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DEPTH-PROFILES OF CORROSION PROPERTIES OF CARBONITRIDED AISI 405 STEEL

GŁĘBOKOŚCIOWE PROFILE WŁAŚCIWOŚCI KOROZYJNYCH WĘGLOAZOTOWANEJ STALI X6Cr13

Electrochemical polarisation characteristics of AISI 405 type stainless steel, carbonitrided in fluid flow, are presented. The evaluation of the corrosion resistance of carbonitrided stainless steel was carried out by using the so called progressive thinning method, consisting in determination of polarisation characteristics on increasingly-deeper situated regions of the top layer. This method made it possible to determine changes in particular corrosion parameters read out from potentiokinetic polarisation curves, thus enabling the depth profiles of these parameters. The resistance of the AISI 405 steel against acid corrosion was determined in acidified 0.5M sulphate solutions having three different pH values, namely 1, 2 and 4. The thickness of the carbonitrided layer has been evaluated on the basis of the spectrophotometric analysis of carbon content and microhardness on the cross section of the surfacial layer.

Keywords: corrosion, depth profile, stainless steel, carbonitrided, fluid flow

W pracy przedstawiono elektrochemiczne charakterystyki polaryzacyjne stali X6Cr13 (AISI 405) poddanej węgloazotowaniu w złożu fluidalnym. Ocenę odporności korozyjnej otrzymanej w wyniku obróbki cieplno-chemicznej warstwy węgloazotowanej przeprowadzono wykorzystując do tego celu metodę postępującego ścieniania, która polega na wykonywaniu polaryzacyjnych testów korozyjnych na coraz głębiej położonych obszarach warstwy wierzchniej. Metoda ta pozwoliła na określenie zmian poszczególnych charakterystycznych parametrów korozyjnych odczytywanych z potencjokinetycznych krzywych polaryzacji. Badania odporności stali X6Cr13 na korozję ogólną wykonano w 0,5M roztworach siarczanowych o trzech wartościach pH: 1, 2 i 4. Grubość powstałej węgloazotowanej warstwy oceniano na podstawie spektrofotometrycznej analizy zawartości węgla oraz mikrotwardości na przekroju poprzecznym obrobionego cieplnie materiału.

1. Introduction

Stainless steel belongs to the broadly applied group of alloy steels with special utility properties [1].The mechanical and corrosion properties of metal alloys can be easy modified by thermochemical treatment of the material surface in suitable atmospheres [2,3]. The processes of carburizing and carbonitriding applied for the stainless steel ensure that the products made of this steel display high operational properties [4-6]. The improvement of mechanical properties of the steel surface is the result of formation of carbide- and nitride inclusions in the outer layers [6,7]. However, the negative effect of the high content of carbon and nitrogen in chromium steel can be precipitation of chromium nitrides and carbides on grain boundaries which results in the decrease in corrosion resistance and plasticity of the steel [1,8,9].

The present study aims at determination of depth profiles of the most important electrochemical corrosion parameters of the low carbon 13wt% chromium stainless steel, carbonitrided in propane-air-ammonia atmosphere with Al_2O_3 powder (particles of 0.1-0.2 μm indiameter) fluid beds.

2. Experimental procedure

2.1. Sample preparation

The subject of testing was AISI 405 (X6Cr13) steel of the following chemical composition (mass %): 0.05C, 12.6Cr, 0.47Mn, 0.5Si, 0.07Ni, 0.02Mo, 0.03Cu, 0.02P i 0.01S. The surface carbonitriding has been carried out inside the fluidized bed where the basis was corundum with graining of 0.1÷0.2 mm. The steel samples were diffusively heated in the corundum fluid beds in the propane and ammonia containing atmosphere at a temperature of 1000°C. After 160 mins lasting heating the

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samples were rapidly quenched in oil and then tempered 2 hours at 200°C in argon and finally cooled in air. The details concerning the carbonitriting method, the composition of gas atmosphere applied, fluid beds characteristics and conditions of its agitation are described in papers [10-12].

The microhardness of the carbonitrided surface has been measured using a Hanemann microhardnesstester at a load of 0.49N along normal to the carbonitrided surface on the cross-section of the samples. The chemical analysis of the samples and carbon content depth profile after the thermochemical treatment have been carried out using quantometer, similarly as described in papers [10, 13].

