M. Suś-Ryszkowska, H. Matysiak, M. Miśkiewicz, E. Skolek, T. Wierzchoń, K. J. Kurzydłowski

Warsaw University of Technology, Faculty of Materials Science and Engineering,
Warsaw

STRUCTURE AND PROPERTIES OF THE GLOW DISCHARGE NITRIDED LAYERS PRODUCED ON AUSTENITIC STEEL

ABSTRACT

The study is concerned with the nitrided layers produced on 'medical' steel of the 316L (00H17N14M2) grade at a temperature of 450°C. The results of the microstructural observations performed by TEM and of the phase analysis of the layers are presented and discussed. The examinations were conducted in the regions extending from the surface down to a depth of about 25 µm. The near-surface zone appeared to contain nitrogen austenite and fine precipitates. There were also certain phases in the lamellar form. Because of the applicative aspect of the glow discharge nitriding of 316 steel, the examinations also included its mechanical strength, in particular the static tensile strength and the low-cycle fatigue strength. The static tensile tests showed no significant differences in the yield stress between the samples in the starting state and those subjected to the low-temperature glow discharge assisted nitriding. The low-cycle fatigue tests (which, in view of the differences between the properties of the untreated material and the nitrided layers, can be classified among the most severe mechanical tests) either, indicated no essential differences in the fatigue properties of the samples subjected to the surface treatments conducted under various conditions.

Key words: nitriding, austenitic steel, glow discharge, ,transmission electron microscopy, fatigue tests

EXAMINATION METHODS

Samples made of 316 steel (0.019%C, 0.327%Si, 1.377%Mn, 17.206%Cr, 10.602%Ni, 2.052%Mo, 0.004%Ti, 0.0431%N, 0.313%Cu, 0.085%Co, 0.026%P, 0.0264%S) were subjected to nitriding under glow discharge conditions at a temperature of 450°C for 4 hours (process 1), 5h (process 2), and 6h (process 3), and, at an elevated frequency of 80kHz, for 6h (process4) in a N₂+H₂ atmosphere (1:1 ratio).

The microstructure was observed in a Hitachi S-3500N scanning electron microscope. The metallographic cross-sections were etched using the Adler reagent of the composition: 3g CuCl₂-2NH₄Cl-2H₂O, 50cm³ HCl, 15cm³ FeCl₃, 20cm³ H₂O. The microstructure was also examined in a JEOL transmission electron microscope at an accelerating voltage of 120kV. The TEM samples were prepared so as to enable observation from the surface down into the material. Fig.1 schematically shows the cross-sections of the layer at the TEM sample. The samples were thinned by ion polishing. This method revealed not only the microstructure formed during the nitriding, but also radiation-induced defects in the form of fine dislocations and dislocation loops.

The chemical composition on the cross-sections of the samples was determined using the EDS method. The microhardness (HV0.05) was measured with a Zwick Materialprufung 322212002 micro-hardnessmeter, the surface roughness - with a Taylor Hobson Form Talysurf scanning profilometer, series 2, and the phase composition - with a Bruker D8 Discover X-ray diffractometer using CuK_α radiation. The static tensile test was conducted at temperatures of 23°C and 600°C using an INSTRON 1115 strength machine equipped with auxiliary equipment. A schematic diagram of the test samples is shown in Fig. 2. The starting straining rate was $4 \times 10^{-4} \text{s}^{-1}$ in all the samples. The stress-strain curves obtained were used for determining the basic strength indices:

- yield strength- R_e ,
- tensile strength - R_m , and
- total elongation - A_c .

The low-cycle fatigue test was performed on 6 axisymmetric samples, in accord with the Polish Standard PN-84/H-04334-2 (Fig.3, 2-initial state, 4-after the surface treatment), using an MTS 810 strength machine with a nominal maximum force of 100kN. The test was conducted within the $\pm 50 \text{kN}$ range with the use of an extensometric force sensor. The samples were fixed stiffly in hydraulic holders. The criterion of failure was taken to be the force reduction to 60% of the maximum force exerted during the last sequence of the 50 cycles. Prior to the test, the hydraulic system was adjusted, over the 25% range, using 316L steel samples with mechanical parameters similar to those of the samples examined.

Fig. 1. Schematic representation of a TEM sample

Fig. 2. Sample intended for static tensile test

Fig. 3. Sample intended for low-cycle fatigue test

RESULTS

Fig. 4 shows the microstructure, surface appearance and element distribution in the nitrided layer produced on 316L steel by glow discharge assisted nitriding at a temperature of 450°C for 5h. The layers thus obtained were about 5 μm thick and had a surface hardness of 1200 HV0.05. The nitrogen penetration depth was about 10 μm . Table 1 gives the values of the stereometric parameters that characterize the surface topography of the material in the starting state and after the glow discharge nitriding at a temperature of 450°C.

