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CORROSION BEHAVIOUR OF GRAPHITE AND STAINLESS STEELS IN PHOSPHORIC ACID

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Abstract:

Corrosion behaviour of graphite and stainless steels was examined in phosphoric acid by electrochemical methods (polarization curves, impedance spectroscopy and SVET). Potentiodynamic curves showed that graphite exhibit an excellent resistance in the acid solution. Effect of the presence of chloride and sulphide ions in 40% H₃PO₄ solution was also investigated at 20°C and 80 °C. At elevated temperature, the current densities increased in the presence of aggressive impurities. Although stainless steels exhibited a good passive behaviour, the best corrosion resistance in chloride and sulphide contaminated H₃PO₄ was shown for the graphite.

Subsequently, the current density at the surface was detected by scanning vibrating electrode technique (SVET). From the data obtained, graphite surface manifested a distinctive behaviour from that of stainless steels.

Keywords: corrosion, phosphoric acid, graphite, stainless steels, SVET.

Introduction:

The manufacture of the phosphoric acid by wet process generates severe corrosion problems. Impurities and additives present in these solutions (chlorides, sulphides, ...) can produce a structural corrosion of materials and reduce their lifetimes. Sulphide ions come from the attack of the phosphate ore by the concentrated sulphuric acid; these ions involve a reduction in the material resistance [1,2], and their effects increase with the temperature and the content of oxygen in the solution [3]. The chloride ions, coming from the phosphate ore and washing water, can be adsorbed on the metal surface to inhibit the passivation process. According to its concentration and the temperature of the solution, the chloride ion causes a localized destruction of passive films and a pitting corrosion [4-6].

Graphite and carbon are attractive materials for industrial applications due to their high strength, excellent thermal shock resistance and light weight. They are widely used as engineering materials, such as high temperature exchangers [7,8]. They are also found application in electrochemical manufacturing processes due to their electrocatalytic activity, high thermal and electrical conductivity and high chemical and electrochemical stability [9]. Nevertheless, there are few papers which deal with the corrosion of carbon in aqueous media [10-14].

The purpose of the present study is to investigate the corrosion behaviour of impregnated graphite in the H₃PO₄ solution in the temperature range from 20°C and 80°C. This work permits to compare the corrosion resistance of graphite and stainless steels in phosphoric acid solution polluted by chloride and sulphide ions. The scanning vibrating electrode technique was used to detect the anodic and cathodic current distribution on the surface of the electrodes.

Experimental:

The samples of Graphite (Gr) and stainless steels UB64, and U50 were tested in the present study. The graphite material is impregnated with a phenolic resin and the chemical composition of the alloys is listed in table1. In all measurements, mechanically polished electrodes were used. Polishing was carried out using successively thinner grade of emery papers (400-4000 grades), then the samples were washed with distilled water and dried.

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The exposed area of the specimen was 0.25 cm². Platinum and saturated calomel electrode (sce) were used as counter and reference electrodes, respectively. The electrolyte used in this study was the phosphoric acid (40% H₃PO₄) without or with addition of 4% of H₂SO₄ and 400 ppm of Chloride. In this last case, the solution was called polluted H₃PO₄ solution.

Anodic polarization curves were drawn potentiodynamically at a scan rate of 0.5 mV/s with a potentiostat/galvanostat (EG&G model 263A). A solartron SI 1250 frequency response analyser was used for electrochemical impedance spectroscopy. EIS diagrams were recorded between 20 KHz and 10 mHz at the open circuit potential (E_{corr}) and the AC amplitude was 10 mV.

