Mechanical and electrochemical behavior of nanocrystalline surface of 304 stainless steel
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Abstract
This paper reports our recent studies on nanocrystalline surface layer of 304 stainless steel (304SS) produced using a sandblasting and annealing process. The grain size of the sandblasted surface layer was less than 20 nm. Mechanical and electrochemical properties of the nanocrystalline surface and its passive film were investigated using nano/micro-indentation, micro-scratch, scanning Kelvin probe (SKP), potentiodynamic scanning and electrochemical scratch techniques. It was demonstrated that the nanocrystalline surface was markedly superior to that of original 304SS with enhanced passive film. The polarization, electrochemical scratch and SKP measurements indicated that the nanocrystalline surface had higher resistance to corrosion, greater capability of repassivation and higher chemistry stability. All results demonstrated that the nanocrystallization surface did not only enhance the mechanical properties of the surface layer and its passive film, but also benefited the passivation capability of the steel with improved corrosion resistance. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Nanocrystallization; Sandblasting; Corrosion; Mechanical properties; Passive film

1. Introduction
Efforts have been continuously made to improve existing materials and to develop new ones which are stronger, lighter, and more resistant to aggressive environments. In recent years, nanocrystalline materials have received considerable interest [1,2]. Their high hardness, improved toughness and superior physical properties have found increasing applications. However, the effect of the nanostructure on the material corrosion resistance has not been well understood although it has been reported that the nanostructured materials exhibit improved corrosion resistance. For example, Ti-implanted H13 steel shows high corrosion resistance due to the formation of nano-scale FeTi2 phase [3]. Studies have also demonstrated that nanocrystalline Ni made by electrodeposition offers superior resistance to localized corrosion [4]. However, the mechanism responsible for such improvement has not been well understood yet. How a nanocrystalline structure of an alloy influences its passivation behavior and properties of its passive film need to be answered.

It is well known that the corrosion resistance of a passive alloy is attributed to the formation of a protective passive film on its surface. The corrosion resistance and electrochemical behavior of passive films on different materials have been widely investigated. It has become possible to evaluate the mechanical properties of passive films thanks to the development of advanced instruments, such as atomic force microscope (AFM) and nanomechanical test instruments [5–7].

The objective of this work is to evaluate the mechanical and electrochemical properties of a nanocrystalline surface of 304 stainless steel (304SS) produced by sandblasting and annealing treatment. In particular, properties of the passive film on the nanocrystalline 304SS’ surface were investigated.

2. Experiment
Specimens having their dimensions of 10 mm in diameter and 5 mm in thickness were machined from a
commercial 304 stainless steel (304SS) (wt.%: C, 0.08; Mn, 2.0; Si, 1.0; P, 0.04; S, 0.03; Cr, 19.0; Ni, 9.0). The surface of the specimens was polished with 600# grit paper, and then blasted by a sand flow of silica particles of 50–70 mesh under 200 kPa for 10 min. The sandblasted specimens were annealed at 350 °C for 60 min. Surfaces of the specimens were polished with alumina particles of 0.05 μm to make them as smooth as possible before testing. Before electrochemical test, a specimen was mounted using epoxy with its surface (Φ, 10 mm) under study exposed to a corrosive medium. The corrosive medium was a 3.5% NaCl solution. For comparison, the as-received and sandblasted specimens were also tested.

Polarization measurement was carried out using a commercial apparatus made by Camry Ltd. During the measurement, a saturated calomel electrode (SCE) was used as the reference electrode, and the platinum plate (Pt) was used as the counter electrode. All electrochemical tests were performed at room temperature.

The performance of the specimens during electrochemical scratch was evaluated using an apparatus that has been described in a previous paper [8]. During the test, a specimen immersed in a corrosive solution was scratched under an applied potential. In this study, two applied potentials were used, which were 50 and 100 mV (SCE) above the free corrosion potential of the specimens in the corrosion medium (E_{corr}), respectively. A diamond tip was used to scratch the surface of a specimen under a normal load, and corresponding changes in current were recorded. For the present study, the applied normal load was 20 g and the tip moving velocity was 8 mm s⁻¹. The duration of scratching was 0.25 s.

