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DEPTH CHARACTERISTICS OF GLOW-DISCHARGE NITRIDED LAYER PRODUCED ON AISI 4140 STEEL

GŁĘBOKOŚCIOWA CHARAKTERYSTYKA WARSTWY WIERZCHNIEJ AZOTOWANEJ JARZENIOWO STALI 42CrMo4

Investigation results under structure and physicochemical properties of glow-discharge nitrided (H_2/N_2 atmosphere, 520°C) AISI 4140 (42CrMo4) steel are presented in the paper. The successive thinning method has been applied to determine corrosion resistance changes within the cross-section of the nitrided layer. The method consists in step by step polarization corrosion measurements for successive surfacial layers. The potentiokinetic polarization tests were carried out in acidified (pH = 2) 0.5 M sulphate solution. Depth and structure of the nitrided layers were evaluated on the basis of microscopic observations as well as microhardness and chemical analysis within nitrided layer. The performed nitriding treatment was prone to clear improvement of corrosion characteristics of the outer layers of the tested steel (up to ca 20 μm) within the passive range. Nitriding did not affect the corrosion behaviour of the tested steel in active range.

Keywords: corrosion resistance, depth profile, steel, glow-discharge nitriding

W pracy przedstawiono wyniki badań nad budową i właściwościami fizykochemicznymi warstw powierzchniowych stali 42CrMo4 (AISI 4140) po procesie azotowania jarzeniowego w atmosferze N_2/H_2 w temperaturze 520°C. Dla określenia zmian w odporności korozyjnej na przekroju poprzecznym warstwy azotowanej wykorzystano metodę postępującego ścieniania, która polega na wykonywaniu polaryzacyjnych testów korozyjnych na coraz głębiej położonych fragmentach warstwy wierzchniej. Badania potencjokinetyczne wykonano w 0,5M roztworze siarczanowym zakwaszonym do pH = 2. Grubość i strukturę powstałej warstwy wierzchniej oceniano na podstawie obserwacji mikroskopowych, zmiany mikrotwardości oraz analizy chemicznej zawartości pierwiastków w warstwie azotowanej. Stwierdzono, że przeprowadzona obróbka azotująca poprawia charakterystykę korozyjną w obrębie stanu pasywnego w najbardziej zewnętrznej części warstwy (do ok. 20 μm). Azotowanie praktycznie nie wpływa na zachowanie korozyjne stali w zakresie aktywnym.

1. Introduction

Nitriding of steel is one of the best known technologies, being widely used in the world's materials engineering. The popularity of nitriding stems mainly from the valuable service properties of the top layer, which include: high hardness, seizure resistance and adhesive wear resistance, high fatigue strength, and improved corrosion resistance [1-3]. Also domestically, advanced surface treatment methods, including those of nitriding different steel grades, have been developed in numerous Poland's scientific centres for a number of years [4-6]. Top layers obtained on constructional steels as the result of nitriding are built chiefly of a mixture of the nitrides ε $Fe_{2-3}N$) and γ' (Fe_4N), with their thickness being dependent on the nitriding parameters, under which there is a diffusion zone α with precipitates of the nitrides of alloying elements: Cr i Mo [7]. So, often, in addition to the iron nitrides ε and γ', also chromium nitrides CrN i Cr_2N occur in the outermost part of the nitrided layer [8]. The presence and concentration of particular phases and precipitates at specific depths of the top layer determine also the corrosion resistance of the material in question. As both the corrosion resistance and mechanical strength of steel are the resultant of the interaction between forming precipitates and the matrix and the amount of Cr in the precipitates, therefore the present work undertakes studies aimed at the understanding of changes in corrosion resistance on the cross-section of the nitrided top layer on chromium-manganese alloy steel.

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2. Experimental procedure

The subject of testing was AISI 4140 (42CrMo4) low-alloy steel of the following chemical composition (mass %): 0.42C, 1.05Cr, 0.81Mn, 0.19Mo, 0.28Si and 0.0077N. The test material was subjected to ion nitriding in an N_2/H_2 atmosphere with the volume ratio of 1:1 at a temperature of 520°C. The surface treatment parameters were selected so as to obtain of a relatively thick surface layer that would have clearly diversified properties on its cross-section.

