

Wear of graphite anodes during electrolysis of acid sulphate solutions

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Received 4 January 1980

Graphite electrodes were prepared by mixing calcined coke and coal tar pitch. They were pressed under 250 kg cm^{-2} and heat treated up to 2800°C . Rectangles measuring $70 \text{ mm} \times 40 \text{ mm} \times 8 \text{ mm}$ were anodically polarized under galvanostatic and potentiostatic conditions. Electrolyses were conducted at $10\text{--}50 \text{ mA cm}^{-2}$ for periods ranging from 10-120 hours in Na_2SO_4 solutions acidified with sulphuric acid to various pH values. The wear of graphite anodes increased with decreasing bath temperature, increasing acid concentration, decreasing pH of the electrolyte and increasing current density. A model is suggested which assumes that corrosion takes place via the formation of a lamellar crystal compound with the formula



The compound is unstable at higher temperatures when corrosion is effected by oxidation of graphite by atomic oxygen. The formation of the carbon ions was found to be a necessary precondition for the formation of the complex.

1. Introduction

The wear of graphite anodes in H_2SO_4 has been ascribed to the attack of atomic oxygen [1-3] and/or the formation of lamellar compounds [4-6]. Fujii [7] reported that the major oxidation path depended on the concentration of the acid, the formation of the lamellar compound being favoured at higher concentrations. Viet [8] showed that the electrochemical oxidation of the carbon by oxygen constituted 40 and 25% of the total wear at 80 and 40°C respectively. Korczynski [9] claimed that the anodic wear of graphitized electrodes decreased with increase in bath temperature in the range $15\text{--}100^\circ \text{C}$. Korczynski and Dylewski [10] found that the anodic corrosion of graphite could be reduced by introducing a depolarizer, increasing the temperature of the electrolyte, controlling the current density or raw material and by using dense electrodes.

Kokhanov and Agapova [11] found that the electrochemical consumption of graphite anodes during the combined discharge of chlorine and

oxygen at a high temperature was independent of the electrolyte pH and the concentration of the alkali produced. Kokhanov and Khanova [12] showed that a linear relation of the wear of the graphite anodes versus temperature was established in terms of an empirical equation: $G_T = 0.23 + 0.014(T - 40)$.

The aim of the present work was to obtain a deeper insight into the corrosion of graphite anodes in sulphuric acid. A lamellar compound was isolated and identified. The influence of sulphate ion concentration, pH, current density and bath temperature on the rate of corrosion are interpreted.

2. Experimental

2.1. *The graphite anodes*

The procedure followed in the preparation of the graphite specimens is given elsewhere [13]. The anodes had an apparent density of 1.64 g cm^{-3} and dimensions of $70 \text{ mm} \times 40 \text{ mm} \times 8 \text{ mm}$.

2.2. The electrolysis cell

This was made from perspex and had the dimensions 25 cm × 18 cm × 15 cm. The tightly fitting cover served as a support for the graphite anode, cathode, mechanical stirrer, heating arrangement, contact thermometer, pH probe, etc. Prior to each experiment, the graphite anode was washed and dried at 125° C and weighed.

2.3. Measurement of corrosion

The total amount of corrosion as well as the rate of corrosion were determined according to the method of Wranglén [14]. The corroded samples were washed repeatedly in distilled water under a vacuum created by a water suction pump until the wash water was free from the sulphate ion. The water was finally evaporated by keeping the anodes overnight in an oven at 125° C. The specimens were then kept in the open air for four hours before weighing. A mean value of weight loss was computed from three measurements (error ± 0.5%).

2.4. Measurements of pore volume and pore size distribution

Measurements of pore volume and pore size distribution were conducted by the liquid pycnometer technique using different fluids [15]. A mercury

porosimeter was used [16] to obtain the pore radius, using the method of Dubinin [17]. The dividing line between micro- and macropore size was taken at a pore radius of 10 nm [18].

2.5. Potentiostatic measurements

An electronic potentiostat, Wenking XXX, was used.

2.6. Infrared studies

The infrared absorption spectrum of the corrosion products was determined with a spectrophotometer, type SP 1000 Unicam.