A scanning Kelvin probe (SKP) was used to measure the surface electron work function (EWF) of the specimens, which reflected their surface electrochemical stability. A gold tip with its diameter equal to 1 mm was used, and the scanning area was 2 × 2 mm. Average EWF values were obtained by measuring 100 points within in the scanning area for each surface. The EWF tests were carried out in open air.

Mechanical properties of passive films on various specimens were evaluated using a triboscope—a combination of a nanomechanical probe and an AFM. The probe was a four-sided pyramidal Vickers indenter made of diamond. During the nanoindentation test, the force–depth curve was recorded. A maximum force of 50 μN was used for the indentation test. Hardness and elastic behavior of the passive films were evaluated based on obtained force–depth curves.

The failure resistance of the passivated film to scratch was evaluated using a universal micro-tribometer (UMT), which had a mechanical probe made of tungsten carbide. During the test, a surface was scratched under a normal load that was increased linearly from 0 to 20 g. Under the applied load, the tip scratched the surface at a velocity of 0.02 mm s⁻¹. During scratching, changes in the contact electrical resistance (CER) with respect to the load were recorded. When the passive film failed under a critical load, the CER dropped steeply. The critical load reflects the resistance of a passive film to failure. Critical loads for passive films on different specimens were measured.

Surface microstructures of the sandblasted and sandblast-annealed specimens were observed under a transmission electron microscope (JEOL 2000FX2, operated under 200 kV). Zones at different distances from the sandblasted surface were observed. Surface chemical compositions of the specimens were determined using an energy dispersive spectrometer (EDS) attached to a scanning electron microscope (HITACHI S-2700). The surface mechanical properties were measured using a micro-indentor (made by Fischer Technology Inc.). The micro-indentation test was performed under a maximum load of 100 mN. Load–depth curves of micro-indentation were determined, from which the surface mechanical properties were evaluated.

3. Results and discussion

3.1. Surface analysis by TEM and EDS

Surface of 304SS was modified by sandblasting and annealing for nanocrystalline structure. The modified surface was examined using TEM. Fig. 1(a) presents TEM micrograph of the layer about 5 μm away from the sandblast-annealed surface. As shown, the size of roughly equiaxed grains in this layer was approximately 20 nm. With an increase in depth, the grain size increased. The grain size was about 100 nm in a transition zone adjacent to the unaffected inner layer as shown in Fig. 1(b). The nano-grains were randomly oriented as indicated by the selected area diffraction patterns in Fig. 1. Typical microstructure of sandblasted surface without annealing is shown in Fig. 2. The blasted surface consisted of heavily deformed grains with size about 20 nm. The TEM observation showed that the annealing treatment did not significantly change the size of grain in the sandblasted surface layer, which should, however, diminish the dislocation density of the surface layer.

The chemical compositions of the sandblasted, sandblast-annealed and the original 304SS surfaces were determined using EDS. No significant difference in compositions between surfaces of the specimens was observed. The EDS analysis results are presented in Table 1.
3.2. Mechanical properties of the nanocrystalline surface

Mechanical properties of the nanocrystalline surface of 304SS were investigated using a micro-mechanical probe. Fig. 3 presents the load–depth curves of different specimens. Two parameters, the indentation depth and the ratio of the recoverable deformation energy to the total deformation energy (η) were determined from the curves. In general, under a certain load, the smaller the indentation depth, the harder is the material. The ratio (η) is a measure of the elastic behavior of the material [9]. The area enclosed by the unloading curve and the maximum depth represents the recoverable deformation energy, and the area enclosed by the loading curve and the maximum depth represents the total deformation energy. The surface mechanical properties obtained from the micro-indentation test are presented in Table 2. It was demonstrated that the sandblasting increased the surface hardness by more than two times. Sandblasting also increased η-value. The annealing treatment further increased hardness and η-value of the sandblasted surface.

