Erosion-corrosion behaviour of innovative hardening treatments and coatings on stainless steels for food industry applications.

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A corrosive environment, wear and the combination of corrosion and wear can cause degradation of equipment. This can cause metal release which is a possible health risks for consumers. Many food products are known to be corrosive. Stainless steel is known for its corrosion resistance, but due to its poor tribological properties there is a risk of material degradation, when exposed to combined corrosion and wear. The aim of this study was to investigate the role of innovative hardening treatments and coatings on stainless steel. Electrochemical measurements have been performed in a food simulant under impingement conditions with suspended alumina particles.

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Introduction

Erosion-corrosion is a combined mechanism by which materials suffer damage due to combined erosion and corrosion. Erosion-corrosion is dominated by two mechanisms; electrochemical corrosion and mechanical wear. When materials are exposed to combined wear and corrosion (tribocorrosion) an interaction between the electrochemical and mechanical processes can become significant and cause material failure earlier than expected.

Stainless steel is often used in the food industry because of its excellent corrosion resistance. Stainless steel is also known to have poor tribological properties and material degradation is likely to occur when wear and corrosion is combined. Examples of erosion-corrosion failures in the food industry are described elsewhere.[1] Nitriding of stainless steel is known to enhance wear resistance but only a small amount of work has been published concerning the tribocorrosive behaviour of nitrided stainless steel.

The present work investigates the erosion-corrosion properties of stainless steel type AISI 316 L. Also the effect of surface modifications as low temperature nitriding and coating with thin layers has been investigated. The erosion-corrosion properties are determined using on-line electrochemical measurements.

Tribocorrosion

Material failure caused by tribocorrosion can be seen in a number of industries, such as mining, mineral processing, chemical processing, pulp and paper production and energy production. The combination of corrosion and wear can cause continuously metal release from equipment. This is a major concern in the food industry since metal release eventually can cause health risks for consumers.[1] Food products can be corrosive due to low pH, high chloride concentrations, high processing temperature as well as cleaning and sanitising agents can act corrosive.

Tribocorrosion can be defined as an irreversible transformation of the material caused by simultaneous physicochemical and mechanical surface interactions taking place in a tribological contact.[2] As indicated in ASTM Standard G119[3] several synergy effects are involved when combining mechanical and electrochemical phenomena.

The total material loss, T, can be considered as in the following equation, where W_0 is the material loss due to wear without corrosion, C_0 is the material loss due to corrosion without wear and S is the material loss due to the total synergism interacting between corrosion and wear.

$$T = W_0 + C_0 + S \qquad (1)$$

The total synergism (*S*) is the sum of the increase of mechanical wear due to corrosion, S´, and the increase of corrosion due to mechanical wear, *S´´*.

$$S = S' + S'' \qquad (2)$$

Electrochemical measurements at constant potential can easily be used to quantify mass loss caused by corrosion, since mass loss is related to charge (and thus the measured current) as described by Faradays law.

$$m = n \cdot M = \frac{Q}{z \cdot F} \cdot M \qquad (3)$$

The mass loss, *m*, is found from at determination of charge, *Q*, the number of electrons, *z*, the molar mass, *M* and Faradays constant, *F*.

The increase in corrosion as a consequence of wear *(S´´)* is illustrated in Figure 1.

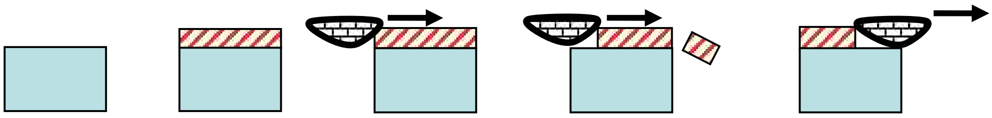


Figure 1 Illustration of tribocorrosion occuring on passivating materials e.g. stainless steel. A passive layer is formed and then an abrasive particle removes the passive layer exposing the bulk material for accelerated corrosion. The surface might repassivate as the solid particle abrasion stops.

The synergy effect describing increased mechanical wear due to corrosion, S´, can occur if corrosion products are released and then acts as third body wear particles. More obvious is the case where a wear resistant coating is corroding and thereby exposing the bulk metal to wear.

As a consequence of tribocorrosion premature material failure might occur if materials are chosen from separate determination of wear and corrosion properties. Therefore it is an advantage to quantify the relative contributions to material degradation from corrosion, wear and synergism when performing failure analysis and designing equipment for corrosive tribosystems.

The electrochemical processes can be monitored by sensitive electrochemical measurements in an erosion-corrosion setup as described in this paper. Such measurements provide further insight into the corrosion related mechanisms in relation to previous examinations based only on weight loss description. Materials applicable for the industry are examined in a flow of fluid and suspended particles and monitored by electrochemical measurements, such as potentiodynamic polarization curves and potentiostatic monitoring of current and potential.

