polished surface. Indeed, the ultra-fine grain layer, acting as a diffusion short circuit, promotes the dissolution of metallic elements and the formation of large crystallites in the outer oxide. While, on polished surface with CS, no large oxide precipitates were observed. There are small oxide precipitates rich in Fe and Ni embedded on the inner oxide's surface for CS sample. According to surface preparation, the evolution of inner oxide thickness follows the same trend for both environments. It increases following G surface, polished surface down to 2400 SiC, and, polished surface with CS. The inner oxide on the G surface is more evolved than on the polished surfaces. For samples exposed to PWR and BWR environments, the donor density increases as the oxide film thickness decreased. On the ground surface for both BWR and PWR the Cr enrichment in the inner layer is higher than for polished surfaces. Thus, the surface state after surface treatment only impacts the oxidation kinetics due to the modifications of the surface. As a result, the density of the outer oxide crystallites is higher for the G sample than for the polished sample down to 2400 SiC. The G sample immersed in the solution oxidizes more rapidly than a polished surface. Indeed, the ultra-fine grain layer, acting as a diffusion short circuit, promotes the dissolution of metallic elements. Regarding the surface preparation process, thicker oxide grows on smoother and less deformed surfaces. The present work shows that stress, ultrafine grain layer, and roughness play a more critical role in corrosion kinetics. However, they don't significantly affect the electrochemical reactivity in the borate buffer solution. Indeed, polarization curves are similar for the three surface states, probably because all oxides have approximately the same composition.

Therefore, surface treatment doesn't significantly impact the chemistry of the oxide.

In summary, for the passive film formed in the borate buffer solution and the oxides formed in the simulated BWR and PWR environments there is some common conclusions. Such as, that the modifications of surface have an impact on certain properties of the passive films and the oxides. And, the surface defects could accelerate the growth kinetics of the passive film and oxides. The more disordered the surface (grinding), the greater the oxidation kinetics. The capacitance of the inner oxide formed on the ground surface is higher than for the other conditions. Moreover, there is a decrease in the donor density with the degree of surface finishing. And, the thicker the inner oxide, the lower the doping density. There are also some differences (Figure 2), at room temperature there is migration of species within the passive film while for water at high temperature there is diffusion of species through the oxide. This is why the thickness of the oxides is greater than that of the passive films. Moreover, chromium oxide behaves like a p-type at room temperature, but like an n-type at higher temperatures.

Last but not least, the oxide grown's electrochemical reactivity is more affected by the environment chemistry than by the surface treatment.
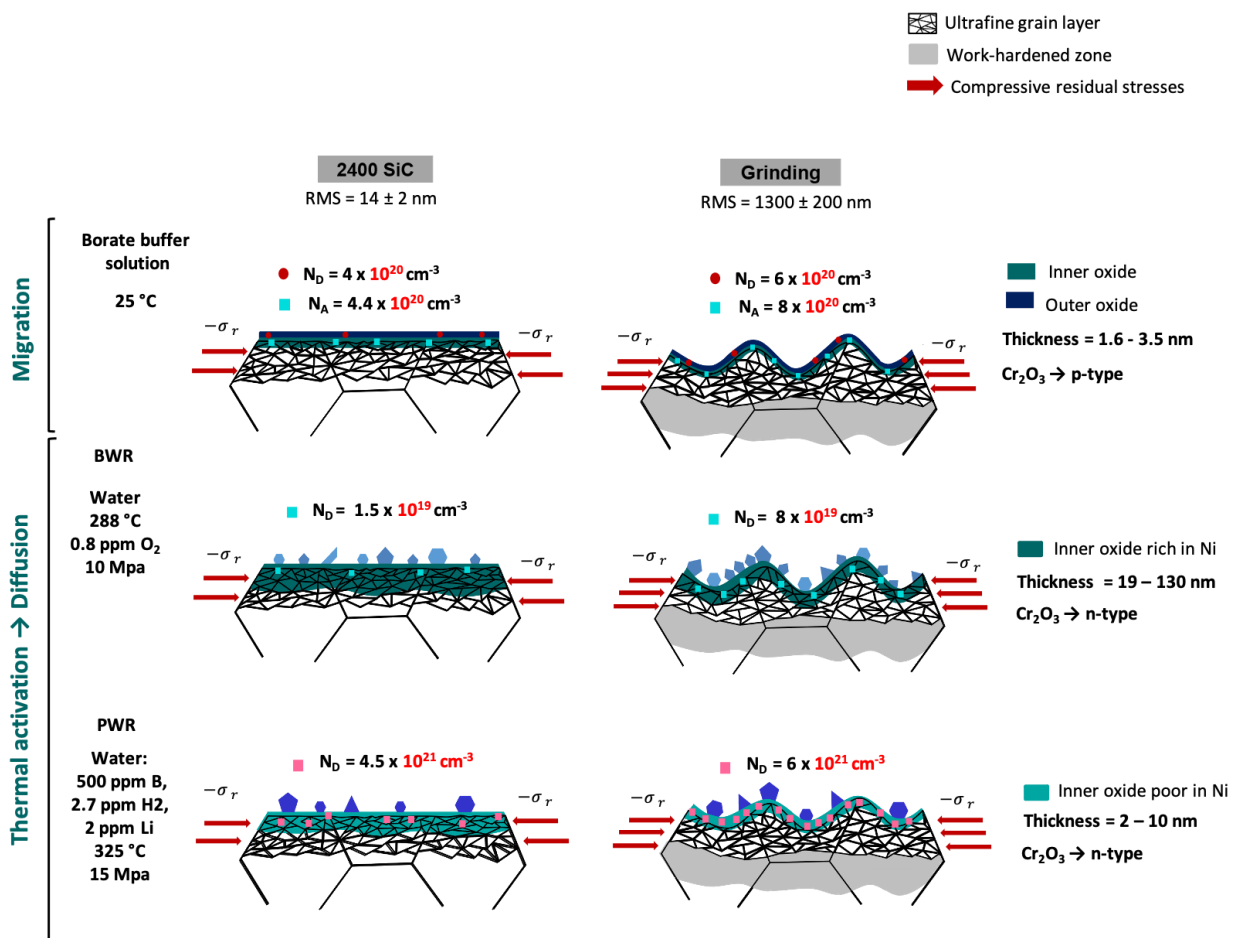

Figure 2. Schematics of passive films formed on polished samples down to 2400 with SiC and grinding process in the borate buffer solution. And, oxides formed on polished samples down to 2400 with SiC and grinding process in the simulated BWR and PWR environments.