The increases in hardness and η-value by sandblasting come from the resultant nanostructure and high-density dislocations. The increased densities of grain boundaries and dislocations blocked the dislocation movement, thus leading to higher hardness. The increased yield strength also raised η-value due to the extension of the elastic deformation range. One may see that the annealing treatment improved the mechanical properties of the sandblasted surface. Since TEM observation showed that the annealing treatment almost did not change the grain size, the improvement in mechanical properties by annealing could be explained as follows. In the sandblasted layer, grain boundaries of the nano-grains (or the dislocation network) were diffuse. This makes them less effective to block dislocation movement. The annealing treatment could result in sharper grain boundaries with larger misorientation between adjacent nano-grains. As a result, the strength could be increased.
Furthermore, the resultant perfect nanocrystalline structure may also improve its elastic behavior. It needs be indicated that, since there were no significant compositional changes, the improvement in mechanical properties of the sandblasted and annealed surfaces should be mainly caused by nanocrystallization.

3.3. Effects of nanocrystallization on the electrochemical behavior of 304SS

Potentiodynamic polarization curves of different specimens in a 3.5% NaCl solution were determined at a scanning rate of 20 mV min\(^{-1}\). Fig. 4 illustrates polarization curves of 304SS, sandblasted 304SS and sandblast-annealed 304SS, respectively. Significant difference in polarization behavior between the specimens was observed. The nanocrystallization considerably improved the polarization behavior of the material. The potentiodynamic polarization curves demonstrated that the sandblast-annealing treatment did not only

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Cr</th>
<th>Ni</th>
<th>Fe</th>
<th>Others</th>
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<tr>
<td>304SS</td>
<td>19.01</td>
<td>7.96</td>
<td>70.25</td>
<td>2.78</td>
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<tr>
<td>Sandblasted 304SS</td>
<td>19.68</td>
<td>9.11</td>
<td>66.59</td>
<td>4.63</td>
</tr>
<tr>
<td>Sandblasted-annealed 304SS</td>
<td>18.76</td>
<td>7.76</td>
<td>69.07</td>
<td>4.41</td>
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</table>

Furthermore, the resultant perfect nanocrystalline structure may also improve its elastic behavior. It needs be
increase $E_{\text{corr}}$, the free corrosion potential, but also reduced the passivation-maintaining current. One may see that the sandblasted 304SS showed the poorest polarization behavior although it was harder than the as-received 304SS.

In order to further understand the effect of nanocrystallization on the corrosion resistance, electrochemical scratch tests were performed for different specimens in a 3.5% NaCl solution under a potentiostatic condition with the applied potentials of 50 and 100 mV (SCE) above $E_{\text{corr}}$, respectively. The current–time curves are shown in Fig. 5. When a passive alloy is scratched in a corrosive solution, fresh metal surface is produced and this will increase the anodic current due to the electrochemical dissolution. When scratching is completed, the current will rapidly decrease due to the repassivation of the scratched surface. Therefore, the current–time curves could be used to evaluate the repassivation capability of an alloy or metal in an electrolyte solution. The starting current ($i_s$) and the maximum current ($i_m$) of different specimens under the different potentials during scratching are given in Table 3. Significant difference in performance between the specimens was observed. The sandblast-annealed specimen showed the lowest maximum current among all specimens. The maximum current of the sandblast-annealed specimen was about one and two orders of magnitude lower than those of the as-received and sandblasted specimens, respectively. This indicates that the nanocrystalline surface is considerably superior to the regularly-grained surface and the sandblasted one with high-density dislocations, in terms of the resistance to electrochemical scratch. The beneficial effect of nanocrystallization may also be seen from the shadowed area under the $i-t$ curve as shown in Fig. 5(a1), which is approximately proportional to the total amount of material dissolution [8]. As demonstrated, the sandblast-annealed specimen with nanocrystalline surface provided significantly higher resistance to electrochemical scratch, compared with the as-received and sandblasted specimens. It should be pointed out that the scratch speed influences the current [10]. The speed used in the present work was not very high (8 mm s$^{-1}$), so that the current increase during scratch could be, more or less, depressed by repassivation of scratched surface. Nevertheless, the experimental data clearly demonstrated the benefit of nanocrystallization to the passivation behavior of 304SS.