Experimental procedure

In this work the corrosion and erosion-corrosion properties of stainless steel AISI 316 L has been studied in a food product simulating solution. The effect of low temperature nitriding of stainless steel AISI 316 L has been studied. Furthermore different DLC coatings have been evaluated as a stand alone coating on the top of stainless steel and as an additional coating on the top of nitrided stainless steel. The reason for studying the last combination is to obtain information concerning the relationship between erosion- corrosion and improved hardness of the base material – in principle studying the corrosion properties as a consequence of improved mechanical resistance to non elastic deformation.

Stainless steel AISI 316 L

Specimens, made from wrought stainless steels, were machined and polished to a final dimension of 15 mm by 15 mm with a wall thickness of 2 mm. All AISI 316 L specimens have been polished to grit 4000 using SiC-paper. Before the specimens are exposed to erosion-corrosion they are passivated in a 25 wt.% solution of nitric acid for 30 minutes at room temperature. The composition of stainless steel AISI 316 L has been determined by OES and is given beneath.

Table 1 Composition of stainless steel AISI 316 L given in wt.%.

	Fe	*Cr*	*Ni*	*Mo*	*Mn*	*Si*	*C*	*P*	*S*	*V*
316L	Rest (68.9)	16.7	10.1	1.9	0.9	0.4	0.03	0.08	0.03	0.1

Low temperature nitriding

Conventionel nitriding is known to improve tribological properties of stainless steel, but on the expense of lowering the corrosion properties. This is caused by the high (> 500 °C) nitriding temperature used in conventional nitriding causing chromium to precipitate as chromium-carbides/nitrides and thereby decreasing the chromium content locally in the matrix.[4] An alternative to conventional nitriding is low temperature nitriding.[5] This is a process for synthesizing a surface layer of expanded austenite with high hardness and apparently without influencing the corrosion properties of stainless steel, since chromium is not depleted from the matrix. A cross section of the surface layer is shown in Figure 2 indicating a layer depth of approximately 7-8 µm.

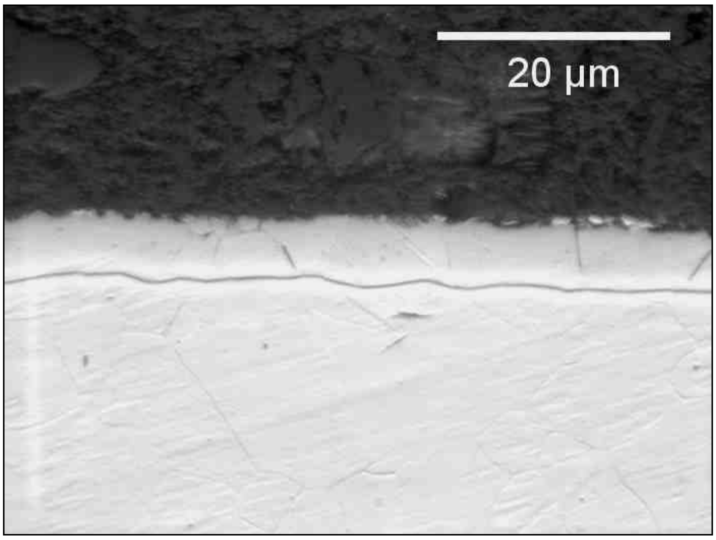


Figure 2 Light optical microscopy picture of the cross section of low temperature nitrided stainless steel. The cracks in the layer can be caused by the preparation due to the brittleness of the layer. The surface has been polished to 1 μm finish and is etched with HCl/HNO_3 solution for 30 seconds.

After polishing the specimens are heat treated at austenitizing temperature (1080 °C) for one minute. The austenitizing is performed in a thermo weight as described elsewhere.[6] The heat treatment proceeds at a rate of 25 °C/min until 1000 °C and with 20 °C/min from 1000 to 1080 °C in a hydrogen atmosphere to minimize oxidation of the surface. The nitriding process takes place in a gas flow consisting of 30 mL/min NH_3 and 20 mL/min H_2. The system was heated with 10 °C/min until 445 °C and this temperature were held for 20 hours.

The effect of hardening has been tested using a micro hardness tester. A Vickers diamond has been loaded to the cross section with a load of 5 gram. Seven repetitions were made across the cross section. The results are presented in Table 2.

Table 2 Micro hardness measurements of the cross section of low temperature nitrided AISI 316 L.

