

ELECTROCHEMICAL PROPERTIES OF TITANIUM CARBIDE

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Polarization curves of hydrogen evolution on TiC electrodes in acidic as well as alkaline media have been measured and dependence of exchange current density on pH of the electrolyte has been established. Chronopotentiometry and voltammetry were used to study hydrogen adsorption on these electrodes. It follows from the results achieved that hydrogen is not adsorbed on a nondestroyed titanium carbide surface. During the long-term cathodic polarization at potentials more negative than -0.5 V, the evolution of hydrogen, however, is simultaneously accompanied by hydrogenation of carbide, when the surface layer is produced containing hydrogen either in the adsorbed form or in the form of the titanium carbohydride.

Transition metal carbides of the IV—VI groups of the periodic system are through many of their properties (appearance, electric and thermal conductivities, chemical resistivity) very similar to metals. These properties are due to donor-acceptor interactions between carbon and metal atoms. In view of the properties quoted, some of the carbides have become subject of electrochemical investigations. The carbides were tested in terms of indicator electrodes for potentiometric measurements¹ as well as in terms of inert electrodes for reduction or oxidation in redox-systems^{2,3}, further as anode for evolution of chlorine from chloride solutions⁴ as well as cathode for evolution of hydrogen from solutions of acids, hydroxides, and neutral salts⁵⁻⁷. They were likewise suggested as charge for decomposers of alkali metal amalgams produced in the mercury cells in the manufacture of chlorine and hydroxides⁸, and also as a catalytic electrode for fuel cells^{9,10}. Corrosion properties of titanium carbides in various media and in various potential regions have been presented in many papers¹¹⁻¹⁵ showing a relative stability of this material against both acidic and alkaline solutions.

In this paper cathodic evolution of hydrogen on titanium carbide and its behaviour under these conditions with respect to the possible application of this material to some electrochemical manufacturing processes has been studied.

EXPERIMENTAL

In order to prepare suitable shape of TiC electrodes, several methods were made use of: a) decomposition of titanium(IV) chloride and toluene vapours in excess of hydrogen on metallic or quartz filaments heated approximately to 1000°C ^{16,17}; b) pressing of powdered $\text{TiC}_{0.95}$ (Alfa Inorganic) with polytetrafluoroethylene as binder at a low temperature, or in a graphite mould at a temperature of about 2800°C and under a pressure of 100 kp/cm^2 ; c) preparation

of electrodes from single-crystal $\text{TiC}_{0.96}$.^{*} The solutions used for the measurements were prepared from H_2SO_4 of the A.R. grade and triple-distilled water. The potassium hydroxide solution was obtained by decomposition of amalgam produced electrolytically. Prior to the measurement the samples were further purified by preelectrolysis directly in the measuring cell employing current of 60 mA for a period of at least 24 hours. To measure the polarization curves a commonly used cell equipped with a stopcock to separate cathode and anode spaces was employed. Oxygen dissolved in the electrolyte was removed by bubbling hydrogen or nitrogen through the solution. The polarization curves of the hydrogen evolution were measured by constant current method, the potential of the electrode being read out after attaining a stationary value set up nearly instantly at cathodic potentials $E < -0.400$ V. (All the potentials presented in this paper relate to the equilibrium potential of the hydrogen electrode in the used electrolyte (RHE)). The capacity of the single crystal electrode was determined from the slope of the potential-time curve for time $t = 0$ at the galvanostatic pulse. Capacity of porous electrodes was determined from the charge passed through the electrode for a small change of the square-wave voltage and recorded by means of $i-t$ curves. Adsorption effects on the TiC electrodes were studied by anodic voltammetry and chronopotentiometry. In the former method potential of the electrode measured was maintained for a time needed at a chosen value by a potentiostat Wenking RS-61. After this period the voltammetric pulse of the linearly increasing voltage was generated by an operational amplifier AS 101 and at repeated pulses by a generator of triangular voltage. In the anodic chronopotentiometry, the electrode was equally as in the previous case prepolarized by the potentiostat at a chosen potential. By means of the relais system the electrode was switched off the potentiostatic circuit at the time chosen and a constant current pulse was switched on the electrode through a resistance from a generator of constant voltage of 200 V. In order to avoid oxidation of the electrode at higher anode potentials, the galvanostatic circuit was switched off after attaining the anode potential selected. The potential or current response in both methods quoted was followed using oscilloscope Tesla BM 430 and recorded photographically. The surface of powdered titanium carbide was established by physical adsorption of nitrogen at a temperature of -196°C using the Nelson and Eggertsen method¹⁸.