Metallographic examination was carried out on Nital-etched specimens using a Neophot 32 optical microscope. Microhardness was measured by the Vickers method with a load of 0,4903 N (HV0.05) along normal to the nitrided surface on the cross-section of samples. Based on the distribution of microhardness, the thickness of the diffusion layer obtained after nitriding was determined. As the limiting criterion, the core hardness plus 150 units was assumed [3]. The examination of chemical composition in the layer cross-section was accomplished by glow discharge optical spectrometry (GDEOS).

2.1. Polarisation corrosion tests

Potentiokinetic polarization tests were carried out in an 0.5M acidified whit H_2SO_4 to pH = 2. Electrodes for the polarization testing of the nitrided AISI 4140 steel had the form of rotating discs (steel sample starting mass ca 19,3891g) with the operating surface area of 0.2 cm^2. Prior to each potentiokinetic measurement, parallel electrode layers of a thickness of 2 ÷ 8 μm were taken off by polishing (waterproof emery paper, grade 1000), while proceeding from the surface into the depth of the steel. After polishing, the electrodes were rinsed with water, degreased in alcohol and dried. The thickness of the layers ground off was determined from the mass loss of the examined disc electrode in relation to its initial mass, established with an accuracy of ±0.02 mg. The methodology described above [9-11] is called the *progressive thinning method*. The potentiokinetic polarization curves have been measured at a temperature of 25 ± 0.1°C, with the disc rotation speed equal to 12 rps and with the potential scan rate of 10 mVs^{-1}, applying the potential scanning from $E_{start} = -1.5V$ up to the value of $E_{end} = 1.9V$. The values of all the electrode potentials are expressed versus the silver/silver chloride reference electrode (SSE) for which $E^{eq}_{Ag/AgCl} = 0.22V$.

3. Results and discussion

Sample photograph of the microstructure of top layer obtained after nitriding of AISI 4140 steel is shown in Fig. 1.

As it follows from Fig. 1, the nitrided layer is built of two zones: the outermost zone of a thickness of approx. 10-15 μm (Fig. 1A), the so called "compounds zone" – rich in precipitates of iron and chromium nitrides [12], and a diffusion layer reaching down to a depth of approx. 600-700 μm (Fig. 1B). Down to a depth comparable to that of the diffusion zone, an enhanced microhardness of the studied material is also observed – Fig. 2. Assuming the core hardness plus 150 as the limiting criterion for the diffusion layer, this layer has attained exactly the thickness of 600 m. It should be noted here that for typical nitriding technologies, slightly thinner layers of up to 300-500 μm are achieved on these types of steel [8,13].

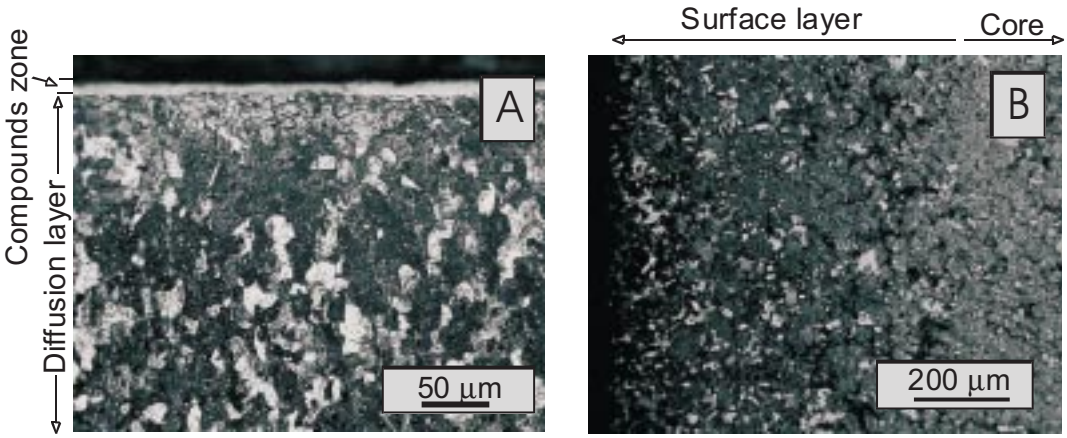

Fig. 1. Microstructure of the surface layer formed on AISI 4140 steel after its nitriding at 520 °C ($V_{N_2}/v_{H_2} = 1 : 1$)

