JOURNAL OF APPLIED ELECTROCHEMISTRY 2 (1972) 143–149

The anodic oxidation of the binary compounds of the transition elements in sulphuric acid

R. D. ARMSTRONG* and A. F. DOUGLAS

The Gas Council, London Research Station, Fulham, London, U.K.

Received 11 October 1971

The anodic oxidation of the silicides and carbides of Ta, W and Mo in M H_2SO_4 has been studied. The rate of corrosion has been shown to be dependent on the solubility of the reaction products. Oxidation of the carbides of Ta and W produces a carbon rich surface. This may be an important factor in the enhanced catalytic activity for hydrogen oxidation shown by anodized tungsten carbide.

Introduction

Several articles [1–6] refer to the use of tungsten carbide and related compounds as electrocatalysts for the anodic oxidation of hydrogen in acid electrolyte fuel cells.

Increased catalytic activity with these materials has been claimed either as a result of controlled anodization [6], the incorporation of small amounts of other carbides [1], or a combination of both of these techniques [1]. It would seem therefore that the catalytic activity of these materials is in part due to surface oxidation. The addition of other carbides probably causes lattice straining and an increase of surface defects which act as active centres.

We feel that the study of these materials is incomplete since very little information is available about the potential region in which they are substantially corrosion resistant. Also the chemical changes which occur at the electrode surface as a result of anodization and their effect on the resulting catalytic activity for anodic hydrogen oxidation has not been adequately explained. This work is an attempt to provide information on these topics.

Experimental

Preparation of electrodes

Two types of electrodes were used: solid electrodes, prepared by hot pressing of the catalyst materials, and gold bonded electrodes, prepared by heating intimate mixtures of powdered gold and powdered catalyst materials. (Gold is inert in the potential region of interest in this work.) Solid electrodes were supplied by Murex Ltd. (U.K.) (WSi_2, $TaSi_2$, $NbSi_2$, $MoSi_2$), Borax Consolidated (U.K.) (TaC), and Ventron (U.S.A.) (WC). Gold bonded electrodes were prepared as follows: powdered catalyst material with average particle size less than 10 μm was mixed with 20% by weight of gold dust (Johnson Matthey). About 2 g of this mixture were cold pressed at 5×10^3 kg cm^{-2} to produce a 1·5 cm diameter disc which was sintered by heating to 950°C for 2 h *in vacuo*. The resulting electrode was mechanically strong but with some open porosity giving a high surface area for reaction compared with the hot pressed solid electrodes.

Characterization of electrode materials

Catalyst materials were examined by X-ray powder diffraction to confirm homogeneity or to

---

* The Electrochemistry Laboratory, Physical Chemistry Department, The University, Newcastle upon Tyne, England.

detect phases present. X-ray fluorescence was used to estimate the concentration of impurity elements in the catalysts. Surface compounds produced by anodic oxidation of the catalyst materials were detected and identified using both X-ray diffraction and electron diffraction techniques.

Electrochemical measurements

A schematic outline of the experimental set-up used is shown in Fig. 1. The working electrode was held in position by a gold clip; a gold counter electrode was used together with a D.H.E. as reference. Analar reagents were used throughout and solutions were prepared from triple distilled water. All measurements were made in 1 M H_2SO_4 at ambient temperatures (25 ± 2°C).

The oxidation properties of the binary compounds were measured at constant current so that steady state conditions were achieved for the quantitative measurement and analysis of the gaseous reaction products. A Perkin Elmer 452 gas chromatography unit was used for gas analysis. An inert gas such as helium or argon was passed at a predetermined flow rate into the anode compartment of the cell to flush the gaseous reaction products out. The concentration of gaseous reaction products was measured at 10 min intervals until a steady state was reached. The carbon monoxide content was measured on a column packed with Molecular Sieve 13X and the carbon dioxide on Chromosorb 102 supplied by Perkin Elmer.