Material	Average Hardness [$HV_{0,005}$]	Results [$HV_{0,005}$]
Untreated AISI 316L	275	282, 277, 269, 286, 277, 265, 286
Low temperature nitrided AISI 316L	1160	1161, 1198, 1198, 1126, 1126, 1161, 1161

DLC and DLC-duplex multilayer coating

Figure 3 schematically shows the structure of the DLC (diamond like carbon) layer and the DLC-duplex multi layer coating.

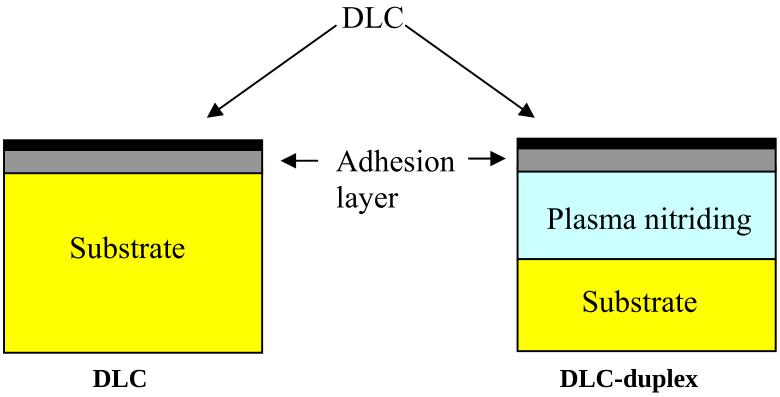
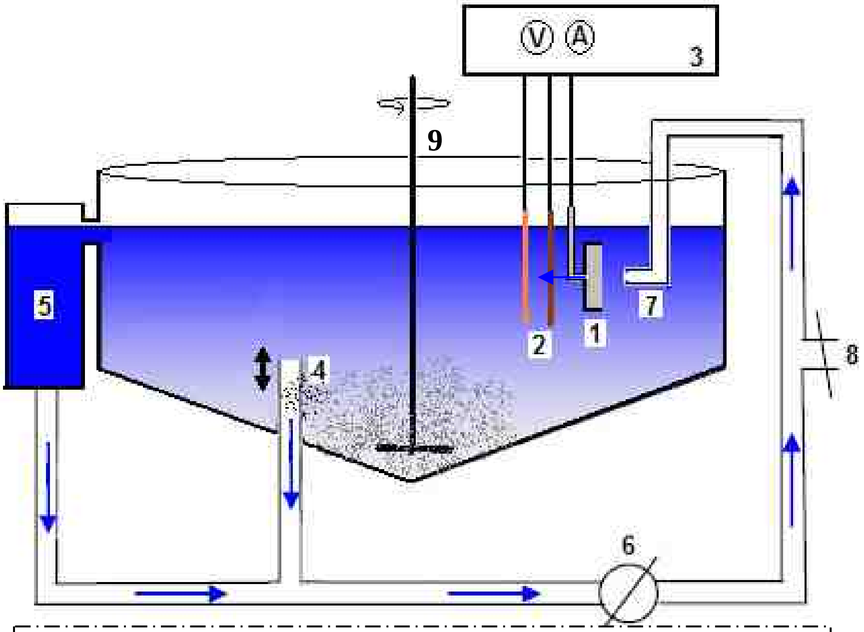


Figure 3 Schematic illustration of DLC and DLC-duplex layer.

Both coatings are layered on a AISI 316 L substrate and consist of an intermediate adhesion layer with a functionally gradient layer for improved adhesion. The DLC-duplex multilayer coating has an underlayer of conventional plasma nitriding (approximately 40 µm of thickness). The plasma nitrided underlayer improves the substrate hardness and supports the top layer when exposed to mechanical impacts.

The erosion-corrosion testing facility

This setup makes it possible to study and compare the erosion-corrosion properties of different materials under simultaneous corrosion and solid particle erosion in a turbulent flow. The test setup allows for corrosion control and monitoring and is similar to the impinging jet apparatus as described elsewhere.[7,8] It consists of a working electrode (the test specimen), an auxiliary electrode (a titanium net) and a standard reference electrode (saturated calomel electrode, SCE) connected to the solution by salt-bridging. The three electrodes are connected to a potentiostat as shown in Figure 4.



1) Working electrode 2) Auxiliary- and reference-electrode 3) Potentiostat
4) Particle outlet 5) Liquid outlet 6) Pump 7) Nozzle 8) Jet outlet 9) Stirrer

Figure 4 Erosion-corrosion experimental setup.