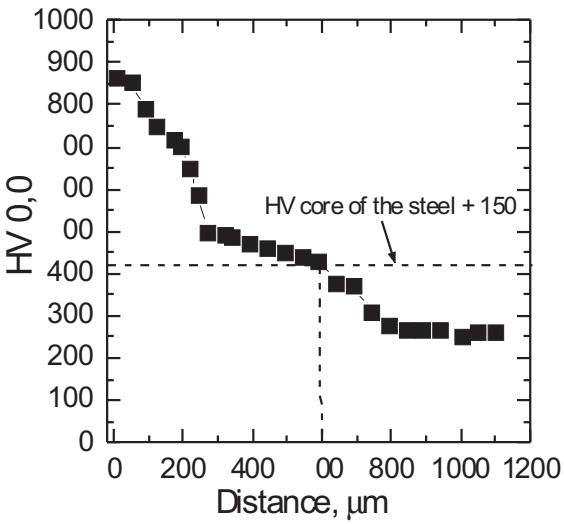

Fig. 2. Microhardness of nitrided AISI 4140 steel as a function of distance from the surface

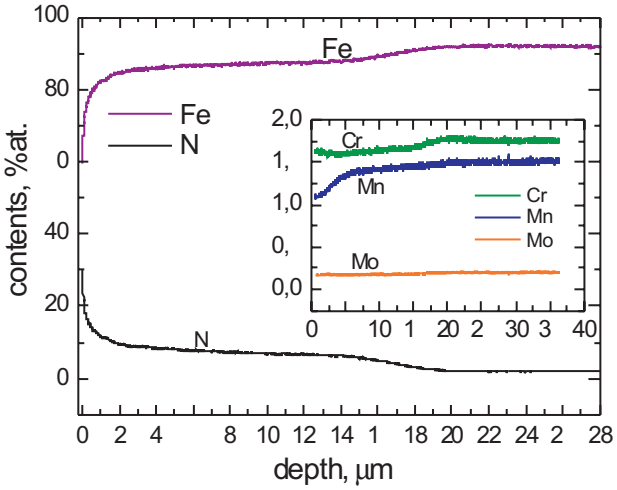

Fig. 3. Depth profiles of the chemical elements on the cross section of the nitrided layer of AISI 4140 steel

As can be seen from Fig. 3, a clearly increased nitrogen content is visible down to a depth of 10-15 μm, i.e. to the depth, where the "compounds zone" is observed for the nitrided low-alloy steel (Fig.1). Although no change in molybdenum content was observed on the cross-section of the nitrided layer, yet a reduction in chromium and manganese contents, though slight, was visible (to a depth of 5 μm). As demonstrated by an X-ray analysis presented in our previous paper [12], the outermost part of the layer is composed of precipitations of both iron and chromium nitrides of the Fe_2N, Fe_4N and Cr_2N types. Similar precipitations were also observed in the diffusion layer (15-600 μm). It should be mentioned that the intensity of the peaks corresponding these precipitations distinctly decreased with increasing distance from the surface; at the same time the intensity of peaks coming from iron increased. The complete disappearance of peaks originating in iron and chromium precipitates was observed at depths greater than 600 μm.

The polarization curves for the nitrided steel, made in a sulphate solution acidified to the pH=2, are shown in Fig.4 The obtained series of curves characterize the corrosion behaviour of the material at several depths from the prior nitrided surface. For a better legibility of the figure, among all polarization curves plotted for successive layers obtained by progressive polishing of the material, only the curves for several selected depths are shown. By taking off successive surface material layers and performing their electrochemical analysis, significant changes in the characteristic parameters of the polarization curves are displayed. These changes enable the determination of the corrosion resistance of the material on the entire cross-section of the top layer. It can be seen from the Fig.4 that nitriding influences the corrosion resistance of steel only in the range of steel transition into the passive state and within the passive range. Generally, no significant differences in the plot of the cathodic polarization curves were observed and within the active dissolution of the steel (directly above E_{cor}). As it results from Fig. 4, the extrapolation of the rectilinear segments of the polarization curves up to E_{cor} leads to comparable corrosion currents (at level of $1 mAcm^{-2}$) for all depths analyzed.