RESULTS

The polarization curves of the hydrogen evolution on several types of electrodes are plotted in Fig. 1. The differing course of the polarization curves and hence also different overvoltage values are due to different methods of the electrode preparation, where – except for the monocrystalline electrode porous electrodes with surfaces of different areas are mostly produced. For the determination of the exchange current density and the charge transfer coefficient on these electrodes, only that part of the polarization curve was utilized, in which the porous electrode behaves as a plane electrode with the polarization curve slope $b \approx 0.120$. For the teflon bonded electrodes it was the region of current densities of $10^{-3} - 10^{-1}$ A/cm² of the geometric surface. In order to determine the real current densities, it was necessary to establish the current-loaded depth of the electrode.

The electrode depth was roughly established by gradual shortening of the electrode stamping with use of grinding by a certain length measured, and after each shorten-

* The samples were kindly supplied by Mr R. Cowling, Laboratoire Suisse de Recherches Horlogères, Neuchatel.

ing, the polarization curve as well as electrode capacity were measured. From the dependence of the polarization curves and electrode capacities on the total length, the working depth of the electrode was then determined. Provided that specific surface area of powdered TiC, determined by an independent adsorption method, was not changed by pressing with teflon considerably, also the electrode working surface could be determined using the electrode working depth found. For the monocrystalline TiC electrode which was ground with powdered carbide of size 30–50 μm and 10–20 μm before the measurement, the roughness factor $f = 6$ was estimated. By using the surface areas thus established, i_0 values and tangents b were obtained of individual kinds of electrodes in a usual way by extrapolation from the linear part of the polarization curve.

Values i_0 and Tafel constants b of hydrogen evolution, at 23°C in 1N-H₂SO₄: electrode-monocrystalline ($i_0 = 1.1 \cdot 10^{-8}$ A/cm²; $b = 0.125$), bonded with teflon ($4.1 \cdot 10^{-8}$; 0.125), high-temperature sintered ($5.9 \cdot 10^{-8}$; 0.120), by decomposition of TiCl₄ + C₇H₈ + H₂ ($2.1 \cdot 10^{-8}$; 0.120), and in 1M-KOH: monocrystalline ($5.8 \cdot 10^{-8}$; 0.120), bonded with teflon ($1.8 \cdot 10^{-7}$; 0.110).

In sulphuric acid solutions of concentrations within 0.05–1.0N, dependence of the rate of hydrogen evolution on the acid concentration has been studied. It was found for the monocrystalline electrode that dependence $(\partial \ln i / \partial \ln c_{\text{H}_3\text{O}^+})_E = 0$. The

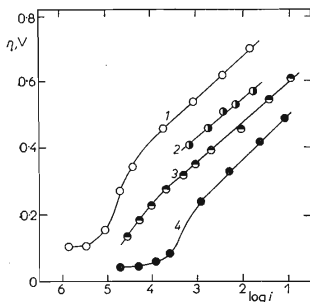


FIG. 1
Polarization Curves of Hydrogen Evolution on TiC Electrodes

1 Single crystal electrode; 2 teflon bonded electrode; 3 high-temperature sintered electrode; 4 electrode prepared by decomposition of TiCl₄ + C₇H₈ + H₂.