Specimens are machined to a final dimension of 15·15·2 mm and polished, appropriately cleaned and dried. The specimen is placed in a holder which exposes an area of 1.64 cm^2 and establishes a contact via a gold plated spring on the backside of the specimen. One kilogram of Al_2O_3 particles size 250 µm is placed in the 60 l tank. A stirrer whirls the sand to a certain extent. A hose connected to the suction side of the pump processes particles and liquid through the pump and the jet impinges the specimen at an angle of 90 degrees. After impingement the particles drops to the bottom of the tank, where they are whirled up again. By adjusting the position of the particle connection hose it is possible to vary the quantity of particles in the jet. Highest amounts of particles are obtained when the hose is closest to the bottom. It is also possible to adjust the stirring velocity, which will have an effect on the particle content. The setup is equipped with an outlet for determining the particle content. Samples of 1 litre are examined by particle filtering and weight determination. The reproducibility is adequate and the equipment is capable of delivering particle loads from 0 to 9 g/l. The pump used is a diaphragm pump driven by air. The pump contains only few parts of metal and the valve balls and seats will inevitably be worn after many hours of service, but can easily be replaced.

Table 3 Erosion-corrosion parameters.

Specimen	***Particles***	***Solution***	***Proces parameters***
AISI 316 L	Al_2O_3 size 250 µm	0.5 % NaCl,	6 l/min = 5.2 m/s
Low temperature nitrided AISI 316		NaAc/citrate buffer,	90 degrees
DLC		pH 4.0	0.6 g/l
DLC-duplex			5 mm distance

The solution is kept at room temperature (22-23 °C) and stirring occurs during all experiments. The applied setting for the pump was to deliver 6.0 litre/min and the nozzle has a diameter of 6 mm which results in a liquid velocity of 5.2 m/s. With the given flow rate and the viscosity the jet has a turbulent flow according to Reynolds number. The distance between the specimen and the jet nozzle is fixed at 5 mm. All the parameters can be seen in Table 3.

Approximate pH values and salt content of various food products are shown in Figure 5. Parameters like processing temperature and the existence of abrasive particles (pips from the vegetable itself or contaminants e.g. grits from gathering) are likely to influence the corrosion and wear properties of materials used for equipment.

Food product	pH	Salt content [mg/100 g]
Milk, cow	6.40 - 6.80	50
Ketchup	3.89 - 3.92	1,042
Mustard	3.55 - 6.00	1,252
Lime juice	2.00 - 2.35	1
Vinegar	2.40 - 3.40	1

Figure 5 Approximate pH and salt content of various food types. [9,10,11]

In this study the solution consists of 40 litre 0.05 M sodiumcitrate/citric acid buffer at pH 4 with a sodium chloride concentration of 0.5 wt. % as a simulant for a food product. Also a solution simulating tap water has been used to study the effect of erosion on stainless steel in such a mildly corrosive solution. Dynamic electrochemical measurements as polarization sweeps and potentiostatic monitoring of current at a fixed potential have been performed.

Microscopy of the eroded specimens has been performed using light optical microscopy (LOM) and scanning electron microscopy (SEM). Non destructive laser measurements have been performed to study the topography on some selected eroded specimens.

Results

The effect of erosion on stainless steel AISI 316 L has been investigated using dynamic electrochemical measurements. The effect of low temperature nitriding is illustrated by monitoring of the open circuit potential during erosion-corrosion. For untreated, DLC and DLC-duplex coated AISI 316 L potentiostatic monitoring of the current at a fixed potential will be presented.

The effect of erosion on the corrosion resistance of stainless steel

To investigate the influence of erosion in a low chloride containing solution polarization curves have been performed in a tap water simulating solution with and without 0.35 g/l particles as shown in Figure 6.

