Mechanical behavior of nitrided 316L austenitic stainless steel coated with a:C-H-Si

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Abstract

The austenitic stainless steel AISI 316L is used in chemical and other industries due to its good corrosion properties; however, it has a poor wear resistance. Plasma assisted treatments such as diffusion process and/or coatings can be used in order to improve the tribological properties. The a:C-H-Si coatings have low friction coefficient and wear resistance; in addition, they are chemically inert although they present adhesion problems when they are deposited on metallic substrates. In this work, the mechanical behavior and adhesion of the a:C-H-Si coatings deposited on nitrided AISI 316L stainless steel (duplex sample) and without nitriding (coated sample) were studied. The coatings were characterized by EDS and Raman. The hardness and Young Modulus were assessed by OM, SEM-FIB and XRD. Pin on disk and linear sliding tests were carried out. The adhesion was evaluated using Indentation Rockwell C and Scratch test. The coatings had high hydrogen content, over 40%, and the film thickness was about 20 μm. The hardness was about 13 GPa and Young’s Modulus was 73 GPa. The friction coefficient was less than 0.2 and the wear resistance was better than in stainless steel without any treatment. In the linear sliding tests, the track depth in the duplex and coated samples was six times lower than in the untreated sample. The nitriding had influence on the adhesion; the critical load was 16.2 N in the duplex sample and of 9.6 N in the coated sample. In the indentation Rockwell C test, the duplex sample also had better adhesion than the only coated sample.

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1. Introduction

Austenitic stainless steels are widely used in industry due to their good corrosion resistance; however, they present poor mechanical properties (Singh et al. (2002), Boromei et al. (2013)). In order to improve their surface properties, different types of coatings such as oxides, nitrides, carbides and “Diamond Like Carbon” (DLC) can be deposited. Carbon-based coatings are included under the name of DLC, and they can be produced by different methods, one of them being PACVD ((Plasma-Assisted Chemical Vapor Deposition). According to the sp3/sp2 ratio and hydrogen content, DLC coatings can be classified in different groups with different mechanical and electrical properties. It is possible to incorporate some dopants and obtain the so called metal-containing amorphous hydrogenated carbon a:C:H-Me. In general, these coatings are characterized by high hardness, low friction coefficient, good wear resistance and chemical inertia as it was reported by Robertson et al. (2002), Grill et al. (1999) and Erdemir et al. (2006). Depending on the hydrogen content the elastic modulus can be high, producing a hard DLC or low, like a polymer, a soft DLC. These two kinds of DLC have different applications, for example, hard DLC films are used in cutting tools, or surgical instruments, and the soft DLC films are appropriate for soft materials or threads where the film must absorb energy without cracking.

In both cases, these coatings have adhesion problems when they are deposited onto metallic substrates, among other reasons because the carbon diffuses into the metals, delaying the DLC coating nucleation and growth. Furthermore, since the thermal expansion coefficients of the steel and the coatings are different, high residual stresses are generated, and consequently, the adhesion turns out poorly (Neto et al. (2009) and Borges et al. (2001)).

In order to overcome these problems, different interlayers or multilayers or diffusion processes such as nitriding have been tried (Borges et al. (2001), Ueda et al. (2007), Snyders et. al. (2007) and Jellesen et al. (2009)). Plasma nitriding is a thermochemical diffusion treatment to enhance steel surface hardness and can be used as pre-treatment for the coatings, generating a suitable interphase between the substrate and the coating with a graded compositional and hardness profile that improves the adhesion. Although several works about DLC coated and nitrided stainless steels were published, each coating and each substrate require a specific study and it is necessary to determine the characteristics of the nitrided layer which should reach good mechanical behavior and be suitable for enhancing adhesion as reported by Borges et al. (2001), Chicot et al. (2011), Podgornik et al. (2001) and Podgornik et al. (2001).

Soft and thick carbon films have not been studied as much as the hard and thin ones, and also adhesion when thickness is over 20 μm is hard to assess and not many references have been found in the literature. In this work, the wear behavior and adhesion of thick and soft DLC coatings, a:C-H-Si, deposited by PACVD on high temperature and high nitrogen nitrided 316L austenitic stainless steel and blank samples were studied.

2. Experimental

The chemical composition in mass percentage of the substrate material, AISI 316L austenitic stainless steel is: 0.017 % C, 0.33 % Si, 1.44 % Mn, 16.25 % Cr, 10.07 % Ni, 2.03 % Mo, 0.24 % Cu and Fe as balance. Disk-type samples of 25 mm in diameter and 6 mm in height were cut from an annealed bar.