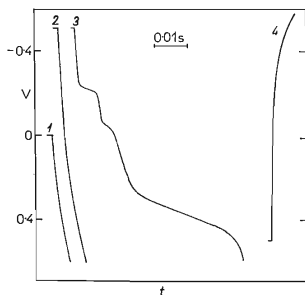


FIG. 2
Chronopotentiometric Curves, 1N-H₂SO₄
Prepolarization at: 1 0.000 V; 2 -0.500 V;
3 -0.500 V; 4 +0.500 V. 1, 2 new electrode;
3, 4 electrode of long-term cathodic polarization.

dependence of the rate of hydrogen evolution on temperature in 1N-H₂SO₄ has been further studied and from the dependence of i_0 upon $1/T$, value of apparent activation energy $\Delta H^+ = 11.1$ kcal/mol has been calculated.

The capacity of the electrode was measured by the methods mentioned above at potentials ranging from 0.0 to -0.6 V; it was shown at the same time that over this potential range the electrode capacity has a nearly constant value $C \approx 12 \mu\text{F}/\text{cm}^2$ of the real surface. Interesting are the rest potential values of the electrode of various origin. On a fresh TiC surface in the 1N-H₂SO₄ solution saturated with hydrogen, a rest potential $E_{i=0}$ within +0.3 to 0.6 V (RHE) was established. On the monocrystalline electrode, however, this rest potential begins to decrease to zero relatively quickly and continues to change gradually towards negative values till the corrosion potential of value -0.10 to -0.17 V is set up. The process of corrosion takes place obviously far more slowly on sintered electrodes and those bonded with teflon, since the electrode keeps a potential $E_{i=0} = +0.3$ to +0.5 V even for a period of many days; only after the long-term polarization, a mixed potential of 0.00 to 0.05 V is set up in the currentless state.

Furthermore, the course of some redox reactions such as oxidation of potassium hexacyanoferrate in neutral medium, oxidation of iron(II)oxalate and reduction of its trivalent form, and reduction of oxygen by the method of linearly increasing voltage on a rotating disc electrode, was examined on these electrodes. All these reactions on the sintered TiC electrode proceed very irreversibly and the limiting current density has not been attained at all. Moreover, the current densities are dependent on the direction of the potential change. If the oxidation or reduction process starts in a more negative region of potentials, the current densities are at equal potential greater than in the opposite procedure, *i.e.* with the outset laying in the region of more positive potentials.

Adsorption of hydrogen on the TiC electrodes has been studied by methods of anodic chronopotentiometry and voltammetry, already described. The shape of the oxidation curves was found greatly dependent on the history of the electrode under investigation, potential, and time of the cathodic prepolarization. On the chronopotentiometric oxidation curves of the electrodes cathodically polarized for a short time only, no oxidation delays are evident and course of all $E-t$ curves of the electrodes prepolarized at potentials from 0.00 to -0.60 V is nearly identical as can be seen in Fig. 2, curves 1,2. Of quite another behaviour is the electrode kept for several hours at a sufficiently negative potential $E < -0.400$ to -0.500 V, or the electrode which has been several times polarized by anodic pulses. In such cases, two and in the prepolarization at potentials $E < -0.500$ V sometimes even three oxidation delays (Fig. 2, curve 3) appear. The length of individual delays is then usually longer after the cathodic prepolarization at more negative potentials after greater number of anodic-cathodic cycles. For the opposite polarity of the galvanostatic pulse, *i.e.* if the cathode current is involved starting from anodic

potentials, the corresponding reduction delays do not appear on the chronopotentiometric curve (Fig. 2, curve 4).

For the anodic pulses, dependence of the charge of individual delays upon the current density of the anodic pulse has been studied. On the basis of the results achieved (Table I) it was not possible to prove an unambiguous dependence, mainly because of the delays being still longer at each of the subsequent pulse. This gives evidence of the fact that with the number of cycles irreversible changes in the surface layers of the TiC electrodes take place, in the course of which the amount of substance capable of being oxidized gradually increases during the cathodic prepolarization.

