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### ELECTROCHEMICAL CHARACTERISTIC OF SOME METAL CARBIDES

Potentiodynamic and quasipotentiostatic method were applied in the electrochemical investigations of carbides. These investigations were conducted with "glued" powder electrodes.

Polarization curves obtained for  $\text{Cr}_3\text{C}_2$ ,  $\text{Cr}_7\text{C}_3$ ,  $\text{Cr}_{23}\text{C}_6$  and Fe,  $\text{Cr}_{23}\text{C}_6$  carbides in 0,5 M  $\text{H}_2\text{SO}_4$  are due to produce a qualitative and quantitative characteristic of the electrodes.

Tafel's coefficients, corrosion potentials and their pH - dependences were obtained.

Investigations of electrosynthesis processes of organic compounds are closely connected with the determination of influence of both medium and electrode material on the course of reaction.

That is bound up with the research of new electrode materials. An application of material carbides as electrode material needs the knowledge of basic electrochemical characteristic of substances in question. Solid carbide electrodes are made usually by pressing caking of specially composed carbide powders.

In this work we have tried to determine the electrochemical properties of chosen carbide powders. The preparation of electrodes was done according to our own method.

During a process of a thermal and mechanical working in alloy steel containing chromium, niobium, titanium, tungsten and slight amounts of carbon, the intercrystalline separation of non-stoichiometric metal carbides takes place.

In certain conditions these carbides can be used as an electrode material whose corrosion characteristic is different from the rest of the steel. In order to obtain this characteristic the investigations should be carried out on the right, pure carbides obtained synthetically or isolated from steel.

The works on electrochemical studies present the potentiodynamic investigations of electrodes made mostly of pressed metal carbides. There is also a work [ 1 ] on the investigation of the carbides deposited in high-speed centrifuges on a platinum, nickel or cobalt base. The carbides deposited by means of a diffusion have been investigated as well [ 2 ] .

A vast thermodynamic and electrochemical characteristic of the carbides has been presented by Ł a s z k o [ 3 ] in his monograph.

The work contains a detailed report on the methods of a chemical and electrochemical separation of the particular phases in steel desintegration. The polarization curves quoted by the author are not sufficient for the precise definition of such parameters as: corrosion potential, Tafel coefficients, etc. The potential ranges typical only of transpassivation processes ( $\varphi > 1,4 V_{SCE}$ ) are well characterized. Being simple to obtain powder electrodes are becoming very popular nowadays. The X - ray investigations of powder metal carbides [ types:  $Cr_7C_3$ ,  $Fe_7C_3$ ,  $(Cr_{1-x}Fe_x)_7C_3$  and  $(Cr_xFe_{1-x})_{23}C_6$  defining their structure were presented in the works [4] and [5] .

### Experimental

In order to obtain the polarization curves of the carbide electrodes in question an equipment consisting of a potentiostat P-20-0,5, a linear sweep generator (A), a log amplifier and two parallel XY recorders BAK.- 4T was used. The polarization of a single sample, while using this equipment, enabled to obtain both the cyclic voltametric and quasipotentiostatic polarization curves in system  $lg_1 = f(\varphi)$ .

A classical three electrode system with a calomel electrode in a KCl saturated solution as a reference electrode SCE and an auxiliary platinum electrode separated from the working

one by means of a porous glass diaphragm was applied in these investigations.

The polarization curves were made for the following carbides:  $\text{Cr}_3\text{C}_2$ ,  $\text{Cr}_7\text{C}_3$ ,  $\text{Cr}_{23}\text{C}_6$ ,  $(\text{Fe}, \text{Cr})_{23}\text{C}_6$  in solution 0,5 M  $(\text{H}_2\text{SO}_4 + \text{K}_2\text{SO}_4)$  of the variable pH value and in 0,5 M  $\text{H}_2\text{SO}_4$  containing ions  $\text{Cl}^-$  of the variable concentration. The carbides in powder came from INSA-Lyon where they were made from the spectra-pure materials and checked by means of an X-ray testing. The carbide insulated from steel  $(\text{Fe}, \text{Cr})_{23}\text{C}_6$  containing about 15 per cent of the phase 5 was acquired from the Institute of Physics and Chemistry of the Silesian University. The investigations presented in this work were carried out while using the electrodes produced on the basis of the so called powder electrode and the carbon-paste electrodes. In order to create them a conductive gel (agar-agar or methylcellulose) was made in  $\text{K}_2\text{SO}_4$  solution and carefully mixed with a weighed quantity of the carbide which was to be an electrode material. The container (Fig. 1) of the volume of 0,5  $\text{cm}^3$  was filled with such prepared paste. In the next stage of the preparatory work the electrode was rinsed, dried in 350 K and cooled down to the room temperature. After filling up the container only with gel the quasipotentiostatic curves have been obtained in each of the investigated solutions. These curves have shown that there was no electrode reaction of platinum contact and the value of current in the considered range of polarization potentials was constant and negligible.

