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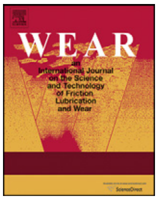

Erosion–corrosion and corrosion properties of DLC coated low temperature gas-nitrided austenitic stainless steel

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ABSTRACT

Low temperature nitriding of stainless steel leads to the formation of a surface zone of so-called expanded austenite, i.e. by dissolution of large amounts of nitrogen in solid solution. In the present work the possibility of using nitrogen expanded austenite “layers” obtained by gaseous nitriding of AISI 316 as substrate for DLC coatings are investigated. Corrosion and erosion–corrosion measurements were carried out on low temperature nitrided stainless steel AISI 316 and on low temperature nitrided stainless steel AISI 316 with a top layer of DLC. The combination of DLC and low temperature nitriding dramatically reduces the amount of erosion–corrosion of stainless steel under impingement of particles in a corrosive medium.

1. Introduction

Stainless steel is used in many industries e.g. the food industry for processing of products potentially aggressive due to low pH, high salt content or high processing temperatures. Stainless steel is normally considered an adequate material solution, but unexpected material failure can occur if the surface is exposed to external influences such as erosive wear caused by abrasive particles. Erosive wear interacting with corrosion is termed erosion–corrosion and is known to degrade materials at higher rates than expected, because of a synergistic effect between wear and corrosion. Research work focusing on improving erosion–corrosion resistance of austenitic stainless steel via advanced surface engineering technologies considering the combined corrosion and wear behaviour has been scarce [1]. Erosion–corrosion failures of stainless steel used in the food industry have been reported [2] and relatively simple surface modifications can be an optimal technological solution to solve such problems. Candidates for such a surface improvement of stainless steel may include diamond-like carbon (DLC) coatings and low temperature surface hardening.

Diamond-like carbon films are known to be chemically inert and show high wear resistance in both ambient air and aqueous environment [3]. DLC coatings can be produced by PVD-techniques with a sputtering target made of graphite. The physical properties of DLC coatings can be similar to the ones of diamond, but the degree of similarity depends strongly on the structure and composition of the DLC coating. The types of bondings in DLC can be described as a mixture of C–C sp^3 (diamond type), C–C sp^2 (graphite type) and C–C sp^1 (the hybridized binding) [4]. Hardness and wear properties depend especially on the content of sp^3 bondings and the hydrogen content in the DLC coating.

Hydrogenized DLC coatings with a mixture of sp^2 and sp^3 are denoted a-C:H (hydrogenized amorphous carbon). If the sp^3 content is increased and the hydrogen content is decreased, it is possible to obtain either the ta-C:H structure (tetrahedral hydrogenized amorphous carbon) or the ta-C structure (tetrahedral amorphous carbon). The latter is the DLC type with maximum sp^3 content and a minimum of hydrogen, making it harder than a-C:H. This DLC type can be grown with deposition techniques involving high energetic ions, such as filtered cathodic arc evaporation. The DLC type called a-C:H has a H content of 20–40 at.%. Such types are usually deposited by reactive sputtering at moderate substrate bias voltages.

DLC films are, however, only a few micrometers thick and when coated on a soft substrate, such as stainless steel, the load bearing capacity is low; the substrate will deform plastically and the DLC film can fall off as flakes [5]. Previous results have shown that stand-alone DLC coatings have improved erosion properties until the layer breaks down, which is followed by an increase in the corrosion rate as compared to untreated stainless steel [6]. In order to circumvent this inherent shortcoming of a stand-alone DLC layer, the load bearing capacity of the relative soft stainless steel can be modified by surface hardening processes. The application of a conventional (plasma) nitriding process, where the hardness increase is obtained from precipitation of nitrides, viz. CrN, for improvement of the load bearing capacity, has been investigated in ref. [7] (designated

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

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

conventional DLC duplex). It was shown that the conventionally nitrided load bearing layer suffered from severe local corrosion after breakthrough of the DLC layer under erosion–corrosion.

An alternative to conventional plasma nitriding is low temperature gaseous nitriding (LTN), which is carried out at temperatures below approximately 450 °C in mixtures of $NH_3/H_2/N_2$ [8]. In this temperature regime the development of CrN is kinetically hindered and the corrosion resistance of the steel is unaltered or even improved [9]. The surface adjacent region is converted into so-called nitrogen expanded austenite, which is a solid solution with high contents of interstitially dissolved nitrogen. The solubility of nitrogen in expanded austenite can be as high as 38 at.% N [10], and the hardness of expanded austenite can reach 1200–1400 HV with a significant improvement of the wear resistance [8,9]. Analogously, low temperature carburizing will result in carbon expanded austenite, although typically with significantly lower content of interstitially dissolved carbon compared to nitrogen [8].