Table-1: Chemical composition of stainless steels

Alloy elements:	Ni	Cr	Mo	Cu	Mn	Si	C	S	P	other
UB64	25.56	20.58	4.67	2.36	1.24	0.72	0.017	0.006	0.019	W:4
U50	8	21	2.5	1.5	2	1	0.03	0.03	0.04	N:0.15

A commercial SVET system from Applied Electronics (USA) was used for local measurements. The ASET Software converted the potential measured by the microelectrode into a current density value. The displacement of the microelectrode was performed using a motorised and computer-controlled XYZ micromanipulators and the electrolyte used for all the investigations was dilute acid solution (1mM) at room temperature. The vibrating probe was carefully placed above the surface of the working electrode at a height of about 100µm. The vibrating amplitude of the scanning probe in both directions, parallel and perpendicular to the surface, was adjusted to about 20µm. SVET scans were carried out after 30 min of immersion under open circuit potential in H₃PO₄ solution (40% H₃PO₄) at different temperatures. Three treatments were carried out for each electrode, and three measurements were taken at various places of each analysed surface. The current density was plotted as a 3-dimensional surface (the current density measured along the z-axis as a function of the x, y plane). In this format, positive and negative current densities represent anodic and cathodic sites respectively.

Results:

Polarization curves of graphite in phosphoric acid solution at 20, 60 and 80°C are illustrated in figure 1. Graphite proves to be an inert material in the phosphoric acid at 20°C. Figure 1 shows that the increase of medium temperature induced an increase in current densities. Corrosion rate is about 0.025 µA/cm² at 20°C and more than 0.1µA/cm² at 80°C.

Figure 2 shows that the addition of chloride and sulphide ions in acid shifts E_{corr} into more positive value (from 170 to 260 mV/sce) and the corrosion rate increases from 0.025 µA/cm² to 0.035 µA/cm² at 20°C. However the corrosion rate and current densities values indicate that graphite exhibit an excellent resistance in the phosphoric acid at 20°C, with a current density which doesn't exceed 1µA/cm² in the potential range from 0.0 to 0.7 V/sce. This is probably due to the formation of surface oxide which blocks the active surface area. It is important to recognize that graphite has a very complex porous structure, and the reaction processes occur within these pores. Some studies [15,16] investigated the electrochemical oxidation of numerous carbons in phosphoric, sulphuric and chloridric acids. Two oxides (a thin protective oxide and a surface oxide) were found to form when anodic current was imposed on carbon electrode.

There were big differences due to more aggressive conditions between polarization curves at 20°C and those at 80°C. The catalytic activity of the aggressive ions adsorbed on the surface increases, and consequently accelerates the dissolution process and the kinetic of exchange between the electrode surface and the electrolyte. From the data obtained, it was clearly seen that the stability of graphite was seriously disturbed by the increase of temperature up to 80°C. The corrosion rate increased from 0.035 µA/cm² at 20°C to 0.3 µA/cm² at 80°C and the corrosion potential increased to more positive value (520 mV/sce).

Temperature effect can be attributed to the appearance of active pores or defects in the graphite surface or to the diffusion of reagent species in the graphite layers. Stonehart et al evaluated the effects of the electrolyte temperature and concentration, the operating potential, the type of carbon, and the nature of carbon surface treatment on the specific carbon corrosion rates [14]. They found that at any given temperature the corrosion currents increased with higher potentials. At a given potential, the corrosion currents also increased with the temperature.