Reaction products in solution were identified and estimated by chemical analysis; solid reaction products were identified either by X-ray powder diffraction or transmission electron diffraction.

Measurements for electrochemical activity for hydrogen oxidation were made under steady state conditions with the solution and atmosphere in the cell saturated with hydrogen. Current readings were taken at 50 mV steps, allowing at least 10 min at each step.

Results

Fig. 2 shows a potential sweep made on a hot pressed tantalum carbide electrode. Identical results were obtained when either hydrogen or nitrogen gas was passed into the cell. The very small currents obtained as a consequence of the small surface area make it difficult to identify any reaction products. Very similar results were obtained with the solid tungsten carbide electrode. For this reason the gold bonded electrodes were prepared and tested. These electrodes have a considerably larger surface area and larger currents were available. From potential sweep measurements, the surface area of the sintered electrodes was 10^2–10^3 times greater than the area of the solid electrodes.

Fig. 3 shows the steady state current for

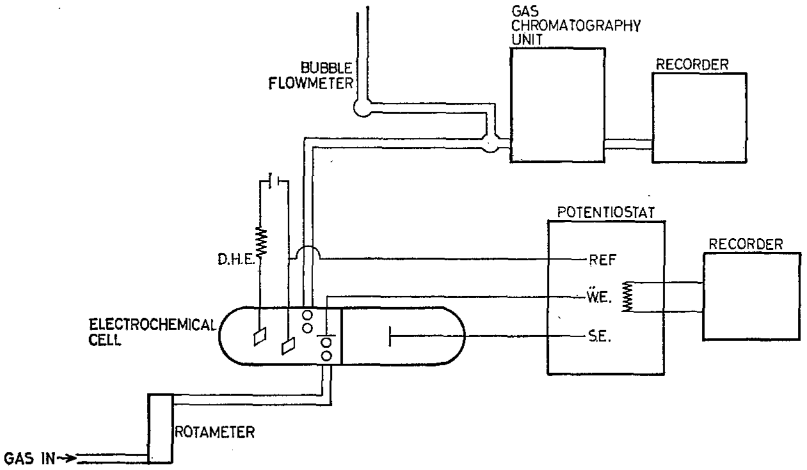

Fig. 1. Schematic outline of the experimental set up.

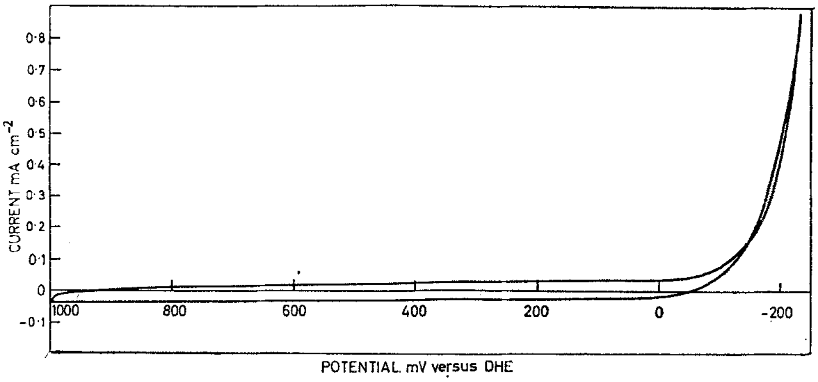

Fig. 2. Current (mA) against potential mV for a potential sweep on a solid hot pressed tantalum carbide electrode; sweep rate = 0·3 V s^{-1}.

