Microstructure and Nanoindentation Characterization of Low Temperature Hybrid Treated layer on Austenitic Stainless Steel

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Abstract. In this work, the hybrid treated layer on austenitic AISI 316L stainless steels were characterized to investigate the improvement on its surface properties. Characterization of this resulting layer was performed by FESEM (Field Emission Scanning Electron Microscope), USPM (Universal Scanning Probe Microscope) and nanoindentation. By using these methods, changes in the mechanical properties due to the diffusion of carbon and nitrogen at low temperature treatments have been traced. This hybrid treated sample has confirmed a considerable increase in hardness and a small rise in the elastic modulus compared to the untreated sample. It is found that all treated samples have enhance E/H ratio which exhibited the decreasing tendency to plastic deformation and reduced the mismatch of properties, while keeping deformation within the elastic range.

1. INTRODUCTION

Austenitic stainless steel (ASS) is used widely owing to its excellent corrosion resistance. However, the application of this material is severely limited by poor wear and friction behaviour. Stainless steel has very good corrosion resistance due to the presence Cr as alloying element to form stable thin passive layer Cr2O3 that protects the steel. Due to its inherent austenitic structure, this material has relatively low hardness as well as poor wear resistance which hinders a wider applicability of the material and may cause problems in existing applications. Consequently, surface engineering treatments for austenitic stainless steel are alternative ways to increase the surface hardness and improving the wear resistance. The gaseous thermochemical treatments to improve surface properties of material are typically carried out in carbon and/or nitrogen bearing gases and usually associated with temperature above 500 °C [1].

On the other hand, there was a phenomena where sensitization occurs which refers to the breakdown in corrosion resistance as a result of exposing the stainless steels in the temperature range from 550 °C to 850 °C. This problem in austenitic steel where precipitation of chromium carbides (Cr23C6) occurs at the grain boundaries at elevated temperatures, typically between 450 to 850°C;
Diffusional reaction in forming chromium nitride/carbide leads to the depletion of Cr from its matrix in austenitic solid solution and consequently unable to produce Cr$_2$O$_3$ passive layer to make stainless feature. As a result, it reduces the corrosion resistance property of the stainless steel. This phenomenon causes reduction in ductility, toughness and aqueous corrosion resistance [2].

Hardening of the nitrided layer and the carburised layer is due to the incorporation of nitrogen and carbon respectively in the austenite lattice, forming a structure termed expanded austenite, which is supersaturated with nitrogen and carbon respectively [3,4]. More recently, a hybrid process has also been developed, which combines the nitriding and carburizing actions in a single process cycle by introducing nitrogen and carbon simultaneously into the austenite lattice to form a hardened zone comprising a nitrogen expanded austenite layer on top of a carbon expanded austenite layer [5-7].

Recent work has shown that low temperature hybrid process of nitriding-carburizing of austenitic stainless steel is possible in conventional tube furnace [8]. The low temperature thermochemical treatments can be performed at temperatures up to 450$^\circ$C to diffuse a large amount of nitrogen and/or carbon in the treated layer of up to 20 µm thick, to form an expanded austenite ($\gamma_x$) ($X=N,C$) layer without formation precipitation of nitride/carbide which related to excellent corrosion resistance as well as wear performances [9,10].

Meanwhile, the surface and near-surface mechanical properties of thin films or coatings can be related to the final performance of materials. As a result, the need of better understanding in the field of depth-sensing nanoindentation would provides a quantitative method for mapping the mechanical properties, such as hardness and elastic modulus of the near-surface region [11, 12]. In order to investigate the high precision measurement of mechanical properties for thin layer Nanomechanical characterizations were performed on all treated and substrate materials. Nanoindentation was carried out to measure the mechanical properties of the implanted surface layers using Nano System 600, manufactured by Micromaterials UK, the schematic diagram for Nano System is shown in Figure 1.

![Figure 1 Schematic diagram of nano test pendulum system][20]
The aims of this paper is to characterize the expanded austenite layer on austenitic stainless steel substrates which representing a harden layer on a softer substrate respectively using the nanoindentation and morphological characterization. The hardness of expanded austenite is initially determined by the Oliver and Pharr method. In order to achieve proper measurement the use of very high applied load is avoided to minimize substrate effect where higher penetration of indenter which probably overtook the diffusion zone and entering the substrate bulk region [13].

2. EXPERIMENTAL

The specimens of 20 mm x 70 mm size rectangular coupon were cut from 2 mm thick hot-rolled plate with standard metallographical preparation for AISI 316L type austenitic stainless steel of the following chemical compositions (in wt.%): 17.018 Cr, 10.045 Ni, 2.000 Mo, 1.530 Mn, 0.030 C, 0.048 Si, 0.084 P, 0.030 S and balance Fe. The sample surface was ground on 320, 600, 800, 1000, 1200 grit SiC papers, and then polished using 1 μm Al₂O₃ pastes to the mirror finished.

Hybrid treatments were performed at 400 and 450°C in a horizontal tube furnace which involving reactive gases both NH₃ (for nitriding) and CH₄ (for carburizing) for a total duration of 8 h. The flow of gases were controlled by Aalborg flowmeter and the linear flow rate of gas mixture through the alumina retort were conditioned by gas mixing tank. In this system the sample were be placed in the quartz boat of about 12 cm in the center of isothermal zone of electric resistance tube furnaces.