The electrochemical stability of a surface reflects its resistance to electrochemical attack, which involves electron transfer. Therefore, for a surface covered by a

![Fig. 5. Current–time curves in a 3.5% NaCl solution during potentiostatic scratching (a1) 304SS specimen under a potential of 50 mV (SCE) above $E_{\text{corr}}$, (a2) 304SS specimen under a potential of 100 mV (SCE) above $E_{\text{corr}}$, (b1) Sandblasted specimen under a potential of 50 mV (SCE) above $E_{\text{corr}}$, (b2) Sandblasted specimen under a potential of 100 mV (SCE) above $E_{\text{corr}}$, (c1) Sandblast-annealed specimen under a potential of 50 mV (SCE) above $E_{\text{corr}}$, (c2) Sandblast-annealed specimen under a potential of 100 mV (SCE) above $E_{\text{corr}}$.](http://example.com/fig5.png)
passive film, the degree of ease for an electron to escape from the Fermi surface to the state of free electron is related to the electrochemical stability and the protective role of the passive film [5]. In this work, a SKP was used to determine the EWF of the passivated surfaces of different specimens. The test results and typical EWFs diagrams are shown in Table 4, Fig. 6, respectively. It was demonstrated that EWF of the sandblast-annealed specimen was the highest, and that of the sandblasted specimen was the lowest.

The better passivation behavior and higher surface chemical stability of the sandblast-annealed specimen may result from its nanocrystalline structure. It has been reported [11] that the decrease in the grain size of a passive alloy increases the density of diffusion paths for elements migrate, thus favoring rapid formation of the protective film. It should be pointed out that higher density of dislocations could also affect the passivation process [12] through changing the diffusion rate. However, as demonstrated in the present work, the sandblasted surface performed the worst. This could be attributed to possibly inferior mechanical properties of the passive film and its possible poor bonding to the sandblasted substrate when high-density dislocations exist in the vicinity of the interface (more discussion has been given in next section). In order to understand why the sandblast-annealed specimen performed much better than the sandblasted specimen, mechanical properties of passive films on different specimens need to be investigated.

### 3.4. Surface nano-mechanical properties

In order to estimate mechanical properties of passive films on different specimens, nano-indentation tests were performed to investigate surface responses of the specimens using an ultra-light indentation load. Results of the tests are shown in Fig. 7, which illustrates force–depth curves of different surfaces under a maximum load of 50 μN. As mentioned earlier, the hardness is related to the maximum indentation depth, and the elastic behavior of a material is related to its ratio (η) of the recoverable deformation energy to the total deformation energy [9]. The mechanical properties obtained from the nano-indentation tests are given in Table 5. One may see that the surface of the sandblast-annealed specimen had the smallest penetration depth and the largest η-value, while the surface of the sandblasted specimen showed the poorest mechanical properties. It is known that the passive film on stainless steel is very thin, usually a few nanometer thick. The thickness of the passive film could also be larger, e.g. it may reach 12.9 nm, depending on the surface treatment [13]. Since in the present study, the indentation depths were very small, e.g. 2–4 nm for natural passive films under the applied load of 50 μN (see Fig. 7), the results could reflect the mechanical properties of the passive films to a considerable degree, although they should be, more or less, influenced by the substrate. As demonstrated, the passive film on the sandblast-annealed surface was harder and more elastic than those on other specimens.

It was shown that the annealing treatment significantly increased the resistance of 304SS to corrosion. Such improvement could result from the nanocrystallization of 304SS surface. In order to evaluate effects of the sandblast-annealing treatment on passive films, surfaces of various specimens after being exposed to