2.2. Polarisation corrosion tests

Potentiodynamic polarization tests were carried out in an acidified 0.5M sulphate solutions with pH = 1, 2 or 4. During the polarization measurement (and 15 minutes before each measurement), the solutions were deaerated with argon. Electrodes for the polarization testing of the carbonitrided AISI 405 steel had the form of rotating discs with the operating surface area of 0.2 cm^2. Prior to each potentiokinetic measurement, parallel elektrode layers of a thickness of 20÷30 μm were taken off by polishing, while proceeding from the surface into the depth of the steel. After polishing, the electrodes were washed in water, degreased in alcohol and dried. The thickness of the layer 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 [13-15] is called the *progressive thinning method*. The potentiodynamic polarization curves have been measured at the temperature of 25±0.1°C, with fast stirring rate to avoid surface

screening by gas bubbles (disc rotation speed equal to 12 rps). The potential scan rate was 10 mV/s, with its moving from E_{start} =-1,0V to the value of E_{end} = 1.9 V. The values of the electrode potentials are expressed versus the saturated calomel electrode (SCE).

3. Results and discussion

In Fig. 1 the depth profiles of carbon concentration of steel and its microhardness are presented. As it results from Fig. 1 the carbon rich area ranges up to 300 μm from the surface. For outer layers (up to 100 μm) the microhardness has not a very high value, however, it distinctly increases in the range of 200–400 μm and then decreases and reaches on values typical for the bulk of the steel. This unexpected depth profile of sample microhardness results from unusual structure of the surfacial layers: the outer layers exhibit structure of the retained austenite with chromium carbides cumulated at grain boundaries [11]. As demonstrated in our previous paper [11], X-ray analysis presented confirms considerable contribution of retained austenite in the outer layers and indicates presence of some kinds of Cr/Fe carbides like $M_{23}C_6$, M_7C_3, M_3C, carbonitrides: $M_7(C,N)_3$ and nitrides: M_xN (where x = 2-4).

In Figure 2 the polarization curves for carbonitrided in the fluidized bed the AISI 405 steel have been presented for three pH values. The curves series characterize the anodic behaviour of the material in several different depths relating to the sample surface which had been previously subjected to the carbonitriding. To make the plots more readable only the polarization curves for a few depths have been chosen out of tens of curves obtained for the consecutive layers removed.
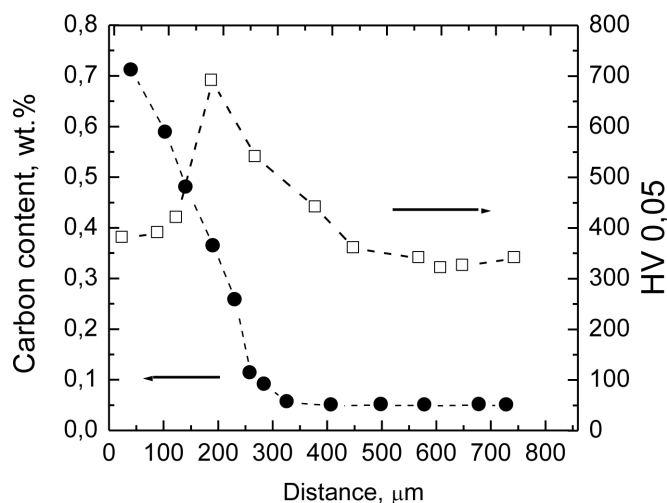

