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Duplex treatment of 304 AISI stainless steel using rf plasma nitriding and carbonitriding

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ABSTRACT

Surface of 304 AISI austenitic stainless steel has been modified using duplex treatment technique of nitriding and carbonitriding. A thick modified nitrided layer, of approximately 20 μm, has been achieved when rf inductively coupled plasma was adjusted at 450 W for processing time of only 10 min. After performing the nitrided layer, the nitrided samples were carbonitrided using the same technique at different acetylene partial pressure ratios ranges from 10% to 70%, the balance was pure nitrogen. Different amount of nitrogen and carbon species are diffused underneath the surface through the nitrided layer during carbonitriding process and are found to be gas composition dependent. The treated samples were characterized by glow discharge optical spectroscopy, X-ray diffractometry, scanning electron microscopy and Vickers microhardness tester. The microstructure of the duplex treated layer indicates the formation of γ'-Fe_4N, Fe_3C, CrN and nitrogen-expanded austenite (γ_N). The thickness of the duplex treated layer increases with increasing the acetylene partial pressure ratio. The surface microhardness of duplex treated samples has been found to be gas composition dependent and increased by 1.29 fold in comparison to the nitrided sample.

1. Introduction

Stainless steels are introduced into various today's industrial applications such as food, storing, chemical, vacuum modeling tools and medical industries for their excellent corrosion resistance. However, they exhibit relatively low wear resistance and relatively low microhardness, which impede some of their specific applications. Thermo-chemical treatments of nitriding, carburizing and nitrocarburizing have been used for a long time as single treatment techniques, essentially to improve their superficial mechanical properties [1–7]. Different plasma techniques have been used for nitriding stainless steels such as ion implantation [8,9], low-energy high-current nitriding [10,11], plasma immersion ion implantation [12–13] and rf plasma nitriding [14–16]. Alternatively, rf plasma carbonitriding has been used recently for surface modification of 304 stainless steel using gas mixture of acetylene and nitrogen [2–3,5,17].

Duplex treatment technique has been recently considered as a newly developed surface treatment method to improve the surface properties of stainless steels and other ceramic alloys [18–28]. It is a surface modification method combined two sequence techniques; a hard coating is performed on the surface treated substrate. It has been found that the substrate should have a sufficient hardness and flow strength to support the coating without plastic deformation when subjected to a high-intensity loading. Duplex treatment of calorizing followed by plasma nitriding [18], plasma nitriding followed by PVD coating [19], preheating followed by PVD coating [20] and plasma electrolytic nitrocarburising coated with diamond-like carbon [21] are mentioned here as examples. Duplex treatment process has been controlled by varying the conditions of specific treatment techniques. An adhered coating of TiN, CrN or carbon deposition which was individually achieved on different nitrided substrates using various duplex treatment processes revealed superficial tribological properties, greater load-bearing capacity and higher corrosion resistance compared to the only nitrided substrates and to the direct coating on un-nitrided substrates [22–24].

It has been found that the carbonitrided layers of austenitic stainless steel exhibit better corrosion resistance in comparison to these treated by pure nitriding or carburizing. This improvement has been revered to the existence of a solid solution phase γ_N [3], which is hard phase and it has a good corrosion resistance with respect to γ-austenite [4]. Blawert and coworkers were found that the chemical compound phases (nitrides and carbides) in the presences of the solid solution phases (nitrogen-expanded austenite and carbon-expanded austenite) are accountable about the significant improvement of surface microhardness [29].

To improve mechanical properties of 304 austenitic stainless steels, duplex surface treatment using inductively coupled rf plasma

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nitriding and carbonitriding has been employed. A carbonitrided layer was formed on the nitrided AISI 304 stainless steel substrate using different gas composition of nitrogen and acetylene with respect to gas pressure ratio. The duplex treated substrates were examined using various analytical techniques of glow discharge optical spectroscopy (GDOS), X-ray diffraction (XRD), scanning electron microscopy (SEM), and Vickers microhardness tester.

2. Experimental

A 1 mm thick of 304 austenitic stainless steels was cut into specimens with dimensions 20 mm × 10 mm × 1 mm, which were cleaned in acetone before the treatment. It has a chemical composition of 0.5 wt.% Si, 1.2 wt.% Mn, 8.5 wt.% Ni, 19.1 wt.% Cr, 0.075 wt.% C and 69.95 wt.% Fe. Duplex surface treatment process was carried out using an inductively coupled rf plasma nitriding and carbonitriding. Rf plasma system consists of a cylindrical quartz tube of 500 mm length and 41.5 mm diameter. The cylindrical quartz tube was evacuated to a typical base pressure of 7×10^{-3} mbar by a rotary pump. In the pretreatment process of rf plasma nitriding, pure nitrogen gas was introduced in the reactor tube to increase the base pressure from 7×10^{-3} mbar to about 8×10^{-2} mbar. The discharge was generated by a three-turn copper induction coil energized from a 13.56 MHz rf power supply through a tunable matching network. The distance between the substrate surface and the rf coil was fixed at 29 mm. The water cooling rate of the substrate was adjusted to be 1500 cm^3/min. The substrates were treated at a fixed input plasma power of 450 W for a processing time of 10 min. The substrate temperature is measured during the rf plasma process by a Chromel-Alumel thermocouple which is attached to the surface of the sample. It was approximately stable during the treatment process at about 450 °C. At the end of the pretreatment process, the nitrided sample was leaved in the evacuated reactor tube until it cool down to the room temperature. Duplex treatment process was employed without initial sputtering or heat treatment prior to nitriding or carbonitriding to remove the native oxide layer from the surface of the untreated substrates. The nitrided samples were carbonitrided using different acetylene partial pressure ratios from 10% to 70%. The total gas pressure was adjusted to be 8×10^{-2} mbar. The distance between the substrate surface and the rf coil was decreased to 24 mm. The water cooling rate of the substrate was reduced to 600 cm^3/min. The nitrided substrates were carbonitrided at the same plasma power (450 W) and plasma processing time (10 min). The treatment temperature of carbonitriding was varied from 520 °C to 590 °C depending on gas composition. Finally, the duplex treated samples were leaved in the evacuated reactor tube until they cool down to the room temperature.

