

ANODE DISSOLUTION CHARACTERISTICS OF TITANIUM, NIOBIUM, AND CHROMIUM CARBIDES

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The potentiodynamic measurements have shown considerable differences in electrochemical behaviour of titanium, niobium, and chromium carbides. With titanium carbide two regions of dissolution appear on the polarization curve in sulphuric acid solutions, the first one at potentials of -200 to 0 mV (S.H.E.) and the second one at oxidation potentials near 1000 mV (S.H.E.). In order to initiate anode dissolution of niobium carbide both in the region of -200 to 0 mV and also at 700 mV (S.H.E.), concentrated solution of sulphuric acid is needed. For chromium carbide, no enhancement of current density in the low-potential region has been observed; at the end of the passivity region, the rate of its dissolution (current densities are considerably lower than for titanium carbide) rises particularly in the transpassivity region. In the solution of concentrated nitric acid ($14.4M$), similar anodic processes as in sulphuric acid solutions have been observed.

Stainless steels of different types are liable in some media to particular and for users of steels often dangerous kinds of corrosion, especially as far as the structure is concerned. In order to make the role of titanium, niobium, and chromium carbides in this corrosion more precise, it is of importance to get acquainted with their electrochemical properties, particularly from the viewpoint of the anode dissolution¹⁻⁷.

Carbides of the transition metals group with cubic face-centered structure of the NaCl type, which possess special properties utilized in industry, are numbered among other solid compounds produced by combination of atoms of these metals and a metalloid, such as carbon. Through their properties, the carbides are reckoned among metals, for they exhibit electron conductivity, paramagnetism (often enhanced), superconductivity of the metallic type at low temperatures, as well as sensitivity to the dissolution in oxidation media, *etc.*⁷⁻¹⁴.

In this paper, electrochemical data on titanium and niobium carbides have been primarily studied in a more detail; orientational study has been made with chromium carbide Cr_3C_2 . Simultaneously, anode dissolution of the carbides has been studied. The data presented in this paper will make it possible to judge more exactly effect of carbides on the behaviour of stainless steels or other alloys, primarily with respect to their type and amount in connection with their chemical composition, but not from the viewpoint of their morphology. The effect of morphology is presented in other papers involving use of electron microscopy^{11,19}.

* The work was carried out by the first author during his stay granted by ASTEF in cooperation with the French Institutions.

EXPERIMENTAL

Some of the methods known may be used for the preparation of transition metals carbides¹⁵⁻¹⁸. We preferred method of powder metallurgy, which allows to prepare samples of various shape, different grain size, satisfactory density and chemical composition. Titanium carbide used for the most part for the measurements was produced from a mixture of TiO_2 and graphite under vacuum (10^{-2} mm Hg) at 1850°C . The mixture contained also 0.5% Cr_2O_3 due to the decrease of the content of free carbon in the final product. The samples having the disc shape, of diameter 10 mm and length 5 mm, thus contained 0.5% of chromium, this fact being not prejudicial to our study, because dendritic carbides produced in superheated stabilized stainless steels contain also small amounts of chromium with traces of other elements, primarily iron¹⁹.

Further samples were made from starting products "Murex" and "Starck" in case of titanium and niobium carbides, respectively.* Density of the produced, samples, however, particularly of the titanium carbide, was considerably lower than that of the niobium carbide samples prepared by the method mentioned above. Orientational electrochemical measurements showed the unfavourable effect of higher porosity of carbide samples, this effect being manifested in a similar way as the surfaces of titanium carbide samples subjected to a very strong corrosion. For the measurements itself, the carbide samples were prepared by mechanical polishing, at first by means of papers, afterwards using diamond paste.

For the experiments, sulphuric acid solutions of several concentrations 0.5M, 2.5M, and 7.2M were used, which allow measurements at various temperatures up to the boiling point of nitric acid, this being significant for the application of the obtained data to stainless steels. For that reason, the experiments with sulphuric acid were followed by those with 14.4M- HNO_3 .

The electrochemical measurements themselves were made potentiodynamically** by means of a potentiostat, logarithmator, electronic millivoltmeter (Tacussel), and XY coordinatograph (Sefram). This arrangement made it possible to record polarization curves of the increasing as well as decreasing potentials at various speeds, this fact being significant to achieve optimum conditions of the experiments and their reproducibility. As reference electrodes the mercurous sulphate electrode with saturated potassium sulphate solution for the measurements in sulphuric acid solutions, and calomel electrode with a bridge of saturated potassium nitrate solution were used. The platinum counter-electrode was separated from the sample by a glass diaphragm.