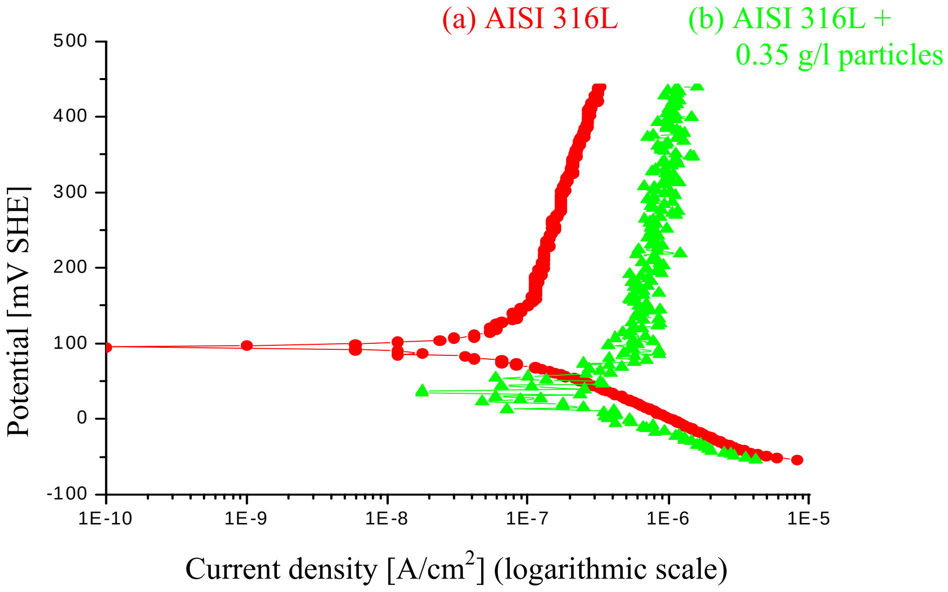


Figure 6 Polarization curve at a scan rate of 1 mV/s for stainless steel AISI 316 L in 0.03 % chloride, 0.1 M acetate buffer at pH 5.5 with (a) erosion 0.35 g/l, 250 µm alumina particles and (b) without erosion.

Figure 6 shows how the corrosion potential decreases about 100 mV under erosive conditions. The corrosion current density can be estimated by the use of Tafel slopes at a value of 0.01 µA/cm^2 under pure corrosion and 0.1 µA/cm^2 during erosion-corrosion. As a consequence of the erosive wear the corrosion rate has increased by a magnitude of ten. The solution used in this experiment is 0.03 wt.% chloride, which corresponds to the limit value of chloride in Danish drinking water. This solution is simulating a mildly aggressive food product and corrosion is not expected to occur at high rate for stainless steel in such a mild solution.

In a higher chloride containing food stimulant solution the resulting current at a fixed potential of 644 mV SHE has been monitored for three erosion time durations: 2, 5 and 15 minutes.

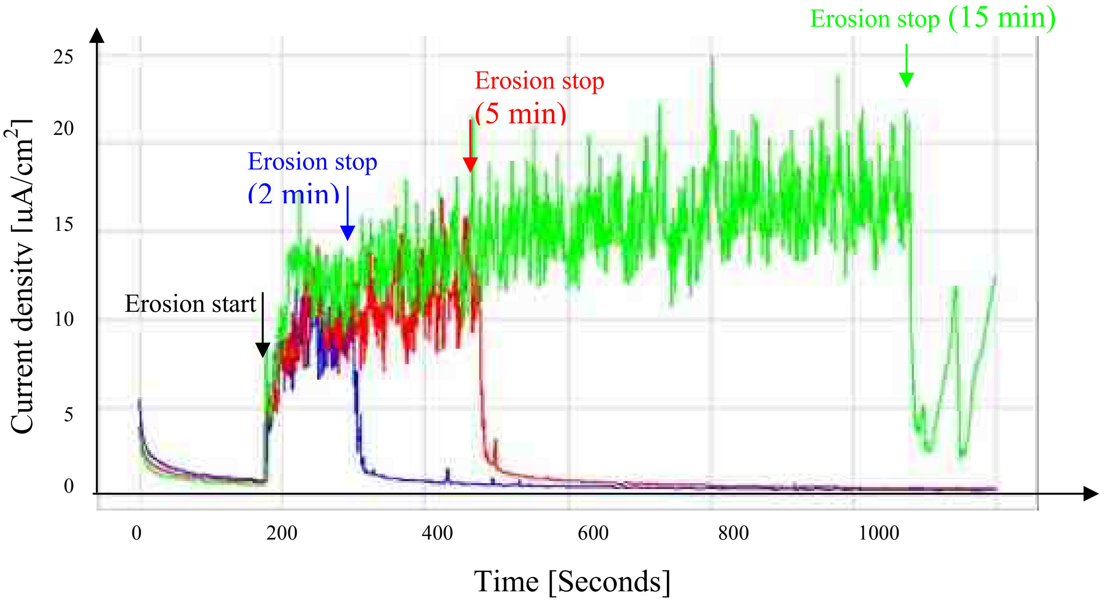


Figure 7 The resulting current at a fixed potential of 644 mV SHE has been monitored for untreated AISI 316 L. Three erosion time durations were made: 2, 5 and 15 minutes. The solution was 0.05 M sodiumcitrate/citric acid buffer at pH 4 with a NaCl concentration of 0.5 wt.% and 0.5 g/l alumina particles size 250 µm.

Figure 7 shows how the three curves are similar until erosion starts as well as during erosion. The fluctuations during erosion are a consequence of particle impacts. The current increase with erosion time is probably due to an area increase of the wear track. As erosion stops repassivation can bee seen, but after 15 minutes of erosion the surface seems to be slightly attacked by local corrosion, which explains the current scattering after erosion has stopped. The enhancement of metastable pitting of stainless steel in chloride solution has been documented previously [12] and is believed to be due to exposure of fresh active sites during erosion.