Plasma nitriding was performed in a semi industrial facility at the University of Applied Sciences in Wels, Austria, for 14 hours in a gas mixture composed of 20 % N2 and 80 % H2 at a temperature of 400°C.

The DLC coatings are in fact a:C-H-Si film (silicon containing amorphous hydrogenated carbon) and they were deposited by the Plasma Assisted Chemical Vapor Deposition technique (PACVD) in the same reactor used for nitriding with HMDSO and acetylene as precursor gas, at 400 °C and a pressure of 2 mbar. The deposition rate was about 1 μm/h. The silicon addition reduces the stresses, improves the adhesion and allows the coating to acquire a greater thickness. Two groups of samples were coated: the nitrided ones so called “duplex” samples in this work, and the blank ones, non nitrided, called “coated”.

The DLC films were characterized by EDS microanalysis and Raman spectroscopy. The nitrided layers were observed by SEM and OM, and the microstructure was analyzed by X-ray diffraction. XRD measurements were performed in a LAB X-XRD-6000 diffractometer with Cu-Kα radiation and a graphite monochromator in the Bragg-Brentano configuration. The hardness and Young’s modulus of the film were measured using a nano-indenteter with 9 mN load. The hardness of the nitrided samples was assessed with a Vickers micro-indenter, with 0.49 N load.
To evaluate the tribological behavior, rotational sliding wear tests were carried out in a pin on disk tribometer with an Al₂O₃ ball (6 mm in diameter) as counterpart, a total wear length of 500 m and a track radius of 7 mm. Linear reciprocating sliding wear tests were also performed with WC (5 mm in diameter) as counterpart, for 90 minutes and an amplitude of 0.48 mm. The wear scars were analyzed by SEM and OM. The DLC films adhesion was characterized using the methods of Rockwell C indentation with 1500 N load and Scratch Test with variable load, at a rate of 5 N/mm, starting with 1 N and with a total distance of 10 mm, with a diamond tip of 200 µm radius. The critical load was defined as the load at which the complete delamination of the coating is observed.

3. Results and discussion

3.1. Characterization of coating and nitrided layer

In the EDS spectrum of the coating (not showed) Si and C were detected, as expected. The Raman spectra for DLC films presented two overlapping bands known as the D and G bands (Fig. 1). The intensity ratio of the D and G peaks ($I_D/I_G$) was about 1.08. Taking into account this value, the G band position and the three stage model proposed by Ferrari et al. (2000), this film can be considered a-C:H-Si with C-C sp³ bonds, around 10%. Also, according to the Full Width at Half Maximum (FWHM) and the $I_D/I_G$ ratio, it could be inferred that the coating is largely amorphous with a cluster size smaller than 2 nm (Ferrari et al. (2000), Casiraghi et al. (2005), Saha et al. (2009)).

![Raman spectrum of the coating.](image)

From the slope of the fitted line to the base of the original spectrum (Ferrari et al. (2000), Casiraghi et al. (2005), Saha et al. (2009)), the hydrogen content was estimated at 43 %. According to the previously mentioned results these coatings are of the soft type with a high hydrogen content and they are indicated by the acronym a-C:H-Si.

The coating thickness was about 20 µm with a well-defined interphase with the substrate in duplex and coated samples as was observed with SEM in a place where the coating was detached during the indentation test (Fig. 2).

In the duplex sample, the nitrided layer was about 40 µm width with a dark area near the surface of 20-23 µm thickness, which corresponds to a nitrides precipitation region. It looked dark after marble etching because Cr is depleted, as a consequence of its involvement in CrN formation, thus passivation was compromised. This layer was followed by a diffusion zone, not etched, that consisted of no precipitates but nitrogen in solid solution (Fig. 3).
The samples were analyzed by XRD and $\gamma$-Fe (retained austenite) peaks were detected in the coated samples; because the film is amorphous and transparent to X-ray radiation (Fig. 4). In the duplex sample, Fe$_4$N, Fe$_3$N and CrN nitrides were identified. They were formed because the nitriding was carried out at high temperature and high nitrogen percentage as was reported by Mingolo et al. (2006), Singh et al. (2002) and Czerwiec et al. (2000).
3.2 Mechanical properties

The coating hardness, measured with the Berkovich indenter, was \((12.6 \pm 0.5)\) GPa. This value of hardness corresponds to the coating because the depth of indentation did not exceed 10% of the film thickness. The Young’s modulus was of \((73 \pm 3)\) GPa. These values of Young’s modulus and hardness confirm that the coating corresponds to the soft type (Robertson et al. (2002)). The nitrided layer hardness was \((911 \pm 34)\) HV\(_{0.05}\), and the austenitic stainless steel was \((250 \pm 10)\) HV\(_{0.05}\).