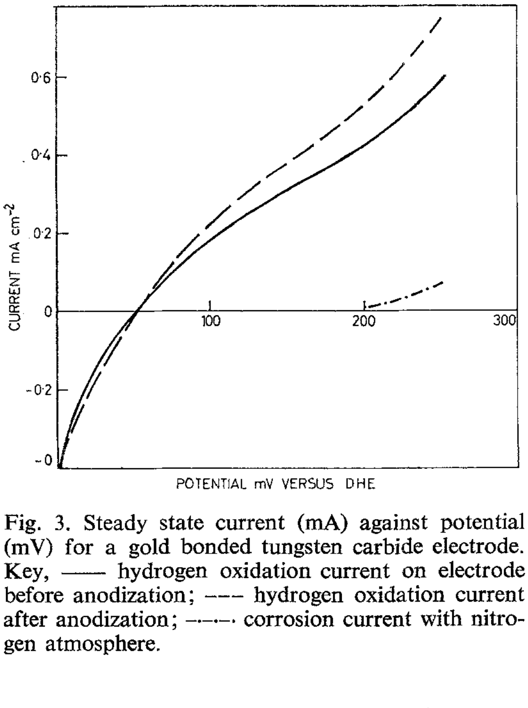

Fig. 3. Steady state current (mA) against potential (mV) for a gold bonded tungsten carbide electrode. Key, —— hydrogen oxidation current on electrode before anodization; – – – hydrogen oxidation current after anodization; –·–· corrosion current with nitrogen atmosphere.

hydrogen oxidation for a gold bonded tungsten carbide electrode immersed in the electrolyte. Almost identical results were obtained after anodization at 700 mV for 4 h.

The steady state oxidation of Mo_2C, TaC, and WC is shown in Fig. 4; Figs. 5 and 6 show the behaviour of the silicides and of the parent compounds respectively under identical conditions. Between 100 and 750 mV the current from $TaSi_2$ was indistinguishable from the background current (<1 μA cm^{-2}).

The time-dependence of the oxidation current at constant potential (1200 mV) is shown in Fig. 7 for $TaSi_2$, WSi_2 and $MoSi_2$. All the compounds tested showed decay of current with time (except for Mo_2C) which means that the 'steady state' currents of Figs. 4 and 5 are somewhat arbitrary.

Table 1 shows the results of analyses of the oxidation products at constant current for the carbides tested. In every case the rate of production of carbon monoxide and carbon dioxide was less than expected from stoichiometric considerations. No attempt was made to analyse the oxidation products of the silicides because of the slow rate of dissolution. On WC, the hydrated oxide $WO_3 . H_2O$ was identified on the surface of the electrode by X-ray diffraction. For Mo_2C the oxide was amorphous and was identified by elemental analysis. On TaC, the oxide was too thin to be detected. Prolonged oxidation of TaC was not possible because of the high rate of current decay.

Discussion

A thermodynamic analysis of the oxidation reactions for the case of WC (Table 2) shows that the equilibrium potentials for the oxidation of the separate elements are very similar to those for the corrosion of the binary compound. This arises from the fact that the free energy of formation of WC is rather low ($\sim$ 10 kcal mole^{-1}) [9]. Similar conclusions are likely to hold for other binary compounds of the transition metals. Thus thermodynamically the oxidation reactions might be expected to be those of a mixture of the component elements.