The effect of low temperature nitriding

Potentiostatic monitoring of the open circuit potential during erosion-corrosion has been performed to investigate the effect of low temperature nitriding of stainless steel.

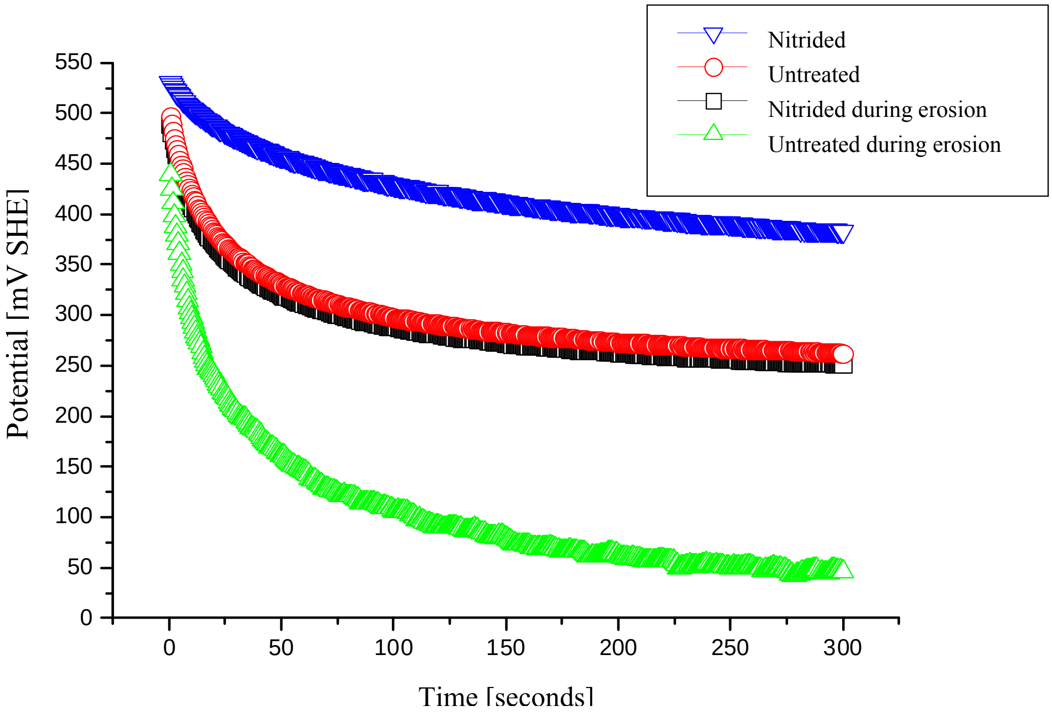


Figure 8 Open circuit potential for AISI 316 L and low temperature nitrided AISI 316 L in 0.03 % chloride, 0.1 M acetate buffer at pH 5.5 with and without erosion of 0.35 g/l, 250 µm alumina particles.

The curves in Figure 8 show how the open circuit potential of untreated AISI 316 L decreases approximately 250 mV as a consequence of erosion. The nitrided AISI 316 L decreases 100 mV and is maintaining similar level as untreated AISI 316 L without erosion. The low temperature nitrided stainless steel has a higher open circuit potential than untreated stainless steel also during erosion. This indicates that the passivating layer properties are affected by the low temperature nitriding process.

DLC and DLC-duplex

The topography of the specimens is generally similar to the one schematically shown in Figure 9, by the use of a non destructive laser measurement.

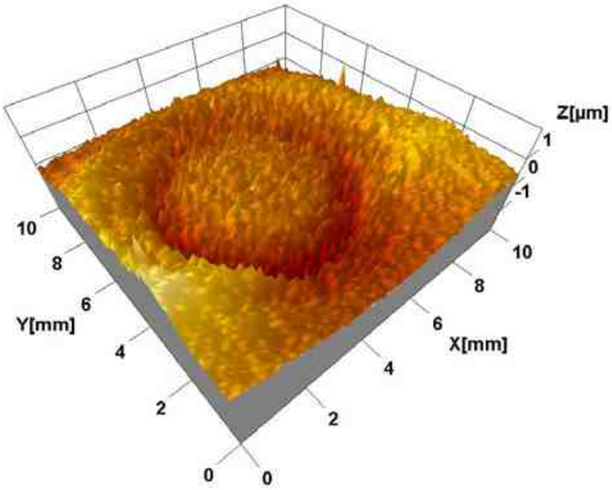


Figure 9 Surface topography made by non destructive laser measurement of DLC coated AISI 316 L after erosion-corrosion in 0.05 M sodiumcitrate/citric acid buffer at pH 4 with a sodium chloride concentration of 0.5 wt.% and 0.5 g/l alumina particles size 250 µm.