In the pin on disk tests with a Hertzian pressure of 0.78 GPa, the friction coefficient of the coatings was smaller than 0.2 in both samples; these low values have also been reported by Robertson et al. (2002), Grill et al. (1999) and Erdemir et al. (2006) for these coatings (Fig. 5).

Fig. 5. Friction coefficients registered in the pin-on-disk tests for different samples

In the friction coefficient versus time curves for duplex and coated samples, a remarkable initial change can be observed, which could be due to the geometry of the contact becoming conformal. The coated sample tribological behavior was more irregular than in the duplex sample; it is possible that coating cracks were produced in the contact zone between the surface and the ball counterpart. At the end of the test, the friction coefficient was lower in the duplex sample. With the coating, the friction coefficient was three times smaller than in the untreated steel, which reached a value of 0.6.

The DLC coatings present low friction coefficient due to the formation of the characteristic graphitic transfer layer of low shear strength, which has a lubricating effect, according to Robertson et al. (2002), Grill et al. (1999) and Erdemir et al. (2006).

The tracks were observed with SEM and the surface damage was similar in both samples; (Fig. 6). The regions where the film was detached were observed in a normal direction to the sliding of the counterpart; the area of these regions was larger in the coated sample than in the duplex sample, and this would correspond to the irregularities observed in the values of the friction coefficient shown in Fig 5. In these tests, the wear volume loss could not be calculated in the coated samples because the track depth was undetectable using the mechanical profilometer.
Fig. 6. SEM micrograph of the wear tracks a) on the coated sample, b) on the duplex sample

Also, the wear behavior of the coatings was evaluated by a linear sliding test using WC as counterpart with a Hertzian pressure of 0.88 GPa. The depth of the tracks in the coated samples was of 20% than in the steel without treatment (Fig. 7). The depth of the track was smaller than 10% of the thickness of the coating; therefore, the wear was produced completely in the coating, and there was not influence on the substrate.

Fig. 7. Depth profile of wear tracks for the different samples.

In the coated samples, lateral ridges of the grooves were not observed, which would indicate that the wear mechanism was only material removal (Fig. 7) without plastic deformation. In the untreated sample, there were material removal and plastic deformation because large protuberances on each side of the tracks are clearly observed (Wu et al. (2010)).
3.3 Adhesion

The adhesion was evaluated by Rockwell C indentation test with 1500 N load. The duplex sample presented good adhesion, there was not coating detachment, only radial cracks could be observed around the indentation. On the other hand, there was a detachment region around the indentation in the coated sample, as can be observed in Fig 8. This indicates that the adhesion was not acceptable using the same observation method used in the VDI 3198 Standard, even though this standard is not applicable for this coatings thickness.

In this test, some plastic deformation was produced below the contact region with the indenter below the contact, but the hard and resistant nitrided layer could support the test better than the untreated steel, resulting in a better adhesion (Vidakis et al. (2003)).

In the Scratch Test, the critical load was 16.2 N for the duplex sample and 9.6 N for the coated sample, which indicates an adhesion improvement with nitriding as a previous treatment. This behavior can be related to the substrate hardness, which is an intrinsic factor in this test. When substrate hardness increases, its bearing capacity is greater and consequently, the required load to produce the coating failure is higher (Chicot et al. (2011), Podgornik et al. (2001a)).

According to the above mentioned results, the nitrided layer composed by nitrides improved the adhesion in both tests, indicating that the modified zone produced at high temperature and high nitrogen percentage was a suitable interlayer for coating deposition. In the DLC coating, the presence of chromium nitrides on the steel surface may be convenient, due to the fact that if there was enough energy to form chromium nitrides, chromium carbides could also be formed, and these carbides improve the nucleation and growth of the coatings as it was reported by Borges et al. (2001), Podgornik et al. (2001a) and Podgornik et al. (2001b).

4. Conclusions

These coatings with high hydrogen content, low C-C sp³ bonds fraction and low hardness in comparison with other DLC coatings whose hardness is typically in the range 20 and 25 GPa, presented good tribological behavior regardless of the pretreatments in the evaluated conditions. However, regarding adhesion, it proved acceptable only with the nitriding pretreatment. The combination of the nitriding with the DLC coating could improve the AISI 316L austenitic stainless steel tribological behavior, and the application would be directed to components which suffer severe deformation because the coating would undergo the mechanical solicitation without breaking due to its low elastic modulus.
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