After immersing the carbide electrode in the electrolyte solution, it was exposed to a cathodic polarization with the evolution of hydrogen for about 10 minutes, brought to the corrosion potential in which it was polarized for 2 minutes and again exposed to the cathodic polarization up to the evolution of hydrogen.

That has assured simultaneously:

1. Testing of exact preparation of the electrode - an electrode being prepared in a wrong way contained hydrogen which had formed on platinum contact .
2. Reproducibility of results with accuracy  $\pm 10\%$ .

After such a treatment the right polarization curves were

taken with a demanded rate of a polarization potential ( $v = 2 \times 10^{-3} \text{ Vs}^{-1}$ ;  $5 \times 10^{-3} \text{ Vs}^{-1}$ ).

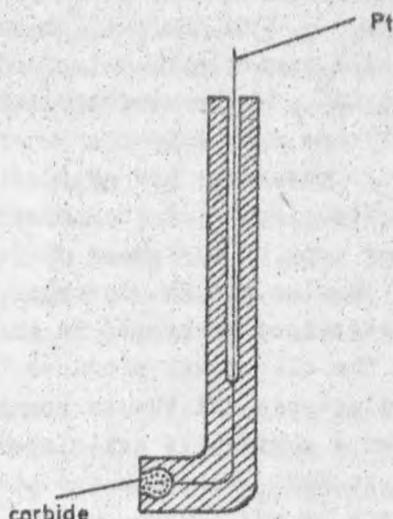


Fig. 1. Working electrode

The basic values of such prepared electrodes were: a well developed surface which enable to observe any weak potential-current (which might be also caused by changes of capacity, however, the investigations of this type were not performed), the ability of putting down the repeated polarization curves and the simplicity their production. Due to the well developed surface of the electrode, its precise definition was impossible here, so the given results were limited to a qualitative description of the polarization curves. On the basis of the graphical extrapolation of the semi-logarithmic curves, Tafel cathodic  $b_-$  and anodic  $b_+$  and the values of the corrosion potentials were obtained using the method proposed by Kelley [6].

### Results and Discussion

The literature on the electrochemical properties of the carbides  $\text{Cr}_3\text{C}_2$  is very scarce and limited to only one work by C i h a l and D e s e s t r e t [7]. This carbide belongs to the ones existing in steels very rarely, so for the purpose of the structural and thermodynamic studies it can be obtained by means of a direct synthesis. The electrochemical studies [7] carried out in 0,5 M  $\text{H}_2\text{SO}_4$  in 293 K revealed only the existence of a current peak with a potential  $\varphi \approx 1.0 \text{ V}_{\text{SHE}}$  and the occurrence of fast processes in the range of the passivation potentials. Polarization curves obtained in this work for the chromium carbide  $\text{Cr}_3\text{C}_2$  in 0,5 M ( $\text{H}_2\text{SO}_4 + \text{K}_2\text{SO}_4$ ) for the different pH values of the solution are presented in Fig. 2.

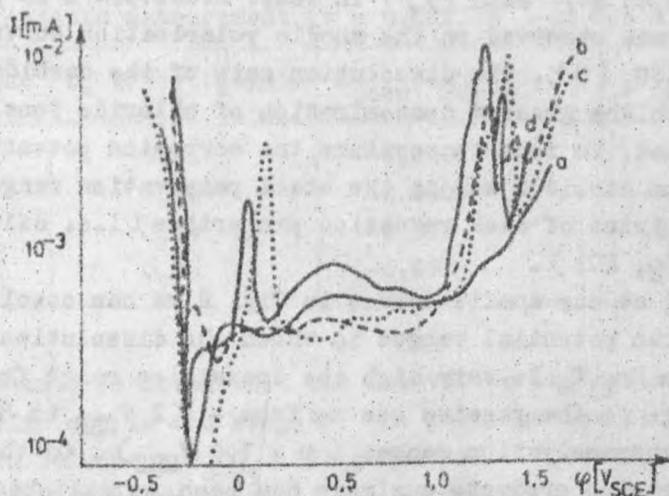


Fig. 2. Quasipotentiostatic ( $v = 0,002 \text{ Vs}^{-1}$ ) polarization curves in 0,5 M  $\text{H}_2\text{SO}_4$ : a -  $\text{Cr}_3\text{C}_2$ ; b -  $\text{Cr}_7\text{C}_3$ ;