Fig. 4. (a) Microstructure of the layer produced on 316L steel by glow discharge nitriding at a temperature of 450°C; (b) the appearance of the surface and (c) distributions of chromium and nitrogen within the layer as a function of the distance down from the surface (process 2)

Table 1. Stereometric parameters characterizing the surface topography of 316L steel in the starting state and after the glow discharge assisted nitriding at a temperature of 450°C

Parameter	Initial state [μm]	Nitrided 450°C [μm]
R _a	0.0591	0.0939
R _q	0.077	0.12
R _p	0.965	0.546
R _v	0.53	0.907
R _t	1.5	1.45
R _z	1.12	1.28

R_a - mean arithmetic deviation of the roughness profile, R_q - mean square deviation of the roughness profile, R_p - maximum height of the roughness profile hill, R_v - maximum depth of the roughness profile valley, R_t - maximum height of the roughness peak (R_t=R_p+R_v), R_z - mean difference between the 5 highest peaks and the 5 deepest valleys of the roughness profile (acc. To ISO 4287/1-1984)

The phase analysis of the layer identified expanded austenite (the so-called phase S) present in the entire volume of the layer and a thin layer ($\leq 0,5 \mu\text{m}$) of iron nitride and chromium nitride CrN on its surface (Fig.5).

Since it is known from the literature that the thickness of the nitrided layer ranges from about 5 to about 30 μm [1, 2] and, depending on the process parameters even to 70 μm [3, 4], we conducted our TEM observations at various depths of the sample. Representative photographs of the nitrided layer are shown in Fig.6.

Fig. 5. Diffraction pattern of the surface of 316L steel after glow discharge nitriding (process 2)

Fig. 6. Microstructure of 316L steel after the glow discharge assisted nitriding

TEM observations show dislocations of high density, especially near the sample surface, i.e. in the nitrided layer. We can infer from our TEM observations, and analyses of the phase composition (and the reported literature data [1, 3]) that the near surface layer contains expanded austenite and, from place to place, CrN precipitates. It is worth noting that the fact that the expanded austenite is a solution super-saturated interstitially by nitrogen greatly affects the structural and diffraction images since such a solution is

liable to lattice distortion and low phase stability. Hence the tendency to form CrN precipitates, especially in the regions far away from the layer surface. Frequently, these two phases occur in a lamellar form (bands 10 to 50nm wide) with even smaller precipitates present within the bands. Similar band shaped structures have been observed by other investigators [1, 3, 7, 8, 11]. Some of the authors suggest that these bands are associated with the stacking faults and dislocations [9] formed as a result of the super-saturation with nitrogen that take place during nitriding. The nitriding process promotes the formation of the band structures, which most probably are initiated by the numerous stacking faults present in the nitrogen saturated austenite of the γ N type. According to the literature reports [e.g. 10], the band-shaped structures are characteristic features of expanded austenite, just as are the regions of high dislocation density with the dark spots of precipitates which can be identified as CrN. Micrographs of the microstructure, together with the diffraction patterns taken at a depth of about 8 μ m are shown in Fig.7.

Fig. 7. Microstructure of nitrided 316L steel and respective diffraction images

MECHANICAL EXAMINATIONS

In order to find how the nitrided layers produced on 316L steel under various glow discharge conditions affect the mechanical properties of the steel, the steel thus nitrided was subjected to low-cycle fatigue tests and to mechanical examinations. The fatigue tests were conducted on axisymmetric samples under the conditions of elastic-plastic

deformation at a constant cycle asymmetry coefficient $R = -1$ ($R = \epsilon_{\min}/\epsilon_{\max}$). For the sake of comparison, the material in the starting state was also subjected to the tests.

Our experiments were based on the assumption that the nitrided layers would improve the tribological properties of the steel with its corrosion resistance being preserved, which was expected to be achieved by increasing the hardness of the steel and reducing its ductility.

The discontinuities formed in the layer during the low-cycle straining may enhance the propagation of the principal crack and, finally, may lead to rapid failure of the product stability. Moreover, in the so-called transition regions, there exists a stress gradient which results from the difference in the expansion coefficients between the materials of the layer and the core. To obviate this drawback and increase the fatigue strength, we should tend to induce compressive stresses in the layer so that they hamper the nucleation and propagation of cracks by closing the crack tips.