Different characterization techniques were used to analyze the duplex-treated samples and the results were compared with those obtained for the nitrided one. A diffractometer with Cr radiation was employed for structure analysis. A glow discharge optical spectroscopy (GDOS) was utilized to measure the elemental concentration depth profiles. Scanning electron microscopy (SEM) was employed to study the microstructure of the duplex treated substrates. Vickers microhardness measurements were taken on the untreated and treated substrates using a load of 100 g at room temperature.

To measure the thickness of the treated layers, the treated samples were cut into small work pieces using ISOMET™ low speed saw. These small parts were cold mounted as cross-sections and grinded using abrasive grit with different grades started by 40 and ended by 400 meshes and polished to mirror like using micro polish of alumina suspensions 0.3 and 0.1 micron. After that, the cross-sectioned samples were etched for 30 s to reveal the surface microstructure under optical microscopy. The etching solution was prepared using 50 ml acetic acid and 50 ml nitric acid added to 50 ml distilled water. Finally, the layer thickness was measured by microhardness tester and visibly confirmed by the optical images.

3. Results and discussion

3.1. Treatment temperature

The austenitic stainless steel substrates are heated up only by the electric field of the inductively coupled rf plasma coil in both processes of nitriding and carbonitriding. At the initial stage of the treatment process, the substrate temperature is increased very fast and stabilized after approximately 2 min of plasma processing time. The substrate temperature has been found to be 450 °C for pure nitriding where the distance between the substrate and rf coil was adjusted at 2.9 cm. The carbonitriding process is carried out at shorter distance of 2.4 cm and lower cooling rate of 600 cm^3/min. Therefore, it is expected that the substrate has higher temperature at nearer distance from the rf coil and lower water cooling rate for the same gas composition. Fig. 1 shows that the effect of gas compositions on the substrate temperature where the other plasma parameters were fixed. It has been observed that the substrate temperature is gradually increased from 520 °C to 590 °C, depending on the acetylene gas pressure ratios. The interplay between the temperature and the gas composition might be caused by the effect of hydrogen species created from the dissociation of acetylene under plasma conditions. The mass difference between hydrogen, carbon and nitrogen plasma species and the ionization potential of atoms can play important role in the resulting plasma temperature (electron and ion temperature) which has a significant influence on the temperature of the substrate. In this case, the ionization potential of hydrogen is 6.4% lower than of that nitrogen and the light hydrogen ions are easily accelerate by the same rf plasma field compared to heavy ions of nitrogen. These ions itself contribute to the plasma heating due to secondary electrons generation by elastic collisions with the plasma species.

3.2. GDOS analysis

Fig. 2 shows the elemental concentration depth profiles of the nitrided sample and duplex treated samples at different acetylene gas pressure ratios of 10% and 30%. Nitrogen and the basic elements of the bulk substrate (Fe, Cr, and Ni) are detected in the investigated depth of the nitrided layer. Furthermore, little concentration of carbon is also detected along the same investigated depth. Detection of carbon is attributed to the hydrocarbon contamination which could be found in the reactor tube during nitriding process [30]. One can observe from the figure that the value of nitrogen concentration (≈16 at.%) is very high compared to that of carbon (≈0.8 at.%). The diffusion mechanism of nitrogen and/or carbon into austenitic stainless steel has been

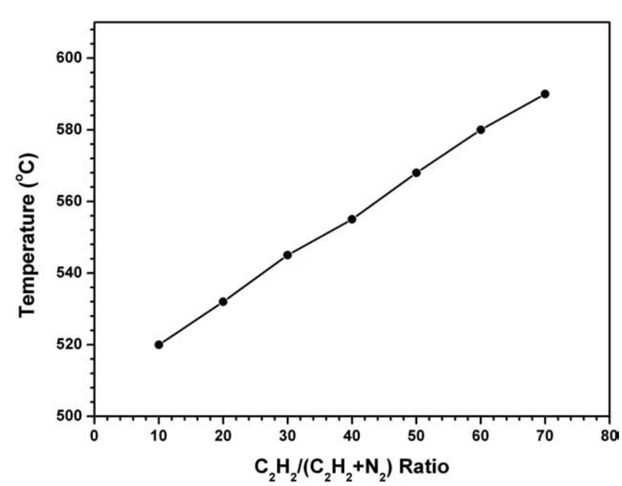

Fig. 1. Treatment temperature variation as a function of the acetylene partial pressure ratio ranges from 10% to 70%.