2.7. Isolation of the intermediate corrosion products

To isolate the intermediate corrosion products, which were retained in the anode pores and not removed by washing, the following procedure was applied. The corroded anodes were thoroughly washed with distilled water until no sulphate ion was traced. The samples were air dried and then crushed and soaked for 24 hours in a small quantity of cold water. The suspension was then filtered and the filtrate evaporated under high vacuum until the volume was reduced to about 50 cm³. The remaining water was removed from the resulting suspension by washing with absolute alcohol, followed by decantation. The compound was finally filtered and dried at room temperature. The product is dark grey to pale brown, insoluble in acetone, absolute alcohol, ethyl acetate or diethyl ether and has a specific gravity which is slightly higher than one. It undergoes hydrolysis in water at temperatures > 65° C. The compound decomposes on heating to give carbon, sulphuric acid and water. It reacts with carbonate with the evolution of carbon dioxide and with barium chloride solution with subsequent precipitation of dirty grey barium sulphate.

3. Results

Fig. 1 shows a plot of the corrosion rate of the graphite anodes against the molarity of sulphuric acid. It can be seen that at concentrations > 2.5 M, the attack becomes very pronounced. A log-log

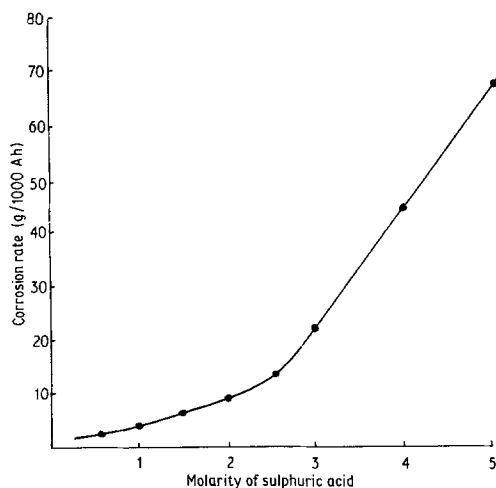


Fig. 1. Effect of sulphuric acid concentration on the rate of corrosion of graphite anodes at 20° C.

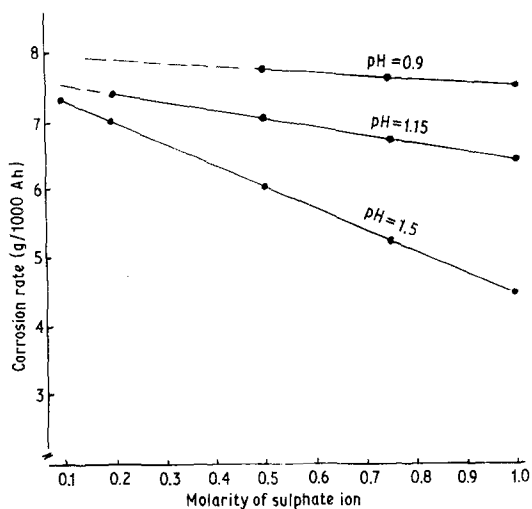


Fig. 2. Effect of sulphate ion concentration on the rate of wear of graphite anodes at 20°C in acidified sulphate solution.

plot of the rate of wear against the acid concentration yields a straight line with a slope of two.

Fig. 2 illustrates that at a constant pH value, the rate of corrosion of the graphite anodes decreases with increasing sulphate ion concentration. It is interesting to note that the decrease is slight at a pH value of 0.9 and becomes more pronounced with increase in the pH of the solution. If the molarity of the sulphate ion is kept constant at 0.5 M, the rate of anodic corrosion decreases

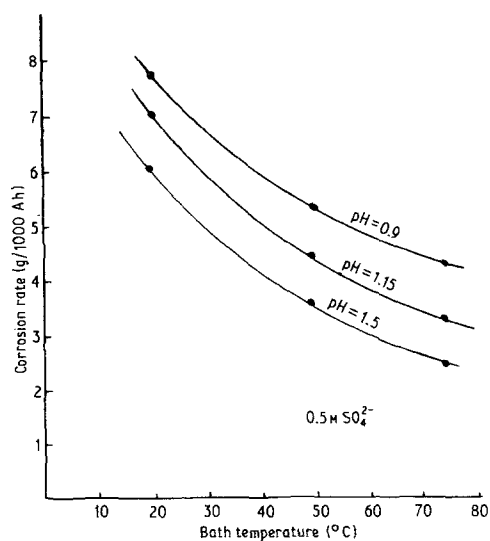


Fig. 3. Effect of bath temperature on the rate of wear of graphite anodes in acidified sulphate solutions.