Also value of the cathode current density at the given potential of the cathodic prepolarization of the electrode is dependent on the instant stage of covering the electrode with the oxidizable substance. Thus, for example, on the electrode surface freshly prepared, at potential $E = -0.500$ V in a $1N-H_2SO_4$ solution thoroughly purified by preelectrolysis, the current density is established which remains nearly unchanged with time of the polarization. On the electrode, however, on which the oxidation delays at the anodic pulse already appeared, after the anodic pulse has been finished and the cathodic potential reapplied the cathode current density exceeds several times its steady state value (Fig. 3). If the oxidation charge is determined at individual nonsteady current densities, it is then evident that a relation exists between

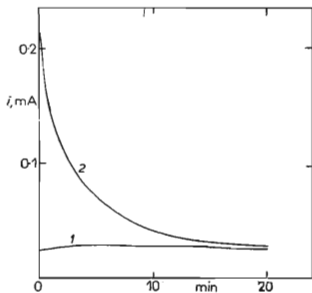


FIG. 3
Time Dependence of Current at $E = -0.500$ V; $1N-H_2SO_4$

1 New electrode; 2 electrode after appearing the oxidation delays.

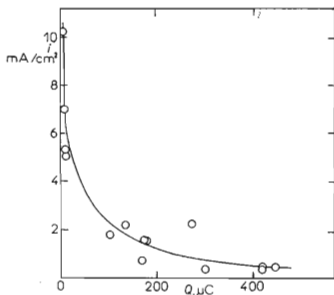


FIG. 4
Dependence of Current Density of the Hydrogen Evolution on the Charge of the Oxidation Delays

TABLE I

Dependence of the Charge of Oxidation on the Current Density of Anodic Pulse

Potential of prepolarization -0.500 V. Q_{Ia} and Q_{II} denote the oxidation delays in the cathodic and anodic regions, respectively.

$i_{\text{cath.}}$ mA/cm ²	Anod. pulse mA/cm ²	Charge of oxidation, μ C/cm ²		
		Q_{Ia}	Q_{Ib}	Q_{II}
- 6.7	303.0	268	76	2.160
-13.4	16.6	490	124	2.150
-12.0	303.0	452	114	2.500
-10.7	16.6	610	120	2.000
-10.3	303.0	530	—	2.500
-16.6	6.7	670	50	2.500

magnitude of this oxidation charge and current density of the hydrogen evolution, as follows from Fig. 4.

Similar results were obtained by voltammetric analysis of the surface layer produced by cathodic prepolarization. On the surface freshly prepared neither oxidation nor reduction peaks are apparent and observable small current densities correspond

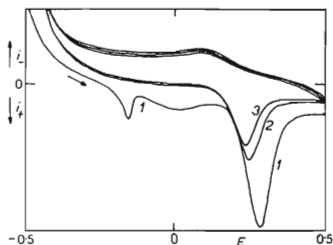


FIG. 5

Voltammetric Curves within the -0.500 to $+0.500$ V Potentials

$$v = 21 \text{ V/s.}$$

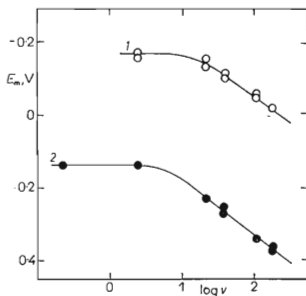


FIG. 6

Dependence of the Current Peaks Potential E_m in Cathodic and Anodic Regions on the Rate of the Increase of the Potential Applied (v , V/s)

to the charging and corrosion current. However, under conditions described above, the oxidation peaks appear, as is inferred from Fig. 5. In the region of negative potentials (at $E \approx -0.1$ V), one peak as a rule appears which is sometimes divided into two peaks, whereas in the region of positive potentials, another usually greater peak arises.