Fig. 1. Concentration of carbon and microhardness of carbonitrided AISI 405 stainless steel after its carbonitriding as a function of distance from the surface
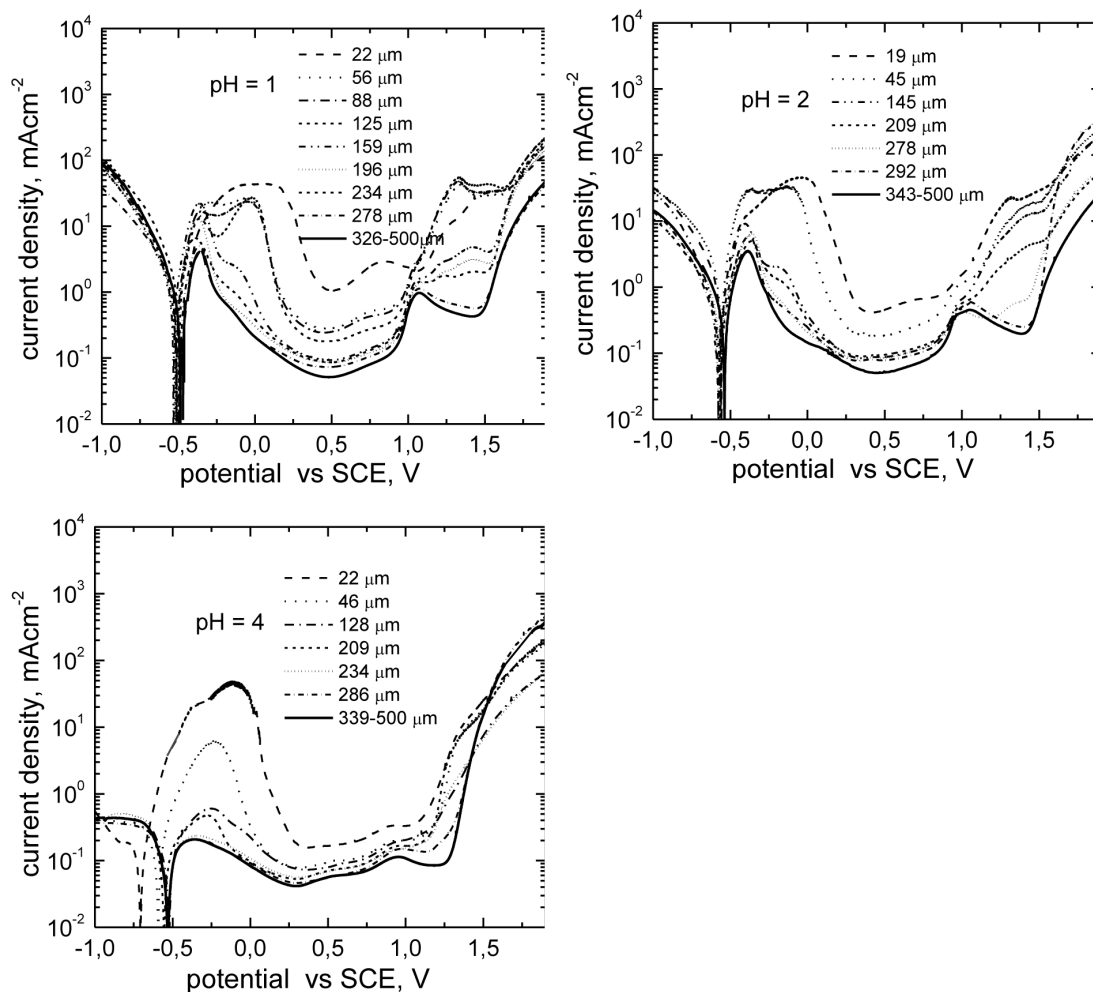
Fig. 2. Potentiokinetic polarisation curves for the AISI 405 steel carbonitrided in the fluid flow and ground away to a specific depth (μm), measured in 0.5 M sulphate solutions at three chosen pH values. Experimental conditions: 25± 0,1°C, electrode rotation speed 12 rps, potential scan rate 10 mVs^{-1})
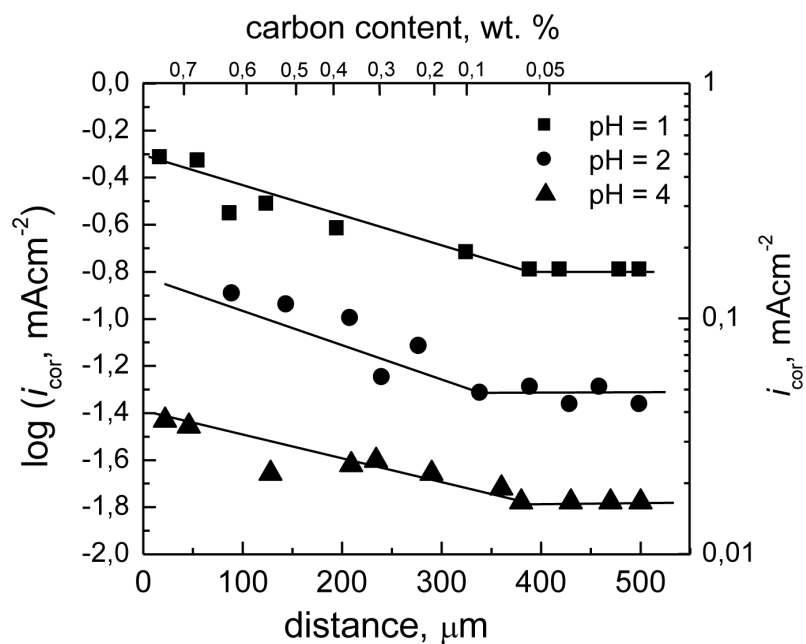