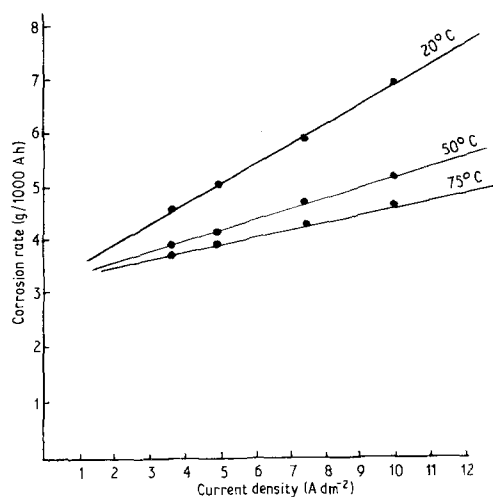


Fig. 4. Effect of anodic current density on the rate of wear of graphite anodes in acidified sulphate solutions at 20, 50 and 75°C.

with increasing bath temperature. The same behaviour is obtained when the pH is fixed at 1.5. The curves shift towards lower corrosion rate with increase of pH (Fig. 3).

Fig. 4 shows that the rate of corrosion increases with increasing current density. The effect becomes less pronounced with increasing bath temperature. Fig. 5 demonstrates that the rate of anodic wear decreases with increasing apparent density of the tested electrode. Fig. 6 shows that

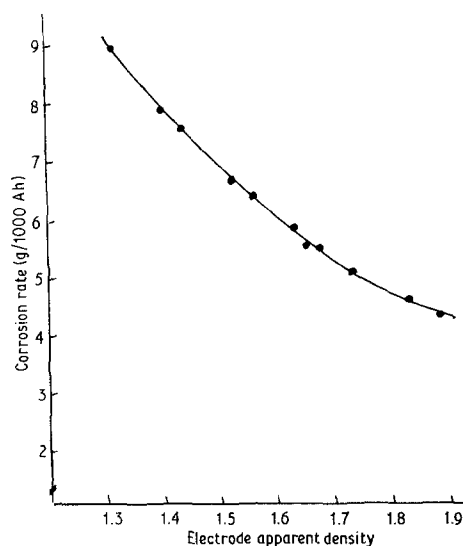


Fig. 5. Effect of apparent density on the rate of wear of graphite anodes in acidified sulphate solutions at 20°C. pH, 1.5; current density, 7.5 A dm².

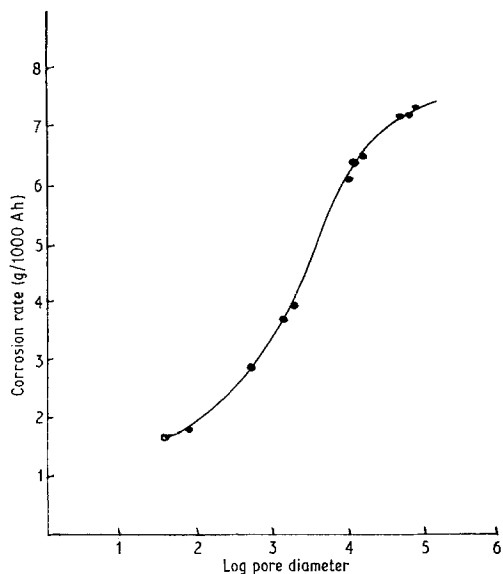


Fig. 6. Effect of pore diameter on the rate of wear of graphite anodes in acidified sulphate solutions at 20°C. pH, 1.5; current density, 7.5 A dm⁻².

within the pore diameter range 75–5000 nm the rate of anodic wear increases with increasing pore diameter. For narrower or wider pores the rate of corrosion is less sensitive to changes in diameter.

Fig. 7 shows two potentiostatic curves obtained at a constant potential value of 500 mV versus SCE for 0.5 and 1.0 M sulphuric acid. It is seen

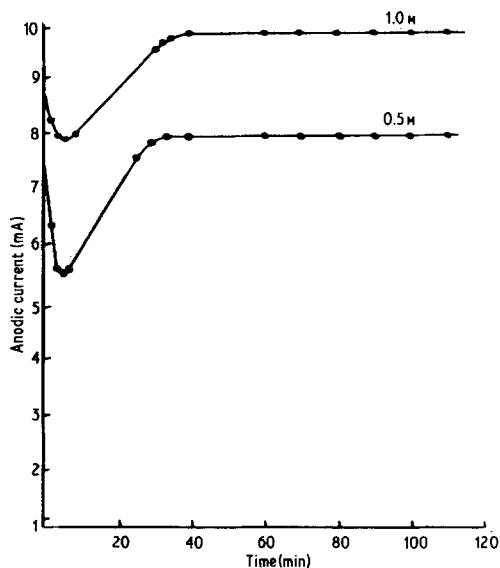


Fig. 7. Potentiostatic current versus time curves at 500 mV (SCE) in 1.0 and 0.5 M sulphuric acid solutions.