Time sequence of the first appearance of the peaks is not identical. At first, a peak in the anode potential region is developed, with the increasing time of the cathodic prepolarization or with the increasing number of anodic-cathodic cycles the peak in the cathode potential region begins to appear and increase. In the cyclic voltammetry employing triangular voltage pulses in the potential range within -0.500 to $+0.500$ V, the cathodic region peak disappears already in the second cycle and in the anodic region the peaks gradually diminished, the maximum potential E_m being simultaneously shifted towards more negative potentials (Fig. 5). Addition of surface active tetrabutylammonium cations at a concentration of $1 \cdot 10^{-3}$ M has no effect on the size of individual peaks. For the opposite direction of polarization, *i.e.* towards the increasing negative potentials one or two small reduction peaks of bad development sometimes appear.

Assuming that the oxidation peaks may be ascribed to the oxidation of hydrogen adsorbed on the surface, and that one titanium atom can combine with one hydrogen atom, the degree of occupation of the electrode surface could be calculated from the charge defined by the anodic peaks area, which for the first peak in the cathodic region and for the second peak in the anodic region attained values $Q \approx 0.5$ and $Q \approx 1.0$, respectively.

Likewise, dependence of the potentials of maximum E_m upon rate of the potential increase, v , has been studied. In order to examine this dependence only a limited number of the experiments could be taken into account, during which the electrode did not change its properties considerably, *i.e.* mainly the concentration of the oxidizable substance did not change. It follows from Fig. 6 that E_m is up to the rate $v \approx 1$ V/s independent of v ; for $v > 10$ V/s potential of the maximum linearly increases with $\log v$, the slope of the straight line being $(dE_m/d \log v) = 0.12$. Also the relation between logarithm of the current maximum i_m and $\log v$ is linear having the slope $k = 1$, starting again from value $v > 10$ V/s.

DISCUSSION

The exchange current value i_0 of the cathodic hydrogen evolution on the TiC electrodes is in fairly good accordance with the data published by Mund and coworkers¹⁰ who found $i_0 = 8 \cdot 10^{-8}$ A/cm². By comparing these values with i_0 of the hydrogen evolution on metallic titanium ($i_0 = 8.5 \cdot 10^{-7} - 7.1 \cdot 10^{-9}$ A/cm²) (ref.^{22,24}), it follows that the rate of the hydrogen evolution is on both kinds of material nearly the same.

The dependences found between the potential or current of maximum E_m and $\log v$ of the anodic voltammetry curves on titanium carbide conform very well to a theoretical model of the oxidation reaction of a substance present on the electrode surface, as has been suggested by Srinivasan and Gileadi¹⁹. For an irreversible reaction, relationship

$$E_m = (RT/\alpha nF) \ln (A\alpha nF/kRT) + (RT/\alpha nF) \ln v \quad (1)$$

holds for E_m , where k is the rate constant of the oxidation reaction and A the charge necessary for the oxidation of the electrode surface covered with a monolayer of the oxidizable substance, and α is the charge transfer coefficient for the oxidation reaction. From the dependence between E_m and $\log v$, found by us, it followed that quantity $\alpha n = 0.5$; thus, under the assumption that $\alpha = 0.5$, a one-electron oxidation reaction would be concerned. Similar dependences between E_m and $\log v$, the transition region of linear parts including, were found by Will and Knorr²⁰ for the oxidation of hydrogen adsorbed on platinum.