c -  $\text{Cr}_{23}\text{C}_6 + \text{a}$ ; d -  $\text{Me}_{23}\text{C}_6$

The slope of the cathodic branch of the polarization curve in Fig 2 does not change when the pH values rise from 0,85 to 9,35, but the corrosion potential shifts to the anodic side ( $dE_{\text{corr}}/dpH = 120 \text{ V}$ ). The carbide  $\text{Cr}_{23}\text{C}_6$  is the most popular one among the carbides existing in alloy steel containing chromium. It occurs there also in mixed carbides. The literature on electrochemical properties of  $\text{Cr}_{23}\text{C}_6$  can be found more easily than the one on the carbide  $\text{Cr}_3\text{C}_2$ .

The pressed chromium carbide  $\text{Cr}_{23}\text{C}_6$  obtained by means of inductive steel melting in 2N  $\text{H}_2\text{SO}_4$  gave the characteristic values of the corrosion potential  $-0,19 \text{ V}_{\text{SHE}}$  and the activation peak  $-0,15 \text{ V}_{\text{SHE}}$  [8]. In the range close to the activation potential the evolution of gas from the carbide surface was observed, but it was not identified [8]. The dependence of the standard potential  $\text{Cr}_{23}\text{C}_6$  upon the concentration of  $\text{H}_2\text{SO}_4$  was expressed directly by the slope  $0,058 \text{ V}$  for the concentration order. With the rise of temperature of the solution the standard potentials were shifted to the negative ones with the coefficient  $0,65 \text{ mV}^\circ \text{ dec}$  [9]. In temp. about  $374 \text{ K}$  no passivation range was observed on the anodic polarization curve in the solution  $\text{H}_2\text{SO}_4$  [8]. The dissolution rate of the carbide increased with the greater concentration of chloride ions. It was observed that, in room temperature the corrosion potential for the chromium carbides was in the steel passivation range for the electrolytes of weak reduction properties (i.e. dilute  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{HCl}$ ).

Looking at our anodic curves in Fig. 2 we can conclude that there are two potential ranges in which the dissolution rate of the carbide  $\text{Cr}_{23}\text{C}_6$  is very high the transition range from the active stage to the passive one ( $\varphi$  from  $-0,2 \text{ V}_{\text{SHE}}$  to  $0,0 \text{ V}_{\text{SHE}}$ ) and the transpassivation range ( $\varphi = 1,1 \text{ V}_{\text{SHE}}$ ). On the basis of the corrosion products analysis has been established that the dissolution of iron-chromium carbides is of an extraction character [3]. In the active, transition and passive ranges the "iron" part of the carbide is dissolved in the first place and then in the transpassivation range its "chromium" part is dissolved.

The investigations conducted for the carbide  $\text{Cr}_7\text{C}_3$  have

shown that its electrochemical properties are similar to those of the carbide  $\text{Cr}_{23}\text{C}_6$  [3]. The polarization curves of the carbides  $\text{Cr}_7\text{C}_3$  and  $\text{Cr}_{23}\text{C}_6$  obtained in our work are presented in Fig. 2 (curves b and c). The difference between them lies mainly in the observed activation peaks and from the electrochemical point of view that is of an essential significance. On the basis of the curves it can be noticed that the cathodic slopes of the polarization curve proper for depolarization processes of hydrogen ions are identical for the carbides question ( $b_- = -120$  mV/dec). The  $E_{\text{corr}}$  values obtained for the investigated carbides  $\text{Cr}_7\text{C}_3$ ,  $\text{Cr}_{23}\text{C}_6$  and  $(\text{Cr, Fe})_{23}\text{C}_6$  are similar and are  $(-0,25 - 0,01 \text{ V}_{\text{SCE}})$  (Table 1). The slope of the curves in this range of the polarization potentials, characterized by the coefficients  $b_+$  are presented in Table 1. The slope  $dE_{\text{corr}}/dpH$  equals 60 mV/dec which support the results of the work [9].

Table 1. Electrochemical parameters of carbides. Quasipotentiostatic measurement ( $v = 0,002 \text{ Vs}^{-1}$ ) in  $0,5 \text{ M H}_2\text{SO}_4$ .