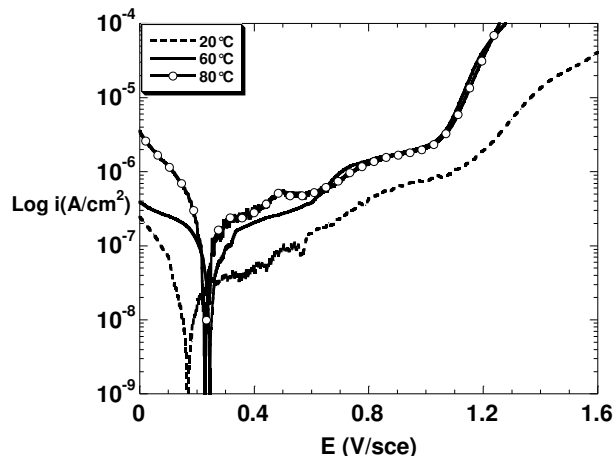


Figure 1: Potentiodynamic curves of graphite in H_3PO_4

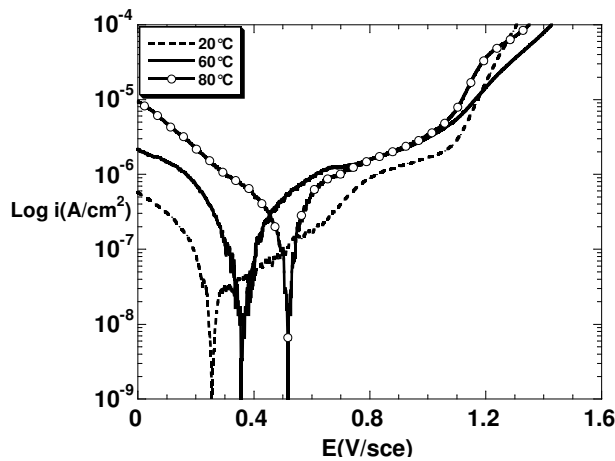


Figure 2: Potentiodynamic curves of graphite in polluted H_3PO_4

In polluted H_3PO_4 solution (figure3), stainless steels have a good passive behaviour with a large passivation domain. This behaviour may be attributed to the chemical composition of the alloy rich on Cr, Ni and Mo ... At the anodic potentials, the formation of Fe, Cr and Ni oxides was expected. Owing to passivation properties of steel and its resistance to acid solution, the chromium oxide (Cr_2O_3) was considered as the main passive component in the formed film [17]. Chromium was a principal element in the alloys which contributed strongly to the formation of passive film. Nickel was another major alloying element, also able to reduce the corrosion rate and passive current density, and molybdenum addition in stainless steels was known to increase the resistance to localized and pitting corrosion [18]. The role of Ni and Mo in the stainless steel at anodic potentials in acid solutions was to stabilise the passive film and to eliminate the active surface sites.

In the same conditions, graphite presented a higher corrosion potential and a smaller corrosion rate. Corrosion rate value was about $2\mu A/cm^2$ for the UB64 and $10\mu A/cm^2$ for U50. Comparing to the graphite corrosion rate (less than $0.1\mu A/cm^2$) one can conclude that stainless steels are more sensitive to the acid attack than graphite.

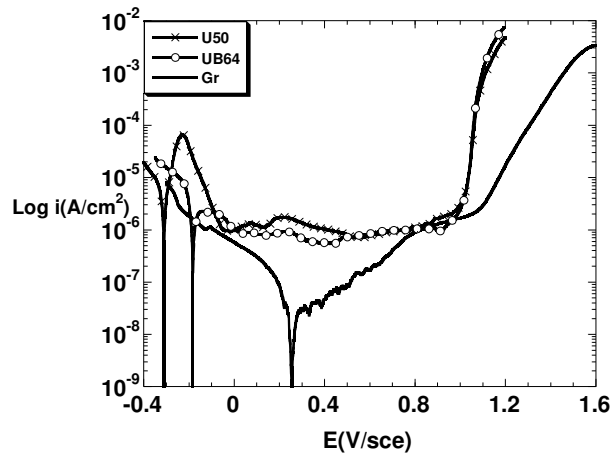


Figure 3: Potentiodynamic curves of graphite and stainless steels in polluted H_3PO_4 at 20°C

Impedance spectra were plotted at open circuit potential in the polluted phosphoric acid at different temperatures. At high frequencies, linear curves were obtained in the Nyquist plots (figure 4a), these lines were not vertical, which indicated that the equivalent circuit of the system included a resistance in addition to the capacitive component [19].

The inclination of the lines, was due to the presence of the finite faradaic resistance R_f in the equivalent circuit. This resistance is relatively large in the acid solution, because of the little rate of the Graphite/electrolyte exchange at the steady-state potential.

