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The effect of surface mechanical attrition treatment on low temperature plasma nitriding of an austenitic stainless steel

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ABSTRACT

The combined effect of superficial nanocrystallisation by SMAT (Surface Mechanical Attrition Treatment) followed by plasma nitriding on the mechanical properties of a medical grade austenitic stainless steel was studied. SMAT conditions were optimised to enhance nitrogen diffusion. Experimental observations (energy dispersive X-ray spectroscopy profiles, cross-sectional optical micrographs, phase analysis by X-ray diffraction and micro-hardness profiles) show that polishing away a very thin layer after SMAT and before nitriding significantly improves nitrogen diffusion into the substrate, yielding a 50% thicker nitrided layer. Possible causes for this improvement are discussed.

1. Introduction

Austenitic stainless steel AISI 316 — ASTM F138 is a typical medical grade material that is used in many industrial and biomedical applications such as orthopaedic implants, due to its excellent corrosion resistance and biocompatibility. However, its hardness and wear resistance are relatively poor [1]. Many attempts have been made in order to harden its surface [2]. For example, at low temperature nitriding [3], the transformation of austenite into expanded austenite (γ_N, or S-phase) increases the surface hardness while keeping a reasonable corrosion resistance [4].

Another process for surface hardening is the Surface Mechanical Attrition Treatment (SMAT) [5]. It generates a nanocrystalline surface layer by severe plastic deformation. This enhances several mechanical properties such as yield and ultimate strengths, but it also decreases the ductility [6]. SMAT has already been combined with other processes such as co-rolling [7], gas nitriding [8,9] or low-temperature plasma nitriding on AISI 321 steel [10]. It has been shown that SMAT combined with nitriding can enhance surface hardness and corrosion resistance [8–10]. The SMAT increases dislocation density and grain boundary fraction near the surface, thereby providing fast diffusion pathways for the nitrogen atoms into the material. Improved nitrogen diffusivity due to smaller grain size was already observed in AISI 304 steel [11]. Conversely, Cemin et al. [12] studied the influence of another mechanical attrition process, ball milling, on low temperature plasma nitriding of AISI 316 steel, and they demonstrated that ball milling oxidises the metal surface, which blocks the nitrogen flux into the bulk material. Several studies have been performed on similar mechanical surface treatments and materials [1,2,10], however no research has been carried out on the duplex treatment SMAT/nitriding of medical grade austenitic stainless steels.

In this work, a medical grade AISI 316 — ASTM F138 stainless steel is first SMATed and then plasma nitrided. The idea is that SMAT will improve the subsequent nitrogen diffusion, so that a thicker nitrided layer is formed, which would enhance several mechanical properties. Based on the thermal stability TTT diagram of γ_N [13], plasma nitriding is carried out for 20 h at 425 °C [2]. However, even if the nanostructure generated by SMAT is known to remain stable for at least 10 min at 600 °C [14], no information is available for longer dwell times. Thus, some of the SMATed samples are annealed at 425 °C for various durations between 5 and 20 h to study the stability of the nanostructure.

The effect of an intermediary polishing step is also investigated. If any oxides would be present, as in [12], this step would remove them. The resulting nitrogen layers obtained with and without polishing are then compared to each other using different techniques (as explained below), as well as to an un-SMATed nitrided sample. Finally, the results are discussed and analysed.

2. Material and methods

2.1. Material and surface treatments

Coupon samples 6 mm thick were cut from 25 mm diameter bars. Their chemical composition is given in Table 1. Several SMATed samples

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Table 1
Composition (wt. %) of the as-received austenitic stainless steel AISI 316 — ASTM F138 (Supplier: ACNIS International).

Element	Fe	C	Mn	Si	P	S	Cr	Ni	Mo	Cu	N	Ti	V
Weight %	48,4	0.013	1.7	0.26	0 .017	0.003	17.37	14.52	2.80	0.08	0.088	<0.005	0.07

were annealed (A) in an air furnace at 425 °C (see Table 2). The other samples were subjected to different combinations of SMAT (S), intermediate polishing (P), and nitriding (N), always in that order (see also Table 2). In each case two samples were used. During the SMAT, spherical shot is set in motion by a high frequency (20 kHz) ultrasonic generator. Random shot impacts at the sample surface generate severe plastic deformation and a superficial nanocrystalline layer [5,15]. This process takes place at standard atmospheric conditions. Suitable SMAT parameters such as processing time (30 min) and shot size (3 mm) were chosen based on previous experiments [16]. An intermediary polishing step is thus carried out to remove a thin superficial layer of 3 ± 0.3 μm. The amount of material removed was measured by successively indenting the surface layer by a Vickers indenter with different loads. Using the projected areas of the indenter, this amount was carefully determined and controlled. Before being placed in the nitriding chamber, the samples were ultrasonically cleaned in an acetone bath. The nitrided samples were all treated in the same manner: they were put into the plasma nitriding furnace simultaneously and at the same distance from the furnace wall. Plasma nitriding was then carried out for 20 h at 425 °C [2] in a 20% $N_2 + 80\%$ H_2 gas mixture at a pressure of 500 Pa [13]. The temperature was measured and controlled by a thermocouple placed inside one of the samples. The nitriding time of 20 h was chosen according to the thermal stability TTT diagram of γ_N [13].