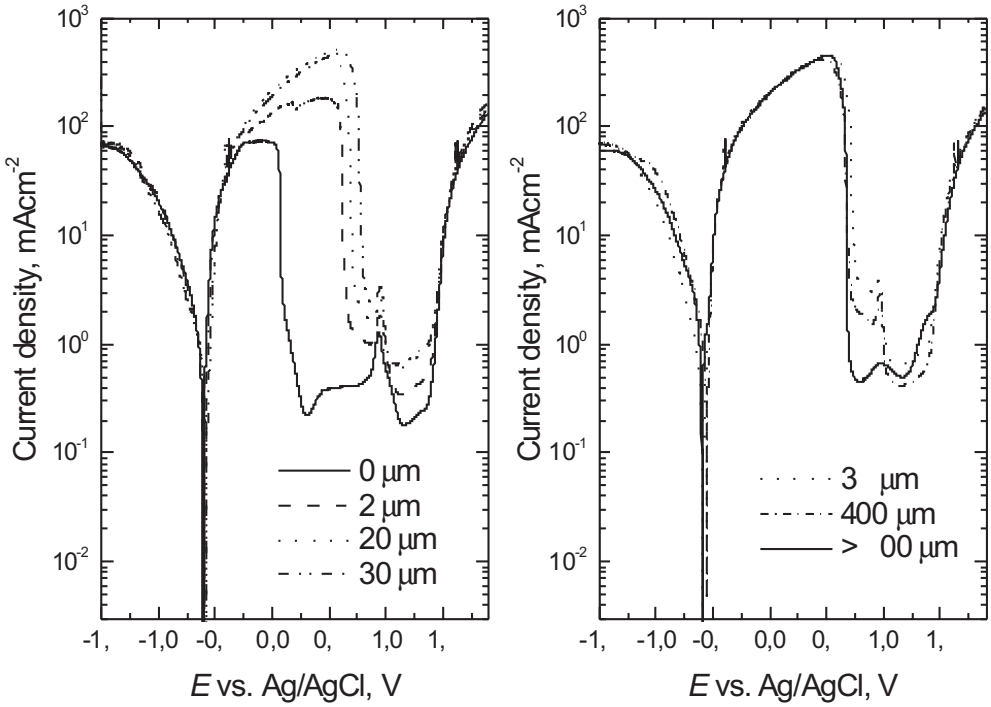

Fig. 4. Potentiodynamic polarization curves of the nitrided AISI 4140 steel measured for different depths from the surface. Experimental conditions: 0.5M sulphate solution, pH = 2, temperature: 25±0.1°C, stirring rate: 12 rps, potential scan rate: 10 mVs^{-1}