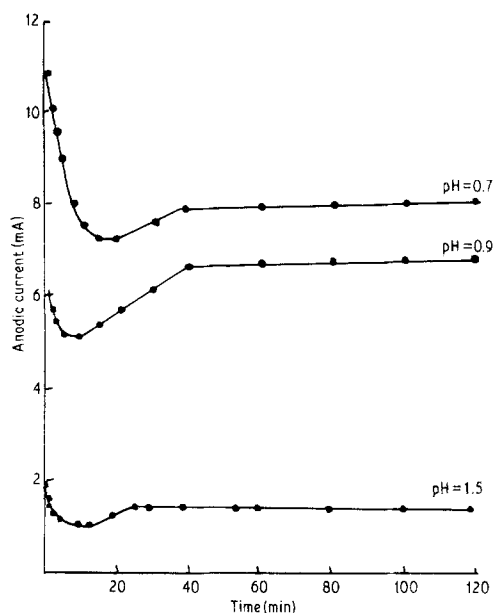


Fig. 8. Potentiostatic current versus time curves at 500 mV in acidified 0.1 M sulphate solutions. pH, 0.7, 0.9 and 1.5.

that the current density decreases, passes through a minimum and rises again before it attains a constant value after 40 minutes. The curves are shifted towards lower current-density values with increase in the acid concentration. A similar set of curves obtained in 1 M sulphate solution and varying pH values (Fig. 8) illustrates that the curves shift towards lower current-density values with increasing pH.

Fig. 9 shows the infrared spectrum of the compound isolated from the corroded electrodes. The spectrum displays three absorption bands at 1100–1180, 3440 and 1630–1730 cm⁻¹, the intensity of the first being the greatest and that of the third the lowest.

4. Discussion

The wear of graphite anodes has been ascribed to one of the following two mechanisms: (a) a direct oxidation of carbon with atomic oxygen ($C + 2O = CO_2$) or (b) the formation of lamellar crystal compounds such as graphite bisulphate [20]. In either case, corrosion proceeds towards the inner surfaces of the anode with the accumulation of acid in the pores [21]. Several lamellar compounds have been reported, e.g. graphite bi-

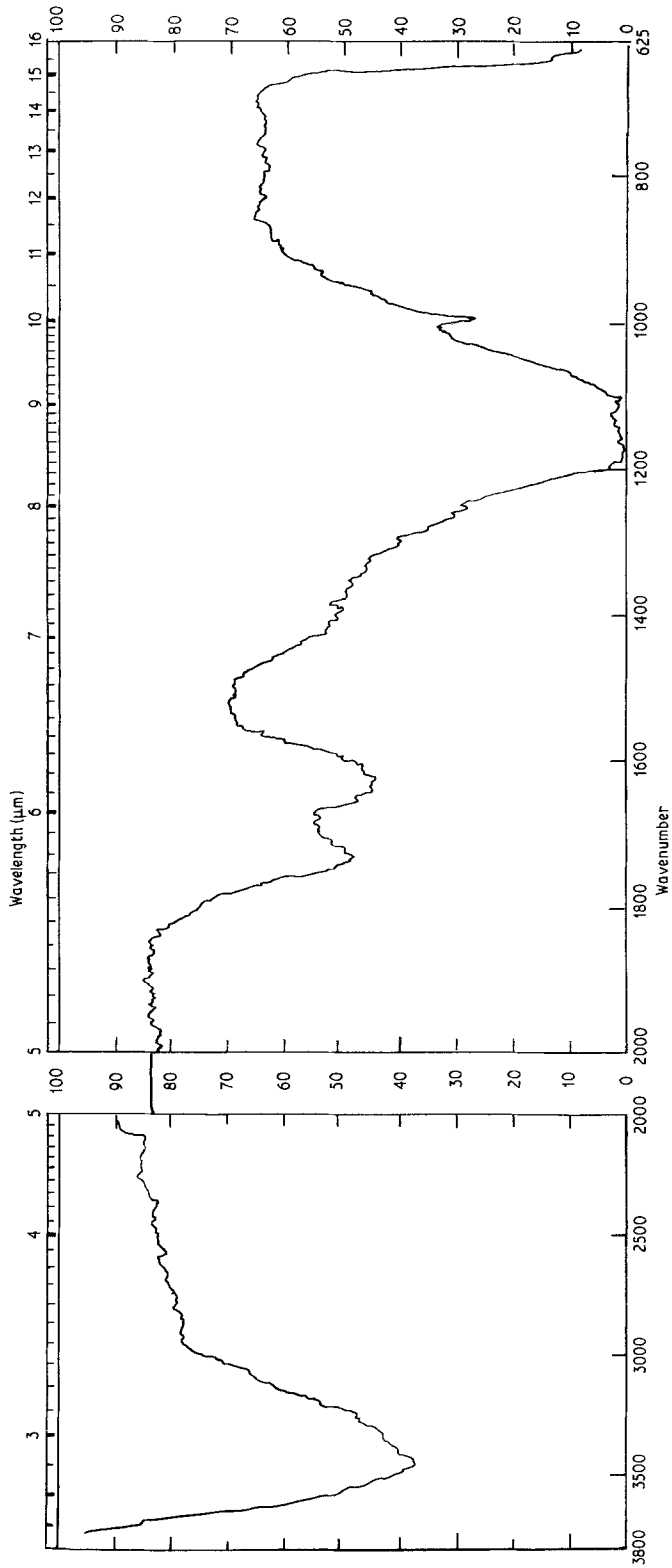
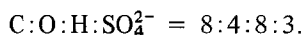