2.2. Material characterisation

The materials were characterised by several techniques. Transverse sections were cut for measuring layer thicknesses and grain sizes using Optical and Scanning Electron Microscopy (OM and SEM) as well as Electron BackScattering Diffraction (EBSD). These sections were polished and etched in a 50 vol.% $HCl + 25\%$ $HNO_3 + 25\%$ H_2O solution to reveal the nitrided layer. Microhardness profiles were measured by a Vickers indenter (Model FM-300e) using a 25 g load. Each data point corresponds to the average of seven indentations. Nitrogen concentration profiles were obtained using a LEO 1450VP SEM with Energy Dispersive X-ray Spectroscopy (EDS). The crystal structure was analysed by X-ray diffraction (XRD) with a Seifert PTS-3000 X-ray diffractometer using CrKα radiation and Bragg–Brentano conditions, directly on the sample surface.

3. Results and discussion

3.1. Thermal stability of the nanostructure generated by SMAT

In order to establish the thermal stability of the nanostructure during the nitriding, the grain sizes of different annealed samples (SS, SA5 and SA20) were determined at 2 μm below the surface from multiple SEM and EBSD observations. Fig. 1 shows a close-up inside the layer affected by SMAT (which extends to beyond 200 μm), of a typical example of one of these microstructures (SS). The average grain sizes are summarised in Table 3. It can be observed that the different annealing treatments hardly affect the average grain size of the nanocrystalline surface, and that a nanocrystalline layer composed of nanograins smaller than 50 nm is still present after 20 h at 425 °C.

Table 2
Sample treatments.

Designation	SMAT	Annealing	Polishing	Nitriding
Untreated	–	–	–	–
SA5	✓	5 h	–	–
SA20	✓	20 h	–	–
SS	✓	–	–	–
N425	–	–	–	20 h at 425 °C
SN425	✓	–	–	20 h at 425 °C
SPN425	✓	–	✓	20 h at 425 °C

3.2. Layer morphology and nitrogen profiles

The thickness of the nitrided layer in each sample was determined by OM (Fig. 2a). Fig. 2a shows that SMAT significantly modifies the thickness and uniformity of the nitrided layer. Samples N425 and SPN425 both have a continuous nitrided layer with relatively uniform thickness, but the one in SPN425 is thicker: 40 ± 2 μm instead of 26 ± 4 μm. Conversely, in sample SN425 only a partial nitrided layer is present and the thicknesses of its nitride islets are generally smaller than the thicknesses of the nitrided layers of N425 and SPN425.

Average nitrogen profiles along the cross-section of different nitrided samples, obtained by EDS, are shown in Fig. 2b. The net counts presented in this figure are supposed to be proportional to the nitrogen concentration. Three zones of each sample were analysed by EDS to check the accuracy and repeatability of the results. The nitrogen curves fluctuate due to the intrinsic scatter of the measurements. As in the optical micrographs, the nitrogen penetration depths again show that nitrogen diffuses furthest into SPN425 and that it hardly diffuses into SN425.

3.3. Micro-hardness profile

In order to have some indication as to how the duplex process affects the hardness, Vickers micro-hardness (HV) was measured through the cross-sections of the samples as shown in Fig. 3. At the surface, SPN425 and N425 have a similar micro-hardness (1118 ± 108 and 1088 ± 110 $HV_{0.025}$ respectively), which is about five times higher than that of the untreated sample. However, the hardness decreases much slower with depth for SPN425 than for N425. This indicates that the nitrided layer of the SPN425 specimen is thicker

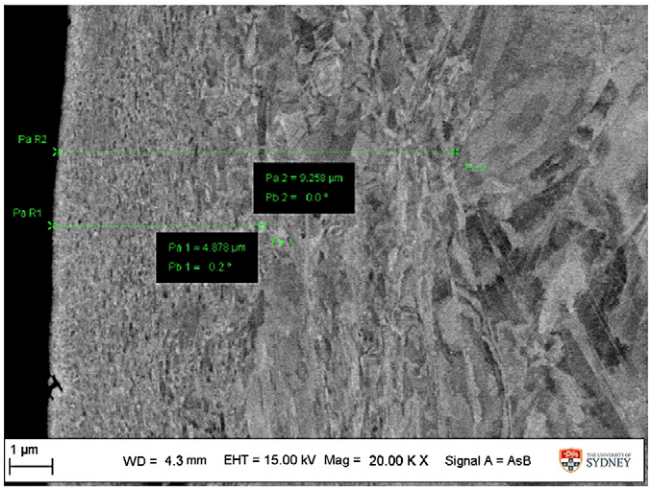

Fig. 1. Cross-sectional SEM micrograph of the SMATed sample (SS). The image shows the grain refinement near the surface inside the zone affected by SMAT. The latter extends to beyond 200 μm (outside of the image).