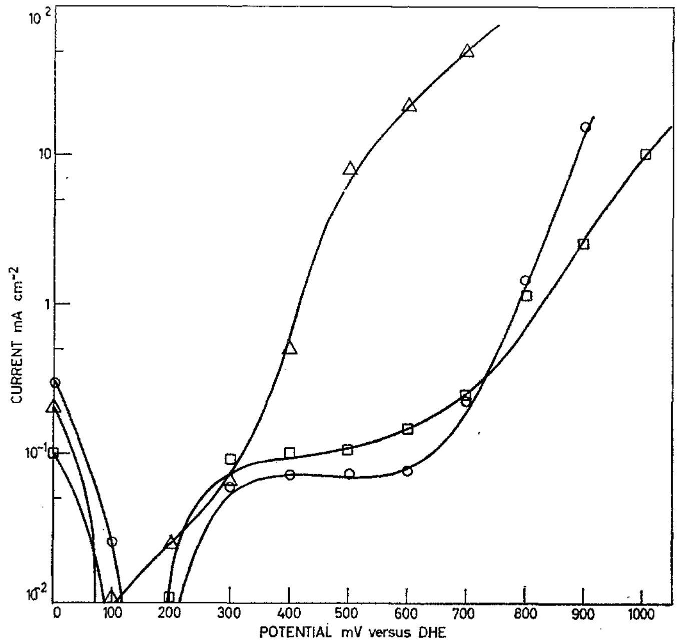

Fig. 4. Steady state oxidation current (mA) against potential (mV) for Mo_2C (△—△); WC (○—○) and TaC (□—□) in a nitrogen saturated solution.

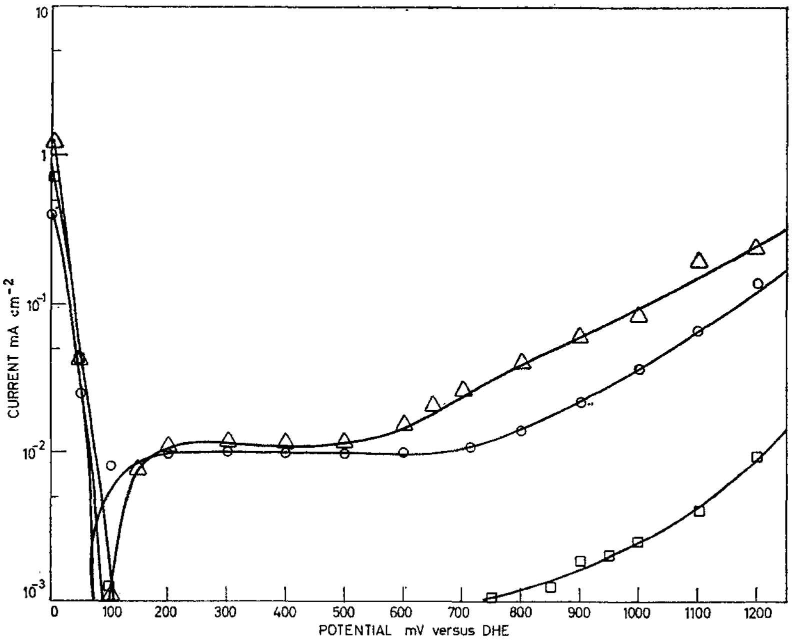

Fig. 5. Steady state oxidation current (mA) against potential (mV) for $MoSi_2$ (△—△); WSi_2 (○—○) and $TaSi_2$ (□—□) in a nitrogen saturated solution.