Fig. 3. Depth profiles for the corrosion current out from the polarisation curves measured for the carbonitrided AISI 405 steel in 0.5M sulphate solutions with pH = 1, 2 and 4
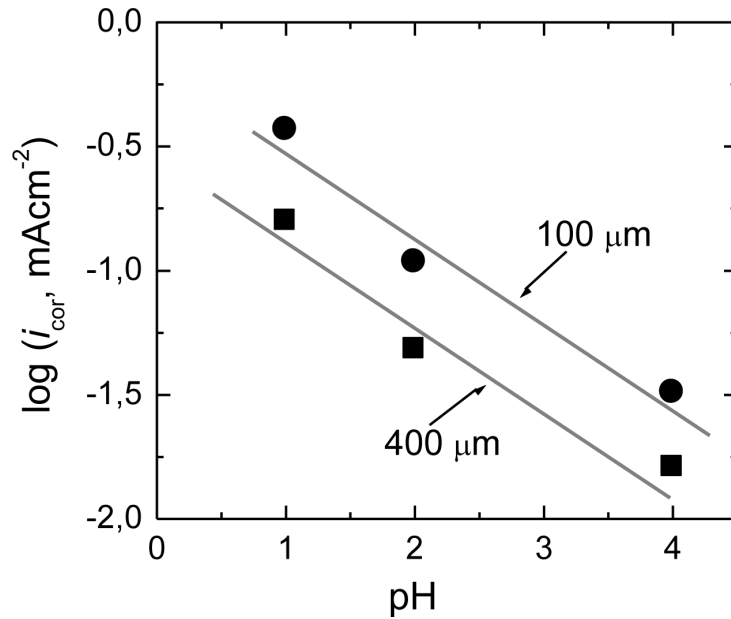
Fig. 4. The corrosion rate of carbonitrided AISI 405 steel at the depths of 100 and 400 μm from the surface as a function of solution pH

As it results from the polarization investigations, the termochemical treatment applied for the AISI 405 steel deteriorates the anodic characteristics of the outer surface layers, which generally manifests itself in distinctly greater anodic current densities for these layers. The changes of characteristic parameters read from the polarization curves for consecutive top layers enable to draw the depth profiles of these values. In Fig. 3, the corrosion current density depth profiles for the tested steel in the three applied sulphate solutions are presented. Additionaly, the carbon concentration for the outer layers is also presented in this figure.

As it results from Fig. 4, both for the carbonitrided area and for the bulk of the material the $\log i_{cor}$ linearly decreases with pH, and

$$\left(\frac{\Delta \log i_{cor}}{\Delta pH}\right)_{T=298K} = -0.4 \qquad (1)$$

holds good. The dependence (1) is similar to that found for active dissolution of pure iron in sulphate solutions at the pH range of 0-2 [16].

The potentiodynamic curves registered for deeper layers of the carbonitrided steel exhibit the systematic decrease in critical passivation current (i_{cp}) as well as (although less clear) the minimal anodic current within the passive range ($i_{min,p}$). In Fig. 5 the depth profiles of critical passivation current (A) and the minimal current within the passive range (B) have been presented.

The decrease of critical passivation current i_{cp} (as well as minimal current within passive range $i_{min,p}$) have

been observed for the investigated steel up to the depth of ca. 300 - 350 μm. For deeper areas further changes of both parameters are insignificant. In Fig. 6 the i_{cp} and $i_{min,p}$ current densities read out for the corresponding pH from the polarization curves at the depth of 100 μm are presented.

As it results from Fig. 6, logarithms of both i_{cp} and $i_{min,p}$ linearly decrease with the increase of pH of sulphate solution with the slopes:

$$\left(\frac{\Delta \log i_{cp}}{\Delta pH}\right)_{100\mu m} = -0.5 \qquad (2)$$

and

$$\left(\frac{\Delta \log i_{min,p}}{\Delta pH}\right)_{100\mu m} = -0.2 \qquad (3)$$

The decrease of i_{cp} along with the increase of pH is much more rapid than the decrease of $i_{min,p}$. It should be mentioned that the partial derivative (2) takes on similar values also for deeper parts of the steel, including those exceeding the carbonitrided area. On the other hand, in case of the $\left(\Delta \log i_{min,p} / \Delta pH\right)$ derivative it has been observed that for sufficiently deep areas it reaches values aimed to zero.