Fig. 9. Infrared absorption spectrum of the intermediate lamellar compound.

sulphate [22] or graphitic oxide [23], with different chemical formulae, such as $(C_6(OH)_3)_n$ [24] and $C_8H_2O_4$ [25]. Hofmann [26] reported that graphitic oxides had varying composition depending on the type of the graphite used and the number of times the oxidation had been repeated.

The chemical analysis of the compound isolated in this work gave the following atomic ratios:



Based on these results, the following formula may be suggested:



The infrared spectrum obtained for this compound shows an absorption band at $1630\text{--}1730\text{ cm}^{-1}$ which may be assigned to the $C=O$ vibration of the keto form. The large absorption band at $1100\text{--}1180\text{ cm}^{-1}$ corresponds to the $C-O$ vibration of the enol form. The OH stretching band appears at 3440 cm^{-1} . Thus it may be concluded that besides the keto-enol equilibrium, the OH and $C-O$ groups may be present. The infrared absorption spectrum may indicate that the oxygen atom is built into the graphite lattice as a heterocyclic atom [27]. The lamellar plane is built up by four hexagons (8 carbon atoms). The HSO_4^- radical is presumably intercalated between the hexagons. It may be assumed that this compound is electrochemically formed in the anode reaction between graphite and the H_2SO_4 solution. The increase in the anodic wear rate with increase in sulphuric acid concentration coupled with the fact that the reaction is second order with respect to H_2SO_4 may be in favour of the suggested formula.

The decrease of the corrosion rate with increase in temperature indicates that the formation of such a lamellar compound is hindered with rise in temperature, probably due to the exothermic nature of one or more of the steps in the reaction sequence. Accordingly, corrosion is mainly effected via direct oxidation of graphite with atomic oxygen.

The decrease in anodic wear with increase in sulphate ion concentration can be explained on the premise that the sulphate ions adsorb on the surface, thus leading to its protection (i.e., they act as an inhibitor). The inhibiting effect of the sulphate ions seems to be directly proportional to the concentration of the adsorbed sulphate ions. The

increase in corrosion rate with decrease in pH (keeping the sulphate ion concentration constant) may be interpreted on the grounds that H^+ ions are essential for the formation of the lamellar compound, as is gleaned from the suggested formula. This assumption finds support in the potentiostatic curves. The initial descending branches may be correlated with the coverage of the graphite anode surface with sulphate ions. The rising branches point to the reaction with H^+ ions to give the lamellar compound. The steady-state value maintained by the current thereafter corresponds to an equilibrium state in which the slow step is the diffusion of the hydrogen ions across a concentration gradient.

The increasing effect of the anodic current density on the corrosion rate is taken to suggest that the number of ionizable, positively charged carbon atoms necessary for the formation of the lamellar compound [28] increases with increasing current density. Such ionizable carbon atoms are less essential for the wear process with increase in temperature as judged from the slopes of the wear-current density curves obtained at different temperatures. Dense electrodes are comparatively more resistant to wear than light electrodes because of the lower pore volume and less internal surface area in the former.

The pore diameter seems to play an important role. Micro-diameters (less than 2 nm) are not accessible for the penetration of the electrolyte into the pores and thus hinder the internal attack. Increasing the pore diameter from 75–5000 nm allows a corresponding increase in both the rate of diffusion of the electrolyte into the pores and the rate of diffusion of the products of the anode reactions from the pores. Further increase in pore diameter is immaterial since the maximum diffusion rates are attained at 5000 nm.

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