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### Table 3

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Potential (mV, SCE)</th>
<th>$i_a$ (A)</th>
<th>$i_m$ (A)</th>
<th>$Q$ (q)</th>
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<tr>
<td>304SS</td>
<td>$E_{corr} + 50$</td>
<td>$3.18 \times 10^{-6}$</td>
<td>$3.88 \times 10^{-6}$</td>
<td>$1.78 \times 10^{-7}$</td>
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<td></td>
<td>$E_{corr} + 100$</td>
<td>$6.83 \times 10^{-6}$</td>
<td>$7.79 \times 10^{-6}$</td>
<td>$2.35 \times 10^{-7}$</td>
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<tr>
<td>Sandblasted 304SS</td>
<td>$E_{corr} + 50$</td>
<td>$3.86 \times 10^{-5}$</td>
<td>$4.88 \times 10^{-5}$</td>
<td>$2.01 \times 10^{-6}$</td>
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<tr>
<td></td>
<td>$E_{corr} + 100$</td>
<td>$5.79 \times 10^{-5}$</td>
<td>$6.34 \times 10^{-5}$</td>
<td>$2.32 \times 10^{-6}$</td>
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<tr>
<td>Sandblast-annealed 304SS</td>
<td>$E_{corr} + 50$</td>
<td>$3.91 \times 10^{-7}$</td>
<td>$4.60 \times 10^{-7}$</td>
<td>$1.71 \times 10^{-8}$</td>
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<tr>
<td></td>
<td>$E_{corr} + 100$</td>
<td>$6.32 \times 10^{-7}$</td>
<td>$6.46 \times 10^{-7}$</td>
<td>$1.13 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

---

### Table 4

<table>
<thead>
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<th>Specimen</th>
<th>EWF (eV)</th>
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<tr>
<td>304SS</td>
<td>$4.46 \pm 0.02$</td>
</tr>
<tr>
<td>Sandblasted 304SS</td>
<td>$4.31 \pm 0.07$</td>
</tr>
<tr>
<td>Sandblast-annealed 304SS</td>
<td>$4.59 \pm 0.03$</td>
</tr>
</tbody>
</table>

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**Fig. 6.** Surface EWFs of different specimens (X and Y are coordinate axes for the scanned area).
3.5% NaCl solution for 16 h were also examined using the nanoindenter. Results of the test are shown in Fig. 8, Table 5, respectively. In the corrosive environment, the hardness and elasticity of passive film on different specimens were impaired to some degree. The mechanical properties of the passive film on the sandblasted-annealed specimen were the best with the highest hardness and \( \eta \)-value. All results indicated that the passive film formed on the nanocrystalline surface was superior to those on the as-received and sandblasted specimens.

The passive films on the specimens were also evaluated using another technique: micro-scratch. The resistance of a thin passive film to scratch failure could be a more appropriate parameter to demonstrate its performance against corrosion and mechanical attack. Compared with the nano-indentation behavior of a thin passive film that could be strongly influenced by the substrate, the scratch resistance of a thin film may directly reflect its integrative behavior. In this work, resistances of passive films on different specimens to scratch failure were evaluated using a micro-scratch technique. During the micro-scratching test, a surface was scratched by a tungsten carbide tip. The normal load applied on the tungsten carbide tip was gradually increased and the CER was simultaneously measured. When the normal load reached a critical value, the passive film failed with a drop in the CER. Fig. 9 illustrates typically changes in CER of the passive films during scratch as the scratching load was linearly increased. The critical load, corresponding to the drop in CER, was a measure of the passive film’s resistance to scratch.

The critical loads for passive films formed on these specimens in air are given in Table 6. The drop in the CER of the sandblasted surface occurred when the load reached about 5.5 g, while that of sandblast-annealed specimen occurred when the load reached about 12.5 g. The drop in CER of 304SS occurred when the load reached about 7.5 g. The scratch test indicated that the passive film on sandblast-annealed surface had the highest resistance to scratch failure. In order to evaluate the effect of corrosive medium on the passive films, the critical loads of different specimens after being exposed to the 3.5% NaCl solution for 16 h were also tested. The results are given in Table 5. In the corrosive environment, passive films on different specimens degraded to some degree. Again, the passive film on the sandblasted specimen was the poorest, while that on the sandblast-annealed specimen was the best. As shown, the critical load at failure was greatly increased for the passive film formed on the nanocrystalline surface. The results of the