RESULTS

Experimental conditions in the 0.5M- H_2SO_4 solution mostly with bubbling nitrogen (only several curves were recorded with bubbling air through the solution - Fig. 1a) at normal temperature and 70°C made it possible to check on the carbide samples the findings achieved up to now^{12,14,19}. The measurements confirmed that on the polarization curve of titanium carbide two dissolution regions were present: The first one at reducing potentials (maximum J_c), the second one at oxidation potential (maximum J_c of TiC). The latter region corresponds to the corrosion of titanium

* The samples were made in the Research Institute of Powder Metallurgy, Šumperk.

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carbides and stainless steels in concentrated nitric acid. It must be mentioned that titanium itself did not exhibit under these conditions changes in the current density within the whole passivity region.

Attention has been drawn to this considerable difference in the electrochemical behaviour of titanium and its carbides⁸.

Niobium carbide behaves under equal conditions quite differently. Only a slight increase of current appears on its polarization curves in the region of reduction potentials; the increase of current density at oxidation potentials up to a distinct maximum was observed in the solution of 7.2M-H₂SO₄ only (Fig. 1b), while the current density values as well as potential of the maximum are considerably lower than in case of titanium carbides.

For chromium carbide, the current density does not increase in the region of reduction potentials (Fig. 1c). In the region of oxidation potentials, the increase of current density is much lower than that of the titanium carbide at potentials corresponding to maximum J_c of TiC. At limiting potentials in the passivity as well as transpassivity regions of the stainless steel, the current intensity strongly increases, similarly as, for example, for chromium itself.

Effect of the concentration of sulphuric acid on the current maxima on the polarization curve of titanium carbide is dependent more or less on the region of potentials. The highest J_c values of TiC were observed in the solution of 2.5M-H₂SO₄. The acid of the latter concentration was successfully employed in the following study on stainless steels, since maximum of dissolution of titanium carbides is most distinct with this acid. In contrast to this, for niobium carbide, it is the 7.2M-H₂SO₄ solution in which the highest current densities were observed (Fig. 1b). It must be mentioned that these

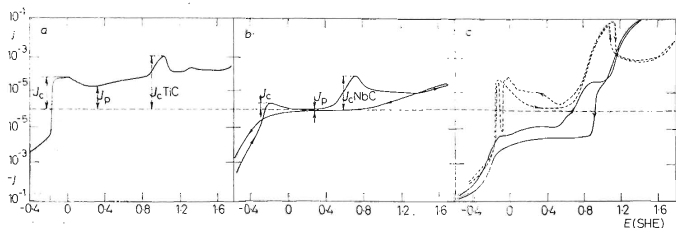


FIG. 1

Polarization Curves of Carbides

J (A/0.5 cm²), E (V). a TiC, 0.5M-H₂SO₄; 20°C; bubbling with N₂, increasing rate of 1 V/h; b NbC, 7.2M-H₂SO₄, 70°C, increasing rate of 3 V/h; c Cr₃C₂ —; TiC ·····, 2.5M-H₂SO₄, 70°C, increasing rate of 9 V/h, decreasing rate of 0.3 V/h.

densities are considerably lower than those for titanium carbide. In addition, the maximum of the anode dissolution of niobium carbide lies at a lower potential than for titanium carbide, where potential of the maximum rises with the increasing acid concentration.

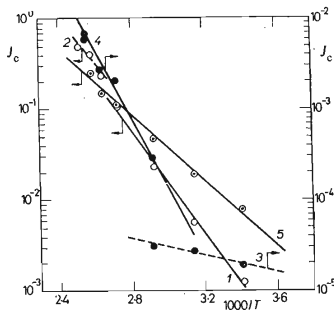


FIG. 2
Plot of J_c (Ac/m^2) against Temperature (K)
Rate of 9 V/h, bubbling with N_2 . \circ TiC
in 7.2M- H_2SO_4 , \bullet NbC in 7.2M- H_2SO_4 ,
 \odot TiC in 14.4M- HNO_3 .