The parameters describing corrosion resistance and anodic behaviour of the carbonitrided steel, determined out of the polarization curves for the material areas deeper than 350 μm, do not show significant differences and practically converge with the curves obtained for these steels after traditional treatment [13,14].
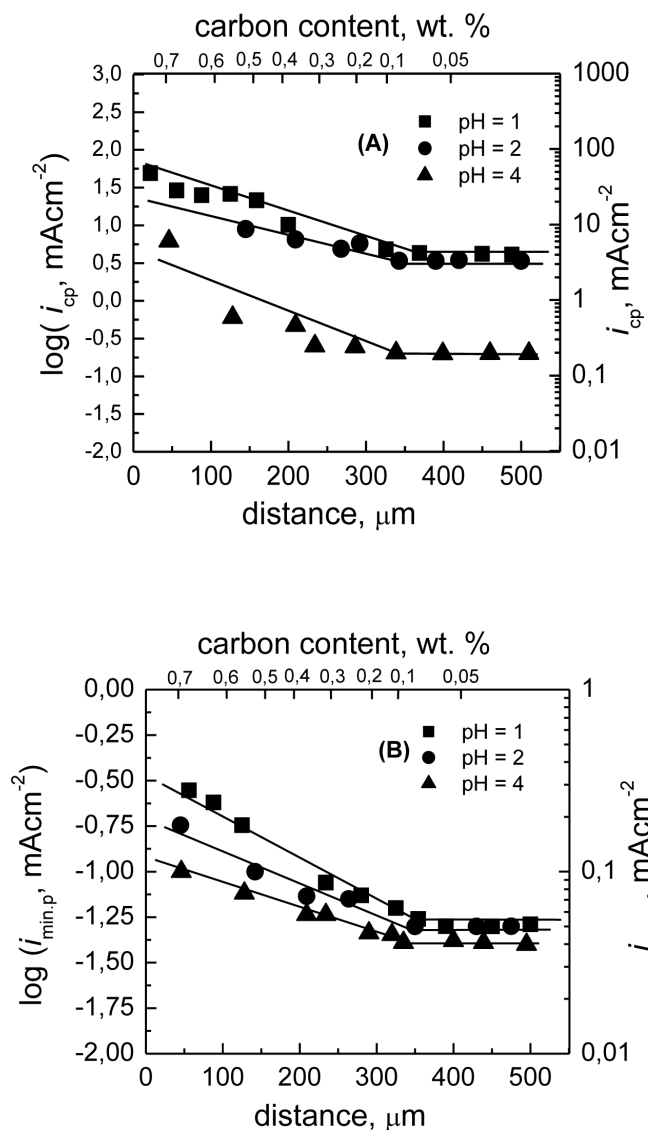
Fig. 5. Depth profiles of the critical passivation current (A) and minimal current within the passive ran ge (B) read out from the polarisation curves measured for carbonitrided AISI 405 steel in 0.5M sulphate solutions with pH = 1, 2 and 4
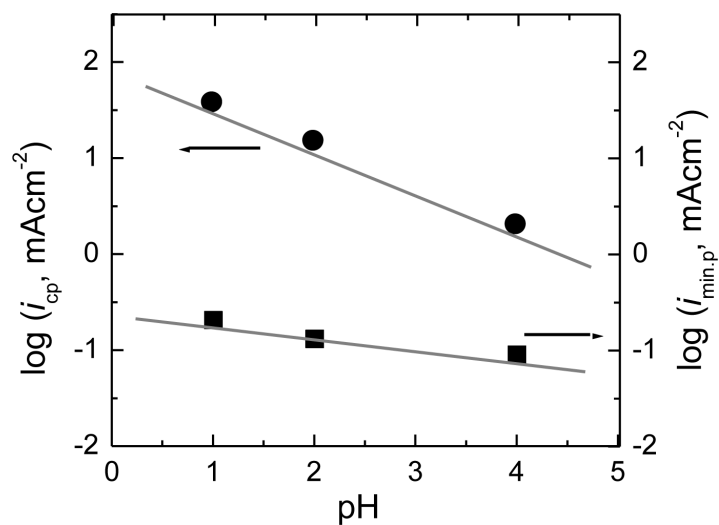

Fig. 6. The effect of pH on the values of i_{cp} and $i_{min,p}$ for the carbonitrided stainless steel at the depth of 100 μm

4. Concluding remarks

–   The thermochemical treatment of the AISI 405 steel leads to a substantial improvement in the hardness and strength of the surface layer of the material. The increase in microhardness is a result of precipitation of carbide and carbonitride phases formed in the top layers reaching to a depth of 350 μm inside the material. The carbide and nitride precipitations involve large amounts of chromium from the matrix, which generally has an unfavourable effect on the corrosion behaviour of the outer layers.

–   Using the examination method applied in the present study, it is possible to register precisely any changes in the corrosion resistance of a material over the entire top layer cross-section.

–   As a result of carbonitriding, the passive state characteristics of the AISI 405 steel undergo deterioration: carbonitriding increases the critical passivation current and moves the potential of transition into a passive state towards more negative values.

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