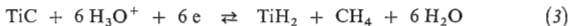
On the basis of the theory presented, it is possible to explain very well the observed shift of E_m for the second and further cycles of the triangular voltage. At $v = \text{const}$ and $k = \text{const}$ the shift of E_m can be caused merely by a change of A according to equation

$$E_{m_1} - E_{m_2} = (RT/\alpha nF) \ln (A_1/A_2). \quad (2)$$

The differences between the values of the shift of the potentials of maximum E_m calculated according to the equation presented, when using measured values of charges spent for oxidation, defined by the peaks, and the measured values of ΔE_m did not exceed 10%. For example, for the case graphically presented in Fig. 5, $\Delta E_m = 0.046$ V was calculated from the anodic pulse area, whereas the ΔE_m measured amounted to 0.041 V. It follows from the behaviour of the electrode in repeated cycles that the degree of occupation of the electrode surface gradually decreases with the increasing number of cycles. It is not quite clear, for the time being, whether this decrease of the surface occupation is due to a low rate of formation of the oxidizable substance in the cathodic region of the voltammetric cycle, or whether a partial blocking or inactivation of the electrode takes place.

It may be assumed from the behaviour described that hydrogen, being in the adsorbed atomic form or as a hydride compound, is the oxidizable substance produced in the cathodic prepolarization on the electrode partially destroyed by the foregoing electrode processes. Contrary to this, on a fresh electrode made of nearly stoichiometric TiC and after cathodic short-time polarization, the amount of the hydrogen thus combined is negligibly small (Fig. 2, curves 1, 2). This finding is in accordance both with theoretical considerations and with the behaviour of TiC during hydrogen

adsorption from the gaseous phase. Goretzki and coworkers²¹ found that a nearly stoichiometric TiC does not react chemically either with atomic hydrogen, nor any adsorption of hydrogen on the surface takes place. Only carbide with deficient carbon content reacts with hydrogen readily to produce carbohydride TiC_xH_y . Thermodynamic analysis of the possibility for a complete hydrogenation reaction of titanium carbide



showed that the standard equilibrium potential E° equals -0.153 V when using thermodynamic data²². From this value it is evident that hydrogenation of titanium carbide during the cathodic polarization at higher cathode potentials is possible, particularly if nonstoichiometric carbohydride is produced. We therefore assume the delays on the chronopotentiometric curves or the current peaks on the voltammetric curves to belong to the oxidation of hydrogen thus combined in carbohydride. According to the number of these delays or peaks and potential regions of their existence it is evident that hydrogen is in these compounds present in two or possibly three forms which differ between themselves in the value of the oxidation potentials. The form capable of being oxidized in the region of anodic potentials probably belongs to the hydride hydrogen. The latter is present both in the surface and volume phases, since the oxidation peaks appear even after grinding the electrode surface layers. Hydrogen, which is oxidized at the negative potentials already, is produced only after attaining certain minimum concentration of the former form of hydrogen and probably represents an unstable supersaturated form of carbohydride. After the oxidation of hydrogen, the rate of its recovery is very low, because this form does not appear with the second pulse of the triangular voltage already.

It is evident from the shape of voltammetric curves and from values of the rest potentials that the oxidation reactions of carbohydride are accompanied by a corrosion reaction which results in the formation of a surface film probably of substoichiometric TiO_{2-x} . Presence of this film of semiconducting nature has been confirmed qualitatively by using the Oše and Rosenfeld method²³ and a very irreversible course of redox reactions, too, gives evidence of it. The formation of the surface suboxide film of TiO_{2-x} might also account even for a decrease of hydrogen overvoltage on TiC in the region of low current densities (Fig. 1), provided that hydrogen overvoltage is on this film lower than on the TiC surface. This assumption may well account also for an observed considerable increase of the current density of the hydrogen evolution after the preceding anodic pulse (Fig. 3, curve 2), where, of course, also a change in the electrode surface properties, due to removal of hydrogen from the electrode surface, can take place.

The mechanism of the hydrogen evolution on titanium carbide could not be defined unambiguously, however, it probably seems (according to values of the Tafel

constant b , dependence of the overvoltage on pH, and very small adsorption of hydrogen in sulphuric acid solutions) the rate determining step to be the discharge of H_3O^+ ions on a fresh and almost stoichiometric titanium carbide whose surface has not changed as yet on account of the hydrogenation or oxidation processes; this is in contrast with metallic titanium for which the electrochemical desorption²⁴ is considered to be the rate determining step.

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