The present work investigates the erosion, corrosion and tribo-corrosion behaviour of surface modified AISI 316 L in a salt containing solution. Investigated surface modifications of AISI 316 L are (1) low temperature gaseous nitriding (LTN) and (2) LTN in combination with a top layer of a deposited DLC coating (LTN-DLC). These surface modified materials are compared to untreated AISI 316 L.

2. Experimental

2.1. Materials and coatings

Specimens of stainless steels were machined to a final dimension of 15 mm × 15 mm with thickness of 2 mm. The composition, as determined with optical emission spectroscopy of the stainless steel type AISI 316 L used is given in Table 1.

A Netzsch STA 449 thermobalance was used for nitriding. All specimens were polished to grit 4000 using SiC paper and were Ni-activated before gaseous nitriding as described elsewhere [11].

LTN was carried out at 445 °C for 22 h in a controlled atmosphere of 9% N_2/55% NH_3/36% H_2. The catalytic Ni layer was removed with dilute HNO_3 after the nitriding process and at same time the samples were passivated. All untreated and nitrided stainless steel specimens were passivated in a 25 wt.% solution of nitric acid for 30 min at room temperature prior to corrosion and erosion–corrosion testing.

The applied DLC layer was a:C–H (amorphous hydrogenated carbon) with a H content of 20–40 at.% film layered on a low temperature nitrided AISI 316 L substrate (see above) with an intermediate adhesion layer consisting of a functional gradient coating (FGC), i.e. with graded carbon content, for improved adhesion. The DLC coating was produced by reactive sputtering in hydrocarbon gas using a conventional chamber.

Adhesion to the substrate depends on the substrate material composition, topography, pre-treatment and the deposition method and parameters used. Stainless steel can be a difficult substrate to adhere to and adhesion properties are often improved by applying intermediate adhesion promoting layers, graded or multilayered structures consisting of CrN, TiC, SiC, Ti or TiN/TiC [12,13].

2.2. Characterisation

The microstructure and layer thicknesses of the nitrided and DLC coated AISI 316 L were studied using a light optical microscope (LOM) after etching with Kahling's reagent for 20 s. The surface hardness was measured using a Futuretech FM 700 microhardness tester with a Vickers diamond applied directly to the surface with a load of 5 g. A JEOL 5900 scanning electron microscope (SEM) was operated under high vacuum conditions to study the effect of erosion–corrosion on the surface morphology.

2.3. Corrosion testing

Potentiodynamic measurements were performed using a Radiometer PGP201 potentiostat. A custom-made sample holder was used, exposing an area of 1.64 cm^2 to solution and with electrical contact established via a gold plated spring on the backside of the specimen. Polarizations are performed using a standard calomel electrode (SCE) at a scan rate of 30 mV/min in 0.5 wt.% NaCl, 0.1 M sodium citrate/citric acid buffer at pH 4.0. This electrolyte simulates a slightly aggressive food product.

2.4. Erosion–corrosion testing

The test setup used allows for corrosion control and monitoring during erosion. The test design has previously been described in details [6] and is similar to the impinging jet apparatus described in refs. [14,15]. The AISI 316 L test specimens is the working electrode, a titanium net functions as an auxiliary electrode and a saturated calomel electrode as a standard reference electrode which is connected to the solution by salt-bridging. The three electrodes were connected to a Radiometer PGP 201 potentiostat. Replicates of all tests were made. The particle concentration in the impinging slurry was estimated by filtering 2 l samples (3 replicates) and determining the weight after filtering dry for exactly 1 min. The fixed parameters used for erosion–corrosion investigation are shown in Table 2.

As described in ASTM standard G119 [16] the total material loss, T, is given by

$$T = W_0 + C_0 + S \tag{1}$$

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.

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

Table 2
Erosion–corrosion parameters.

Specimens	Particles	Solution	Process parameters
Untreated AISI 316 L LTN AISI 316 L LTN AISI 316 L DLC coated	Al_2O_3 size 250 μm	0.5 wt.% NaCl in a 0.1 M $Na_3C_6H_5O_7$, $C_6H_8O_7$ buffer at pH 4.0	6 l/min = 5.2 m/s 1.9 g Al_2O_3/l Impact angle = 90° 4 mm distance from jet Erosion period = 38 min Temperature 22–23 °C