It is seen from Fig. 4 that the transition of the steel into the passive state is particularly easy for the outermost nitrided layers. For the first layer (0 m), the potential of transition into the passive region is approx. +0.2V, and the minimal current within the passive range reaches a value of approx. 0.2 $mAcm^{-2}$. This observation is consistent with the results obtained by Mańkowski and Zych [14,15]. However, starting from the depth of 2 μm, a distinctly more positive passivation potential (~0.5 V) and increasingly higher current densities in the passive range are measured. Starting from the depth of 30 μm, the passivation potential settles at the level of 0.6 V. Another important phenomenon, this time appearing within the passive state range (0.5 – 1.5V), is the occurrence of an anodic peak at E=0.9V. This peak divides the passive range into two distinct parts. For the left-hand part of the passive range (0.5 – 0.9 V), the anodic currents are generally 2-4 times higher than these for the right-hand part (0.9 – 1.5 V). The peak under consideration practically vanishes for depths typical for the interior of the sample (> 700 μm), thus its occurrence should be associated with the presence of nitride precipitates. Its occurrence as the result of the transpassive oxidation of both Cr (1.05% in the steel) and Mn (0.81%) should be rejected, since at pH=2 these processes occur at more positive potentials: 1.0 ÷ 1.2 V [9,16]. It is also unlikely that the anodic peak at 0.9V could reflect the oxidation of passive layer components ($Fe(OH)_2 \rightarrow FeOOH$), as it was suggested by Kuczyńska-Wydorska et al [17], as in acidified media this type of transition Fe(II) → Fe(III) takes place at less noble potentials (ca 0.65 V vs Ag/AgCl). Taking into account the results obtained by Jagielska et al [9,16] for carburized and carbonitrided stainless steels, the hypothesis can be put forward that the observed peaks (0.9 V) reflect the transpassive dissolution of nitride precipitates. Bearing in mind the enrichment of these precipitates in Cr, as described earlier [12], it could be inferred that the products of this dissolution are CrO_4^{2-} ions (with nitrogen passing into the solution in the form of NH_4^+):

$$Cr_2N + 8H_2O - 9e \rightarrow 2CrO_4^{2-} + NH_4^+ + 12H^+ \qquad (1)$$

Thus, the oxidation of Cr nitride precipitates at E = 0.9V comes down to their removal from the surface, which results in an improvement in the effectiveness of the surface passive properties (i.e. a distinct decrease of the anodic current in the range of 0.9 – 1.5V). In Table 1 the parameters read out from Fig. 4, which describe the ability of AISI 4140 steel to passivation, i.e. corrosion potential E_{cor}, corrosion current i_{cor}, critical passivation potential and current E_{cp} and i_{cp}, as well as the minimum anodic currents within the left- and right-hand parts of the passive range under are presented for comparison.

TABLE 1

Parameters which define the ability of AISI 4140 steel to passivation, i.e. E_{cor}, i_{cor}, E_{cp}, i_{cp}, as well as the minimum anodic currents in the left- (i_l^{min}) and right-hand (i_p^{min}) parts of the passive range. The current densities expressed in mAcm^{-2}

Distance, [μm]	E_{cor}, [V]	i_{cor}	E_{cp}, [V]	i_{cp}	i_l^{min}	i_p^{min}
0	-0.60±0.02	100±5	0.020±0.002	72±5	0.20	0.16
2÷20	-0.57±0.03	100±10	0.50±0.04	190±10	1.0	0.30
25÷30	-0.56±0.02	140±10	0.54±0.05	495±15	1.6	0.60
35÷400	-0.55±0.04	100±5	0.60±0.04	490±10	2.0	0.60
400÷600	-0.58±0.03	100±5	0.60±0.02	490±10	2.5	0.60
Core (>600)	-0.58±0.02	100±5	0.60±0.02	490±10	0.48	0.49

As it has already been mentioned, nitriding practically does not affect the steel behaviour both in the cathodic region and within the active anodic dissolution range, hence the corrosion rates in the active state are comparable for all the tested depths. For strongly cathodic potentials (< – 1.2V), the reduction of hydrogen ions is controlled by diffusion, with the limiting current being $i_{H^+,lim}$ = 60 - 70 mAcm^{-2}, which is fully consistent with other literature data [18]. Nitriding does not affect the kinetics of anodic oxygen evolution either (see the polarization curves for E > 1.5 V) – the respective anodic curves practically coincide, showing a slope of b_{a,O_2} = 0.12V.

4. Concluding remarks

- Nitriding of AISI 4140 steel surface has little effect on its general corrosion at pH = 2, especially in active state.
- The corrosion resistance of the passivated nitride layer is closely related with its composition and phase structure. The best protective properties in the passive range are revealed by the outermost compounds zone of the nitrided layer.
- As a result of nitriding, the passive state characteristics of the AISI 4140 steel are improved: nitriding decreases the critical passivation current and moves the potential of transition into a passive state towards more negative values.
- Within the passive range of nitrided steel an anodic peak occurs at E = 0.9V that can be ascribed to the transpassive dissolution of Cr-rich nitride precipitates.

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