Our results show that the nitrided layers do not degrade the fatigue properties of 316L steel, and even slightly improve them depending on the thickness of the expanded austenite layer. Taking into account the stochastic character of the fatigue processes, and hence a possible spread of the results obtained, we may state that the nitrided layers and the untreated material withstand a similar number of the loading cycles until failure (Table 2).

Fig. 8. Appearance of a nitrided layer on 316L steel after a low-cycle fatigue test (process 3)

During the cyclic deformation process, a crack network was observed to form on the surfaces of all the layers examined. An example of such macro-cracks is shown in Fig.8. These cracks did not however enhance the crack nucleation processes or the development of the critical cracks that would reduce drastically the fatigue strength. Observations of the layer surface revealed small mass losses. No delamination was however observed, which is evidence that the bond between the layer and the substrate was effective and could successfully withstand the cyclic loading.

As can be seen from Table 2, it is only the nitrogen austenite layer produced by nitriding at a frequency of 80kHz (process 4), whose fatigue strength is significantly reduced compared to that of the starting material. Radial cracks and mass losses appeared on its entire circumference as early as during the first loading cycles, leading to stress concentration and defect accumulation in this region and, in consequence, to the reduction of the fatigue strength. The number of cycles recorded until failure, N_f , was here reduced by a factor of 2.

The static tensile test of this layer shows a decrease of the total elongation with respect to that measured in the other layers and in the starting material, with the values of the characteristic stresses $R_{0.2}$ and R_m being preserved. Fig.9 compares the tensile curves obtained at room temperature for 316L steel in the starting state and the steel with the nitrided layers formed on its surface. Table 3 gives the basic strength parameters of these materials measured at room temperature and at a temperature of 600°C.

Table 2. Mechanical properties of the steel 316L compared to the properties of the nitrided steel

Sample	Deformation amplitude	Minimum test stress [MPa]	Maximum test stress [MPa]	Number of cycles until failure N_f
316L steel initial state 2	2% ($\pm 1\%$)	-418	447	927
316L steel – nitriding (process 1)	2% ($\pm 1\%$)	-512	498.5	1191
316L steel - nitriding (process 2)	2% ($\pm 1\%$)	-514	500.5	1087
316L steel - nitriding (process 3)	2% ($\pm 1\%$)	-536	510	911
316L steel - nitriding (process 4)	2% ($\pm 1\%$)	-633.404	520	475

Fig. 9. Tensile curves obtained for 316L steel in the starting state and after nitriding

Based on the results of the static tensile test we can state that the strength parameters, in particular the yield stress, tensile strength and total elongation, of the samples in the starting state and those subjected to the surface treatment do not differ essentially. The only exception is the material treated in the high-frequency plasma, whose total elongation, measured at room temperature and at an elevated temperature, is smaller.

Table 3. Basic strength parameters of 316L steel in the starting state and after nitriding, measured at room temperature and at 600°C

T [°C]	R _{0,2} [MPa] Yield stress	R _m [MPa] Tensile strength	A _c [%] Total elongation
316L steel - initial state			
23	579	716	36.0
600	369	448	17.8
316L (process 1)			
23	559	720	35.7
600	315	440	17.0
316L - (process 2)			
23	560	711	38.8
600	408	504	17.8
316L - (process 3)			
23	548	717	39.8
600	449	516	12.5
316L - (process 4)			
23	512	687	16.0
600	345	466	10.5

FINAL REMARKS

The glow discharge assisted nitriding of 316L steel at a temperature of 450°C yielded nitrided layers 10-30µm thick with a surface hardness of about 1200 HV0.05 (starting material - 230HV0.05).

The layers contained nitrogen austenite (known as the phase S) in their entire volumes, and iron nitride Fe₄N and chromium nitride CrN in the near-surface zones.

TEM observations confirmed the presence of expanded austenite (γ_N) and CrN precipitates in the layer microstructure. Other characteristic features of the layers are numerous stacking faults and high dislocation density. The sub-structure of the stacking faults is formed as a result of the saturation austenite with nitrogen, since this reduces the stacking fault energy [14].

Nitrided layers on steel 316L, formed at temperature 450°C, do not degrade its mechanical properties of steel. These layers are increasing wear resistance of friction

and slightly its corrosion resistance [2].

Process of glow discharge nitriding (frequency of 80 kHz) leads to decreasing of strength properties of steel 316L. It is caused by the fact, that the layer thickness to the level of about 30µm.

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