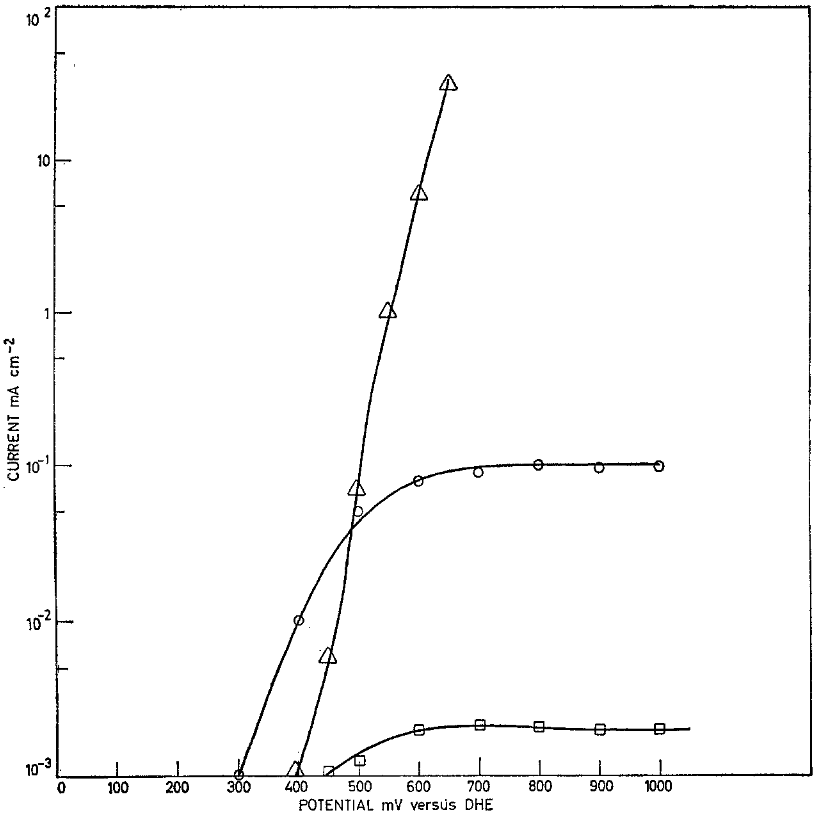

Fig. 6. Steady state currents (mA) against potential (mV) for Mo (△—△); W (○—○) and Ta (□—□) metal in a nitrogen saturated solution.

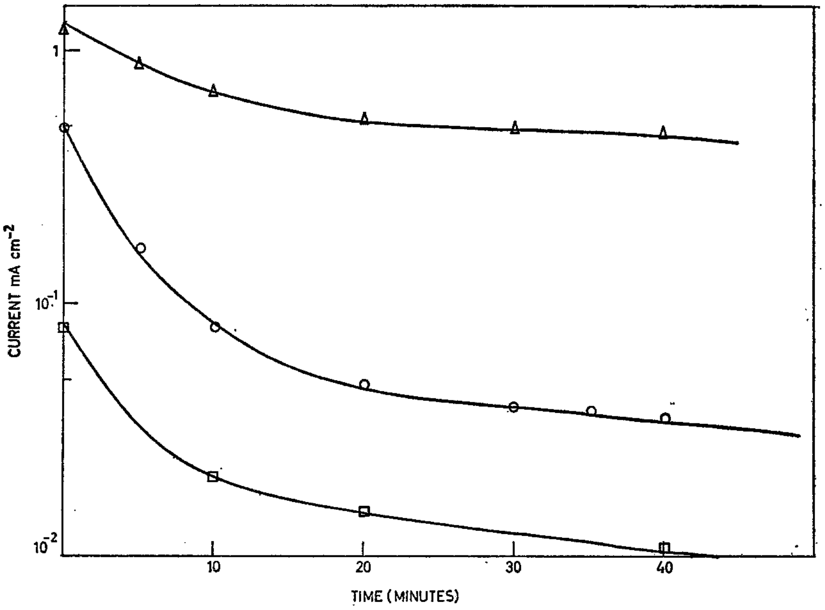

Fig. 7. Current (mA) against time (min) at constant potential (1,200 mV) for oxidation of MoSi$_2$ (△—△); WSi$_2$ (○—○) and TaSi$_2$ (□—□) in a nitrogen saturated solution.

Table 1. Analysis of oxidation products of Mo_2C, WC, TaC and C

Compound	*C.D. mA*	*mV*	*Reaction products identified as fraction of total current*				
			Gaseous %			*Soluble*	*Solid*
			CO_2	CO	O_2		
Mo_2C	40	552	—	—	—	Mo$^{(III)}$ Mo$^{(VI)}$	MoO_3
Mo_2C	80	550	0·4	0·7	—		
Mo_2C	110	675	11·4	0·2	—		
Mo_2C	215	765	10·9	0·4	—		
Mo metal	10	570				Mo$^{(VI)}$	
	200	660				Mo$^{(VI)}$	MoO_3
WC	14	850	16·0	2·3	—	W$^{(VI)}$	WO_3H_2O
	50	910–960	17·2	2·8	—		
TaC	12	890	3·3	1·3	—	none detected	none detected
	40	1,100–1,400	7·8	0·6	—	—	—
Glassy carbon strip	10	2,250	78·5	4·5		—	—
	100	2,600	61·1	2·8			