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Maximum depth (nm)</th>
<th>( \eta ) (%)</th>
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</thead>
<tbody>
<tr>
<td>As-received 304SS</td>
<td>3.1</td>
<td>39.3</td>
</tr>
<tr>
<td>As-received 304SS after being exposed to 3.5% NaCl for 16 h</td>
<td>4.8</td>
<td>11.2</td>
</tr>
<tr>
<td>Sandblasted 304SS</td>
<td>3.9</td>
<td>67.8</td>
</tr>
<tr>
<td>Sandblasted 304SS after being exposed to 3.5% NaCl for 16 h</td>
<td>6.4</td>
<td>58.5</td>
</tr>
<tr>
<td>Sandblast-annealed 304SS</td>
<td>2.3</td>
<td>98.8</td>
</tr>
<tr>
<td>Sandblast-annealed 304SS after being exposed to 3.5% NaCl for 16 h</td>
<td>3.0</td>
<td>78.2</td>
</tr>
</tbody>
</table>

Fig. 7. Load–depth curves of passive films under a maximum load of 50 \( \mu \)N. (a) 304SS, (b) Sandblasted 304SS and (c) Sandblast-annealed 304SS.

Table 5

The maximum indentation depth and \( \eta \) ratio under an ultra-light load of 50 \( \mu \)N.
micro-scratch were consistent with those of the nano-indentation test.

The difference in mechanical properties between passive films on different surfaces could be attributed to possible changes in structure of the passive films and their adherence to the substrate. The high corrosion resistance of stainless steel results from the formation of a chromium-enriched passive film, which protects the steel from corrosion, attack [14]. When a surface layer is nanocrystalline, the high-density grain boundaries could promote the diffusion of Cr to surface, thus forming a passive film containing richer Cr that may strengthen the film. This might be reason why the passive film on sandblast-annealed specimen exhibited superior mechanical properties. It should be mentioned that since the passive film is so thin that its mechanical behavior is also affected by the interfacial bonding between the film and the substrate. The poor mechanical behavior of the passive film on sandblasted specimen could result from possibly poor interfacial bonding between the film and the substrate. Since the sandblasted surface layer contained high-density dislocations and diffuse grain boundaries, Cr could also diffuse easily to form Cr-rich passive film. However, the interface between the passive film and the substrate with high-density dislocations and possibly other defects is similar to an ‘incoherent’ interface. The bonding of such an interface is usually weak. A poor interfacial bond could also lead the film to have inferior response to external mechanical force. This could be the reason why the passive film on the sandblasted surface performed poorly, compared with that on the sandblast-annealed specimen, during scratch and indentation tests.

The above-discussed is only a possible mechanism responsible for the difference in mechanical behavior and scratch resistance between the passive film on the sandblast-annealed specimen and that on the sandblasted specimen. Complete understanding of this difference needs systematic studies on the structure and adherence of the passive films.

Table 6
Critical loads (g) at failure during scratching

<table>
<thead>
<tr>
<th>Conditions</th>
<th>304SS</th>
<th>Sandblasted 304SS</th>
<th>Sandblast-annealed 304SS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Passive film formed in air</td>
<td>7.5 ± 1.7</td>
<td>5.5 ± 1.2</td>
<td>12.5 ± 3.0</td>
</tr>
<tr>
<td>Exposed to 3.5% NaCl for 16 h</td>
<td>6.6 ± 1.4</td>
<td>4.8 ± 1.6</td>
<td>11.0 ± 2.3</td>
</tr>
</tbody>
</table>

Fig. 8. Load–depth curves of passive films after being exposed to a 3.5% NaCl solution for 16 h under a maximum load of 50 μN. (a) 304SS, (b) Sandblasted 304SS and (c) Sandblast-annealed 304SS.

Fig. 9. Typical changes in the CER for the passive film on the sandblast-annealed specimen during micro-scratch.
4. Conclusion

Mechanical and electrochemical properties of nano-crystalline 304SS surface made by sandblasting and annealing were investigated, in comparison with those of sandblasted and as-received 304SSs. It was demonstrated that the nanocrystalline surface showed superior mechanical and electrochemical properties. In particular, the performance of the passive film on the nanocrystalline 304SS surface was considerably better than those on the as-received and sandblasted specimens. The mechanism responsible for such improvement resulting from the nanocrystallization is discussed.

Acknowledgements

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