Prior to treating, the specimens were soaked in concentrated HCl (2 M) solution for 15 minutes duration with the purpose to remove the native oxide film that commonly forms on stainless steel and protects the metal matrix from corrosion. This oxide layer is believed to act as a barrier for diffusional nitrogen transport [14,15]. After thermochemical treatments, the specimens were quenched in water. The cross sectioned treated specimens were first characterized by metallographic examination. To reveal the microstructure, the polished surface were etched in Marble’s solution (4g CuSO₄ + 20 ml HCl + 20 ml distilled water). The structure and morphology of specimens were characterized using Field Emission Scanning Electron Microscope-FESEM (Zeiss Supra 55VP) and Universal Scanning Electron Microscope-USPM (NanoNavi: E-sweep) to reveal 3D surface topographical profile at higher resolutions.

| Treatment                        | Time (h) | Temp (°C) | CH₄ | NH₃ | N₂ | Layer Thickness (μm) |
|----------------------------------|----------|-----------|-----|-----|----|----------------------|
| Hybrid process 316L             | 8        | 400       | 5   | 20  | 75 | 3.421                |
| Hybrid process 316L             | 8        | 450       | 5   | 20  | 75 | 6.425                |

Table 2 Instrumented hardness settings

| Variable                         | Value          |
|----------------------------------|----------------|
| Type of experiment               | Depth vs. Load |
| Type of indentor                 | Berkovich pyramid |
| Maximum load                     | 300 mN         |
| Maximum depth                    | 200nm          |
| Dwelling time at maximum load    | 5 s            |
| Loading rate                     | 3.99 mN/s      |
Nanotest equipment which located at AMREC SIRIM Malaysia is made by Micro Materials Ltd. from UK and it is a nanomechanical property testing system with a Berkovich tip. The sample support was attached to a mechanism which permitted: (1) the sample to be brought into contact with the test probe of a NanoTest, (2) the applied normal force and the resulting depth of penetration to be monitored continuously. In the NanoTest unit as shown in the Figure 1, forces are generated by means of a coil and magnet system located at the top of a pendulum arrangement and displacements of the probe into the surface are monitored with a sensitive capacitor plate arrangement. In the recent measurement, the nanoindentation techniques were set as described in Table 2.

3. RESULTS AND DISCUSSION

3.1 Layer morphology and surface topography analysis

Hardened layers with different morphologies were observed as a result of the various treatment conditions and the thicknesses of the layers produced in different specimens are shown in Table 1. According to the micrograph in Figure 2, expanded austenite layer is recognized as a featureless surface layer. For a similar treatment duration, the Plasma process is reported [16] to produce about 18 µm thick layer which is much higher compared to that of the present conventional hybrid treatment in horizontal tube furnace. In plasma process, the native oxide layer was removed mostly by bombardment of the plasma gas which is completely absent in conventional process. This is one of the reasons why conventional horizontal tube furnace produced small layer thickness compared to the corresponding plasma nitriding. Previous investigation revealed that nitriding at 450°C became effective after treatment for 6 h where a continuous treated layer was produced [17]. The two specimens processed under hybrid treatment conditions as shown in Figure 2, actually produced duplex layers although not clearly revealed in the present micrograph, this separation of dual structures are observable under SEM.

3.2 Nanoindentation measurement profile

The instrumented hardness tests conducted on AISI 316L untreated and hybrid treated samples has confirmed a considerable increase in hardness 4 to 5 order and a small rise in the elastic modulus of the material after the hybrid thermochemical treatments as describe in Table 3. The curves in Figure 3 illustrate the applied load against the displacement of the indenter.

Previous investigation had explained that, the resilience and toughness of the material are of significant importance, and the ratio of hardness to elastic modulus has been reported to be a more appropriate index than the mere hardness, to rank the wear resistance [18,19]. Meanwhile, the best tribological performances have been reported for combinations of high surface hardness and relatively low elastic modulus, to reduce the tendency to plastic deformation and reduce the mismatch of
properties, while keeping deformation within the elastic range which is an agreement with recent findings as describes in Table 3.

### Table 3 Roughness, indentation hardness and elastic modulus for each hybrid treatment.

| Treatment (°C) | Roughness, Ra (μm) | Hardness (GPa) | Elastic Modulus (GPa) | E/H  |
|---------------|--------------------|----------------|---------------------|------|
| Untreated     | 0.12               | 2 ± 0.2        | 210 ± 2             | 97.22|
| Hybrid 400 °C | 0.22               | 7.892 ± 0.7    | 167.518 ± 4.2       | 21.226 |
| Hybrid 450 °C | 0.28               | 8.471 ± 0.5    | 173.64 ± 3.1        | 20.50|

In relation with surface roughness after thermochemical treatments as shown in Figure 1(a), Table 3 presents the general characteristics of the hybrid treated layers, due to the high nitrogen and/or carbon contents in the layers resulting from deposition process as describes elsewhere [5], a characteristics relief is usually observed which results in an increase in the surface roughness.

![Figure 2](image_url)  
**Figure 2** Depth-sensing indentations performed on a) hybrid treated layer, b) hybrid 400 °C and c) hybrid 450 °C.
4. Conclusions

The thermochemical treatments of AISI 316L stainless steel in a horizontal tube process at 400 and 450°C have been demonstrated to produce hard layers of an expanded austenite phase without precipitation of chromium carbide/nitride as confirmed by FESEM images. The layer produced in horizontal tube process is not uniform in thickness under the same treatment conditions. The layer thickness of hybrid treated at 400°C is 6.425 μm while at 400°C gave much smaller thicknesses for the same processing conditions. USPM observation of all treated surfaces shows a higher surface roughness after treatments. Nanoindentation tests reveal a higher elastic modulus and hardness for all treated samples compared to the untreated. It is found that all treated samples have enhance E/H ratio exhibit the decreasing tendency to plastic deformation and reduce the mismatch of properties, while keeping deformation within the elastic range.

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