Electrode	$b_+$ V/dec ( $\pm 0,01$ )	$E_{\text{Corr}}/\text{V}_{\text{SCE}} (\pm 0,01)$	$dE_{\text{corr}}/dpH (\pm 0,01)$
$\text{Cr}_3\text{C}_2$	0,05	-0,240	+0,120
$\text{Cr}_7\text{C}_3$	0,06	-0,250	+0,060
$\text{Cr}_{23}\text{C}_6$	0,09	-0,250	+0,050
$\text{Me}_{23}\text{C}_6$	0,09	-0,250	+0,060

It should be noted that the activation processes the metal dissolution are in the range of the polarization potentials in which (in solutions  $\text{H}_2\text{SO}_4$ ) the passivation "plateaux" for chromium steel has been recorded. The chromium carbides undergo a polarization process starting from the values of the polarization potential  $\varphi = 0,3 \text{ V}_{\text{SCE}}$  up till  $\varphi = 1,0 \text{ V}_{\text{SCE}}$ . For the higher potential values ( $\varphi > 1,2 \text{ V}_{\text{SCE}}$ ) one can notice a transpassivation process and a subsequent oxygen evolution on the electrodes.

Chloride ions cause a strong activation of the electrodes, the activation peak is very sharp (Fig. 3), but the passive range decreases and for the polarization potential of about  $1,5 V_{SCE}$  the transpassivation processes can be observed. The dependence  $dE_{corr}/dpCl^-$  is  $-30 mV$ .

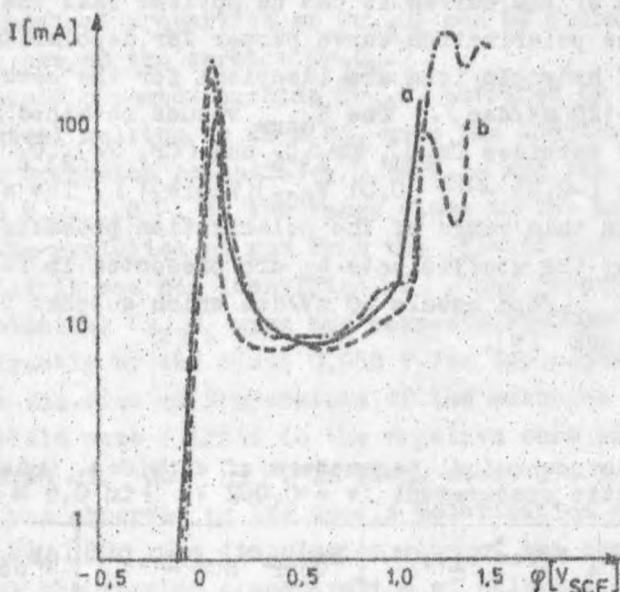


Fig. 3. Polarization curves ( $v = 0,002 \text{ Vs}^{-1}$ )  $\text{Cr}_{23}\text{C}_6$  in  $0,5 \text{ M H}_2\text{SO}_4$ . Versus  $\text{Cl}^-$  concentrating: a -  $p\text{Cl}^- = 4,0$  ;  
b -  $p\text{Cl}^- = 3,0$ ; c -  $p\text{Cl}^- = 2,2$  .

Fig. 2 presents also a polarization curve for the mixed carbide  $\text{Fe}_{23}\text{C}_6$ . This carbide was insulated from alloy steel and it contains the carbides  $(\text{Fe}_{1-x}\text{Cr}_x)_{23}\text{C}_6$ ,  $(\text{Fe}_{1-x}\text{Cr}_x)_7\text{C}_3$  and about 15 per cent of the phase  $\delta$  which remained during the carbide insulation. The curve given in Fig 2. is to some degree, the total curve of the partial ones for the carbides  $\text{Cr}_7\text{C}_3$  and  $\text{Cr}_{23}\text{C}_6$ .

The products of reactions under controlled potential were not investigated, so we do not discuss the course of their processes.

"Glued" powder electrodes made of the metal carbides, which

were used in these investigations, allowed us to obtain, in quick and easy way, the polarization characteristic of the electrode material very useful in the subsequent studies on alloy steel.

Future investigations will be continued in the case of electrodes made of pressed carbides.

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## CHARAKTERYSTYKA ELEKTROCHEMICZNA WYBRANYCH WĘGLIKÓW METALI

Do elektrochemicznych badań węglików metodami quasipotencjo-  
statycznymi i potencjodynamicznymi zaproponowano proszkowe,  
klejone elektrody. Otrzymano krzywe polaryzacyjne węglików:  
 $Cr_3C_2$ ,  $Cr_7C_3$ ,  $Cr_{23}C_6$  i  $(Fe, Cr)_{23}C_6$  w 0,5 M  $H_2SO_4$  pozwala-  
jące na jakościową i ilościową charakterystykę materiału elek-  
trodego. Wyznaczono wartości współczynników Tafela, potenc-  
jałów korozji i wpływu pH na wartości potencjałów korozji.