In view of the potentiodynamic method selected, likewise effect of the rate of the potential change on character of the polarization curve was followed in detail. Generally, it may be assumed that the rate affects the J_c values of both TiC and NbC negligibly. An exception is niobium carbide, if it is subjected to 0.5M- H_2SO_4 ; under these conditions, however, a distinct current maximum cannot be observed. At very low rates, also increase of the J_c value of TiC was observed, this fact being obviously in connection with the enlargement of the sample surface, due to the increasing corrosion under considerably aggressive conditions. This phenomenon appears more distinctly at increasing potentials. As far as the J_c and J_p values are concerned, the effect of the rate of potential change is analogous for both carbides, regardless of the conditions. These values increase with the increasing rate.

A great effect on electrochemical characteristics of carbides has the temperature. Because of the experiments being carried out under normal pressure, the concentration of 7.2M- H_2SO_4 was chosen which allows measurements within a wide range of the temperatures including temperature corresponding to the boiling point of 65% nitric acid, *i.e.* under conditions which are most convenient for comparison of the behaviour of the carbides tested. The behaviour of titanium carbides is affected by the temperature already in the neighbourhood of normal temperature, whereas for niobium carbides, this is the case after 70°C only. Even at the high rate of the potential change (5 V/min) the temperature effect is distinct, this giving evidence of a great intensity of the reactions involving the anode dissolution of carbides in the upper part of the passivity region. Generally, it can be assumed from the measurements under various conditions that effect of temperature is analogous for both carbides,

only the rate of dissolution of titanium carbide is several times higher. A proof for this is also the fact that activation energies for the maximum of the anode dissolution are comparable for both carbides, even though conditions of their dissolution are different in both cases (values Q or A read out from Fig. 2 for TiC are 12.7 kcal/mol or $3.55 \cdot 10^6$, respectively, those for NbC are 12.1 kcal/mol or $2.47 \cdot 10^7$, resp.). An increase of temperature obviously changes also shape of the polarization curve of chromium carbide (Fig. 3). The current density in the region of potentials corresponding to maximum J_e of TiC rises with temperature, but without formation of a distinct maximum. In the transpassivity region, the current density increases in the same way as for chromium.

Analogous measurements as in sulphuric acid were made in nitric acid in which the conditions of dissolution are quite different (Fig. 4). Effect of temperature on the current density is in the region of the maximum J_e of TiC smaller in nitric acid than in sulphuric acid. The starting current density under normal temperature, however, is greater and increases more slightly with the temperature (Fig. 2, curve 5; $Q = 3.60$ kcal/mol; $A = 2.77 \cdot 10^{-2}$). The values measured for niobium carbide are very low and also a distinct effect of temperature was not observed. The behaviour of tested carbides in nitric acid is quite different. Niobium carbide is covered by an adhesive layer of light-yellow colour, whose X-ray analysis suggests a mixture of nitrides

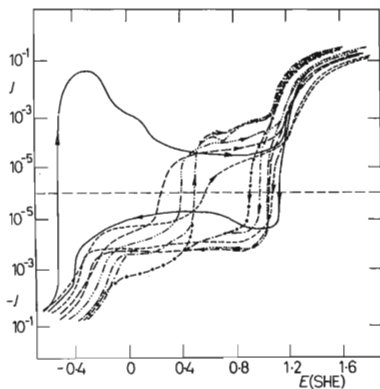


FIG. 3

Polarization Curves of Cr_3C_2 in $2.5\text{M-H}_2\text{SO}_4$ at 9 V/h

J ($\text{A}/0.5 \text{ cm}^2$), E (V). 20, ---- 40, - · - · 70, - - - - 95, and - + - + - 105°C;
 — 99.9 Cr at 70°C under equal conditions.

and nitrates. The formation of this layer strongly slows down dissolution of niobium carbide. Chromium carbide exhibits a slight increase of current density at the interface between the passive and transpassive regions of the stainless steel. Its behaviour is different from that of titanium carbide, whose maximum is still quite in the passivity region. An appreciable increase of the current density for chromium carbide can be observed in the transpassivity region only.

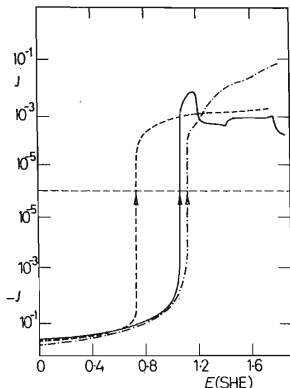


FIG. 4

Polarization Curves in 14.4M-HNO₃
70°C, 0.3 V/h, bubbling with air,
J (A/0.5 cm²), E (V) — TiC, ---- NbC,
- · - · - Cr₃C₂.

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