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Oxygen argon plasma treatment effect on hydrogen uptake in austenitic stainless steels

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ABSTRACT

In this study, oxygen argon plasma (OArP) treatment was introduced as a new method for controlling hydrogen uptake in austenitic stainless steels during cathodic protection. It was determined that a 5-min treatment with OArP did not affect the nanomechanical properties of the material or the dislocation nucleation process, but it greatly inhibited the effect of hydrogen when the surfaces were in situ electrochemically hydrogen charged. Moreover, the cyclic voltammetry and X-ray photoelectron spectroscopy tests showed that the applied treatment influenced the composition of the surface oxide which in turn influences the hydrogen uptake from the surface.

Introduction

Super duplex stainless steels (SDSS) and austenitic stainless steels (ASS) are widely used in many industrial applications because of their cost efficiency, high mechanical properties, and good stress corrosion cracking resistance. However, under appropriate conditions they can undergo hydrogen embrittlement [1–9]. Specifically, within the sub-sea applications where due to the cathodic protection a continuous source of hydrogen exist on the surface [10]. It is known that SDSS can often fail due to hydrogen being released during cathodic protection, leading to hydrogen embrittlement (HE) [11–15].

In the presence of an external hydrogen source, such as hydrogen transportation pipelines or sub-sea pipelines under cathodic protection, one possible approach for controlling HE is to inhibit the *uptake* of hydrogen from the surface. Hydrogen uptake is a complicated process that happens through different steps depending on the source of the hydrogen i.e. gaseous or electrochemical. In the case of electrochemical hydrogen, hydrogen uptake involves the whole steps within the hydrogen evolution reaction as well as atomic hydrogen absorption on the surface and its diffusion through the different phases which are present on the surface [6,16]. The rate of hydrogen uptake is controlled by the kinetic of the slowest step involved. For a given alloy, the most convenient way to reduce the rate of hydrogen uptake is by modification

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Table 1 – Chemical composition of materials investigated in this study (wt%).

	C	Si	Mn	S	P	Cr	Ni	W	Mo	Cu	N	Al
SDSS	0.017	0.23	0.51	0.001	0.027	24.92	7.31	0.53	3.6	0.6	0.253	0.005
316L	0.015	0.38	1.25	0.0005	0.027	16.39	10.16	–	2.09	–	0.04	–

of its surface. This can be done by surface treatment which alters the kinetic of hydrogen evolution on the surface and/or formation of a surface film with a very low diffusivity for hydrogen. For example, studies have shown that a pulsed plasma nitride layer reduces the hydrogen uptake [17–21] while at the same time enhances the mechanical properties in presence of the hydrogen [21–23]. The exact mechanism of how the hydrogen uptake through nitriding is reduced, is not clear yet. Primary studies shows that the nitriding mainly affects the transportation and the solubility of the hydrogen on the surface layer [18]. In a recent study, Izawa et al. showed that the oxide film on the surface of the ASS can alter its mechanical behaviour in hydrogen atmosphere [24].

Recently, electrochemical nanoindentation (ECNI) technique [25–32], has been extensively used to study the effect of hydrogen on mechanical properties [26,33,34]. The ECNI method provides a rapid possibility to evaluate the hydrogen effect on the nanomechanical properties in a relatively small sample with a high statistics. In comparison to the conventional mechanical testing methods for hydrogen embrittlement e.g. tensile test in hydrogen atmosphere, ECNI is simpler, cheaper and material-conservative. As an example we can refer to the Zamanzade et al. work on evaluation of the hydrogen effect on nanomechanical properties of intermetallic iron aluminide alloys with different Cr concentration [35,36]. Within a similar experimental approach in this study, we examined the hydrogen effect on naomechanical properties of two different austenitic phases: austenite phase of 25% Cr SDSS (UNS S32760) and 316L ASS, with two different surface treatments. An oxygen argon plasma (OArP) is used to alter the freshly electropolished (EP) surface of the both steels, and the subsequent changes in mechanical properties are studied by means of nanoindentation in both hydrogen charged and uncharged conditions. The surface compositional changes and electrochemical properties are studied using X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry (CV).

Materials and methods

Materials and sample preparation

The chemical compositions of EN1.4501 (UNS S32760) SDSS and 316L ASS are presented in Table 1. The heat treatments were applied to the samples according to Table 2, which resulted in microstructures with a very low dislocation density and coarse grains. The dimensions of the samples used were 1 mm–2 mm in thickness and 12 mm in diameter for SDSS and 10.6 mm in diameter for 316L. The preparation of the samples began by grinding with silicon-carbide papers up to 2400 grade, followed by mechanical polishing with a water-based diamond suspension up to 1 μm. The final step was electropolishing using the parameters presented in Table 3 to remove the microscopic work-hardened layer of material caused by mechanical polishing [37].

Methods

Oxygen–argon plasma treatment

The OArP treatment was performed with Fishione 1020 PC equipment. The freshly EP samples were treated for 5 min with a mixture of 25% oxygen and 75% argon. This treatment was originally developed for cleaning hydrocarbon contamination from SEM samples. An oscillating electromagnetic field accelerates free electrons to high velocities and the excited gas atoms create the plasma. The energies with which plasma ions collide on the surface are less than 12eV, which is below the typical sample sputtering threshold. The same treatment with the same parameters was applied to both the SDSS and 316L samples.

Electron backscatter diffraction mapping

A low vacuum field emission SEM (LV-FESEM), Zeiss Supra 55 VP was used for electron backscatter diffraction (EBSD) mapping of the samples prior testing, and TSL OIM software was used for the data analysis. The samples were tilted by 70°, the acceleration voltage was 30 kV, the working distance was 21 mm and a step size of 200 nm was used for EBSD mapping. Fig. 1(a) presents the phase map of SDSS and Fig. 1(b and c) presents the inverse pole figure maps which give information regarding the grain orientations of both SDSS and 316L samples respectively. To exclude the crystallographic orientation effect, all sets of nanoindentations were performed within the same grain. In the SDSS sample, an austenite grain orientated close to the (001) plane was tested, while a grain orientated close to the (101) plane was investigated in the 316L sample, as indicated by the straight arrows in Fig. 1(b and c). The selection of these orientations made based on availability of large size grain with low index close to the centre of the sample for ease of performing in situ electrochemical nanoindentation. For easier identification of theses grains, each sample was marked with several microindents (dotted arrows) where the

Table 2 – Heat treatments applied to materials.

	Heat treatment	Temp. (°C)	Time	Cooling
SDSS	Annealing	1130	7 h	Water quenching
316L [21]	Annealing	1150	8 days	In furnace

Table 3 – Parameters used for electropolishing.

	Electrolyte	Pot. (V)	Flow rate	Time (s)	Temp. (°C)
SDSS	Methanol/H_2SO_4	35	12	30	21
316L	Methanol/H_2SO_4	20	12	30	21