Table 2. Thermodynamic data for oxidation of WC

Reaction	*Free energy change (k cal mole^{-1})*	*Potential versus normal hydrogen electrode (V)*
$W+3H_2O \rightarrow WO_3+3H_2$	−12·4	−0·09
$C+2H_2O \rightarrow CO_2+2H_2$	+19·2	+0·21
$WC+3H_2O \rightarrow C+WO_3+3H_2$	−2·3	−0·02
$WC+2H_2O \rightarrow CO_2+2H_2+W$	+29·2	+0·32
$WC+5H_2O \rightarrow WO_3+CO_2+5H_2$	+16·8	+0·07

Kinetically however these considerations must be modified since if either element forms an insoluble film, passivation of both elements may occur. Thus where both of the reaction products are insoluble as for $TaSi_2$, in which we assume that $Si \rightarrow SiO_2$, the rate of oxidation drops rapidly as the surface layers are formed. In the oxidation of WC, TaC, WSi_2 and $MoSi_2$, one of the reaction products is insoluble and the blocking of active sites is not so efficient but the rate of oxidation is still considerably less than that for Mo_2C where no passivating layer occurs. Both TaC and WC show a large increase in oxidation rate above 650 mV and this coincides with CO_2 evolution. Below this potential it is probable that only metal oxidation is occurring, giving rise to a plateau region. This is in line with the thermodynamic data of Table 2 which suggests that WC will oxidize to WO_3+C preferentially.

The oxidation of the carbides is important for reasons set out in the introduction and the results showed that irrespective of the potential and of the metallic element the oxidation of the carbon proceeded at a lower rate than that of the metal. Assuming that oxidation proceeded at the same rate for both elements in any one compound then the fraction of current producing CO_2 should be as shown in Table 3.

The actual amount shown in Table 1 is

Table 3. CO_2 contents with stoichiometric oxidation for carbides

Reaction	*% Current to produce CO_2*
$Mo_2C \rightarrow 2MoO_3 + CO_2$	24
$WC \rightarrow WO_3 + CO_2$	40
$TaC \rightarrow Ta_2O_5 + CO_2$	44·4

considerably lower. We conclude that the oxidation of TaC and WC at potentials above 600–700 mV produces a carbon-rich oxidized surface. The oxidation of Mo_2C presents a different case since both of the reaction products are soluble, leading to a high rate of corrosion. However in every case the resistance to oxidation is in the order $Ta > W > Mo$.

The tungsten oxides have been shown to be active electrocatalysts provided that they are present only as a thin layer on a conductive substrate [7, 8]. The advantage of anodized WC as a catalyst may be due to the formation of a carbon-rich WO_3 layer in which the excess carbon acts as current collector in the semiconducting oxide.

References

[1] British Patent 1,234,014.

[2] J. Heidemeyer, D. Babesel, W. Gellert and P. Schavner, *Coll. Czech. Chem. Comm.*, **35** (1971) 944.

[3] K. Mund, G. Richter and F. V. Sturm, *ibid.*, **35** (1971) 439.

[4] R. D. Armstrong, A. F. Douglas and D. E. Keene, *J. Electrochem. Soc.*, **118** (1971) 568.

[5] H. Bohm, *Electrochim. Acta*, **15** (1970) 1273.

[6] H. Binder, A. Kohling, W. Kuhn, W. Lindner and G. Sandstede, *Nature*, **224** (1969) 1299.

[7] Brevet D'Invention, 1,585,070.

[8] G. Feuillade, J. Bouet and B. Chenaux, *Third International Symposium on Fuel Cells*, Brussels, 300, June 1969.

[9] E. K. Sturms, 'The Refractory Carbides', Academic Press, 1967.