The surface topography indicates how the middle of the wear track has degraded to a lesser extent than the outer circle of the wear track.

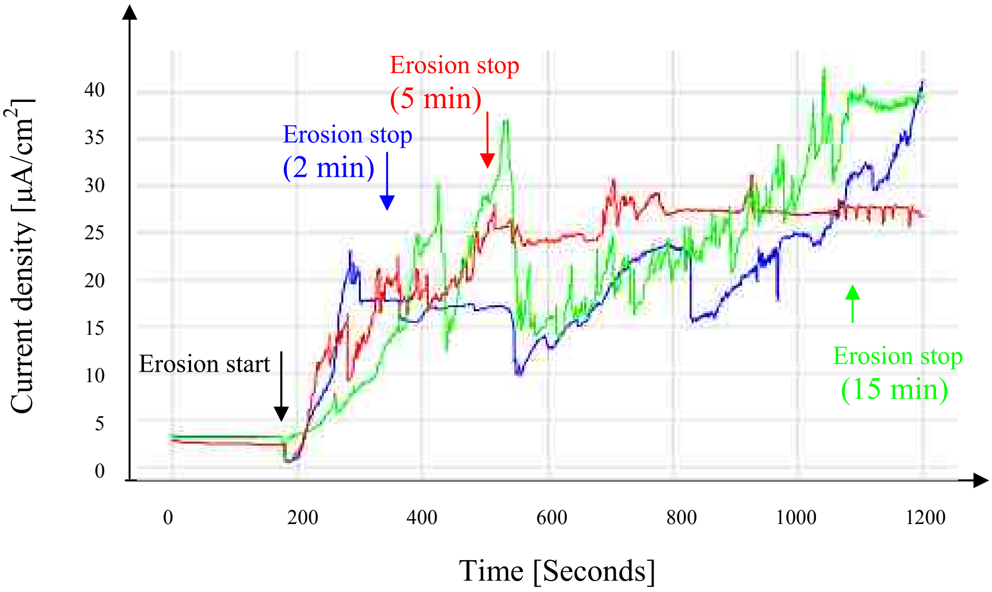


Figure 10 The resulting current of the DLC coating has been monitored at a fixed potential of 644 mV SHE for three erosion time durations: 2, 5 and 15 minutes in 0.05 M sodiumcitrate/citric acid buffer at pH 4 with a sodium chloride concentration of 0.5 wt. % and 0.5 g/l alumina particles size 250 µm.

Figure 10 shows how the three curves are similar until erosion starts. After erosion no repassivation can bee seen. The current measured are higher than for untreated AISI 316 L as shown in Figure 7.

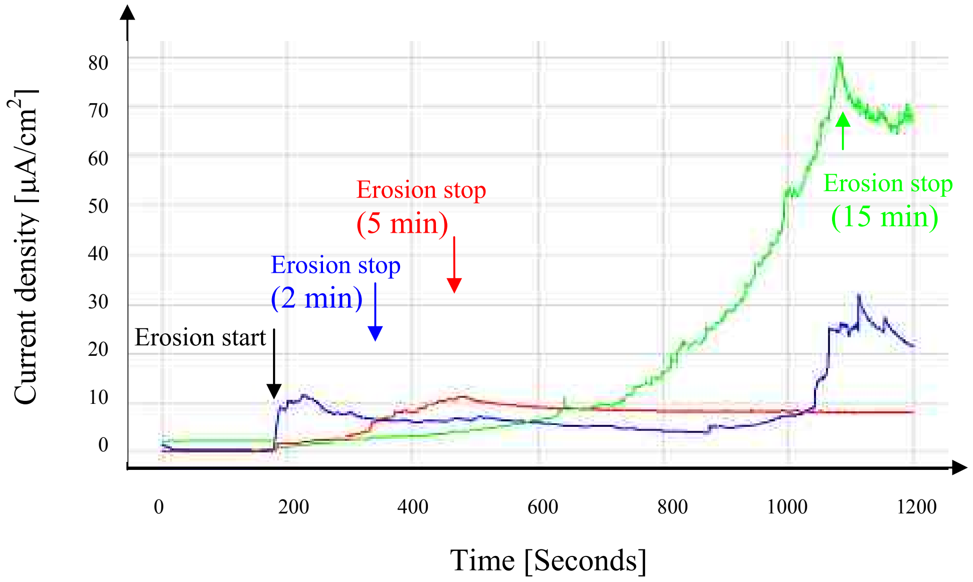


Figure 11 The resulting current of the DLC-duplex multilayer coating has been monitored at a fixed potential of 644 mV SHE for three erosion time durations: 2, 5 and 15 minutes in 0.05 M sodiumcitrate/citric acid buffer at pH 4 with a sodium chloride concentration of 0.5 wt. % and 0.5 g/l alumina particles size 250 µm.

The three curves shown in Figure 11 are again similar until erosive conditions starts. After erosion repassivation are not seen. The currents measured for the 2 min and 5 min erosion duration are lower than for DLC, shown in Figure 10. The specimen exposed to erosion for 15 min shows a drastic increase after approximately 700 seconds indicating that the coating has been worn through or microcracks has been introduced in the DLC-duplex coating, because of the mechanical impact from the particles. After this the current increases to a value of 80 µA/cm^2.

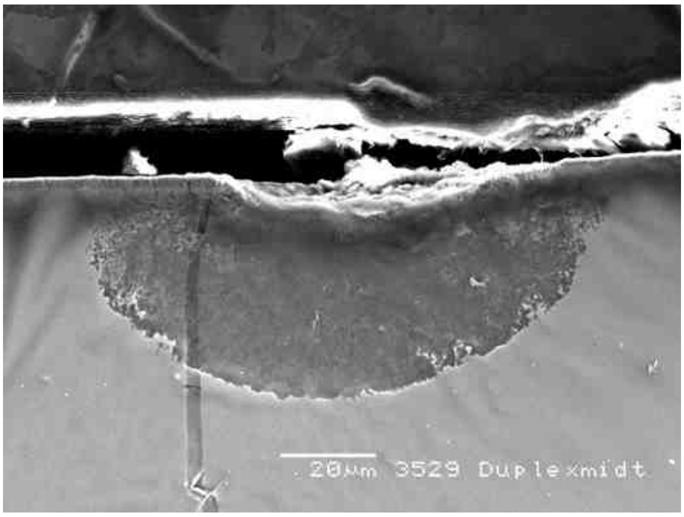


Figure 12 DLC-duplex after erosion-corrosion in 0.05 M sodiumcitrat/citric acid buffer at pH 4 with a NaCl concentration of 0.5 wt. %, showing under-corrosion of the conventional nitrided stainless steel substrate.

It is evident that the conventional nitrided layer has inferior corrosion resistance than the DLC layer as indicated in Figure 12, showing local corrosion of the conventional nitrided layer beneath the DLC layer. A crack seems to have been initiated at the edge of the DLC coating and is propagating through the nitrided layer. This could be an effect of the preparation of the cross section.

Conclusion

Erosion-corrosion is a tribocorrosion process known to degrade materials at higher rate than expected due to a synergistic effect between wear and corrosion. Stainless steel is often used in the food industry for processing of food products which can act corrosive due to low pH, high salt content and high processing temperatures. Furthermore cleaning and sanitizing agents can be corrosive to equipment used in the food industry. Unexpected material failure can occur if the stainless steel surface is exposed to erosive wear caused by abrasive particles combined with a corrosive solution.

To optimize the surface of stainless steel to withstand erosion-corrosion there is a need for determining the material degradation caused by erosion and corrosion respectively as well as the combined effect. A setup as described in this paper can be used for this purpose. The setup allows specimens to undergo erosion-corrosion while electrochemical measurements are performed online, real time. The results can be used to optimize the surface properties, estimate life time of process equipment and evaluate the effect of environment composition, particle concentration, fluid velocity etc. Following results have been obtained:

● Erosion with only 0.35 g/l alumina particles has shown a significant change in corrosion resistance of stainless steel even in a mildly corrosive solution. A more distinct synergy effect between erosion and corrosion is likely to appear if the solution pH decreases and salt content increases, which can be the case for various food products like juices or other acidic products.

● Low temperature nitriding is a process for hardening the surface of stainless steel with expanded austenite without deterioration of the corrosion properties. Low temperature nitriding has shown not only to decrease the wear rate as compared to untreated stainless steel, but also doing so without deteriorating the corrosion properties of stainless steel. Results have shown an increase of hardness for the expanded austenite phase to 1160 HV and an improvement of resistance to localised corrosion attacks.

● Thin layer coatings have been characterised in respect to erosion-corrosion properties. For the case of the DLC-coating the properties have improved until the layer breaks down and the corrosion rate increases compared to untreated stainless steel. This effect is even more clear in the case of DLC-duplex, where the underlayer of conventional high temperature nitrided layer has shown poor resistance to local corrosion attacks. Repassivation has not been seen for the coated layers, as were the case with untreated stainless steel. The high corrosion current values for the coated layers as compared to stainless steel are probably related to local corrosion taking place.

Future work is ongoing to improve the corrosion resistance of such conventional multilayer coatings with an under layer of low temperature nitrided stainless steel. Such a coating is expected to resist local corrosion attacks if the top layer breaks down locally.

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