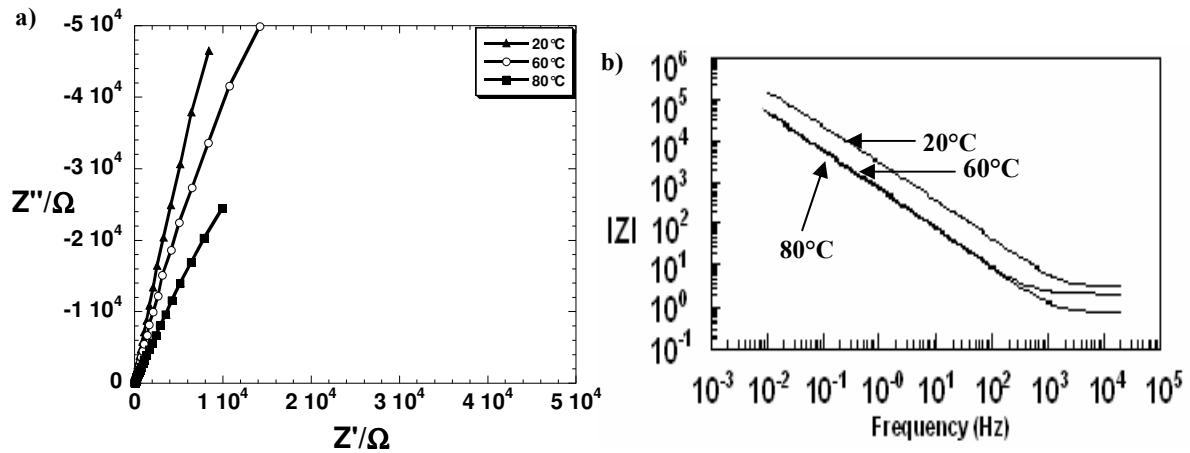


Figure 4: Impedance spectroscopy curves of graphite at different temperature in polluted H_3PO_4

a) Nyquist plots . b) Bode plots.

Figure 4b shows that there is a decrease in the total impedance values when the temperature of the electrolyte increases, revealing an increase of the corrosion rate. More the total impedance at 10^{-2} Hz was initially around $15 \cdot 10^4 \Omega \text{ cm}^2$ and decreases to value above $4 \cdot 10^4 \Omega \text{ cm}^2$ after increasing temperature to 80 °C. This evolution suggested an evolution of the charge exchange between the material and the solution occurring at the surface. The R_f value decreased when the temperature of acid medium increase (inclination of the plot was more pronounced) due to the enhanced rate of charge transfer at the interface revealing that the response of the system changed from a capacitive to a resistive behaviour. This evolution revealed that the corrosion processes become more possible.

Impedance measurements showed that graphite had a good resistance in the phosphoric solution in agreement with I-E curves results, but the increase of medium temperature had a negative effect.

SVET scans are presented in figure 5. It can be seen from the current maps that stainless steel and graphite surfaces reacted differently. After 30min of immersion, the anodic and cathodic sites were distributed on the surface with different sizes and intensities. The sites of the metal dissolution or the formation of the surface oxides were indicated by the anodic zones, which were adjacent to the sites of the reaction of oxygen reduction indicated by the cathodic zones.

Stainless steel surface showed big corrosion attack zones indicating a metallic corrosion activity with an anodic current density which attained $120\mu\text{A}/\text{cm}^2$ after immersion at free potential in the solution at room temperature (map A).

Graphite samples showed a quasi-symmetric current distribution between anodic and cathodic sites, with size not exceeded a few tens of μm s (map C). Different sites are dispersed arbitrarily on the graphite surface and illustrate a uniform corrosion with a weak current densities (less than $20\mu\text{A}/\text{cm}^2$).

When the samples were immersed in solution at higher temperature (80°C), bigger current densities were recorded and anodic sites were broader. The anodic activity of the stainless steels gave current density of at most $120\mu\text{A}/\text{cm}^2$ at 20°C and which exceeded $300\mu\text{A}/\text{cm}^2$ at 80°C (map B). The increase of temperature was confirmed to accelerate the dissolution kinetic on the metal surface.

On the other hand, graphite surface was less affected by the increase of temperature, the current densities remained always moderate, but were also higher than those recorded at 20°C and the anodic sites are more numerous (map D). This was due to the increase of exchange rate in the active sites on the graphite surface and consequently the resistance of material decreased.

From all the results obtained, the corrosion phenomenon of graphite in the phosphoric acid solution, can be classed in general corrosion in term of the large distribution of the active sites on the surface. Stainless steels showed a localized corrosion behaviour with big corrosion areas indicating a local metal dissolution.

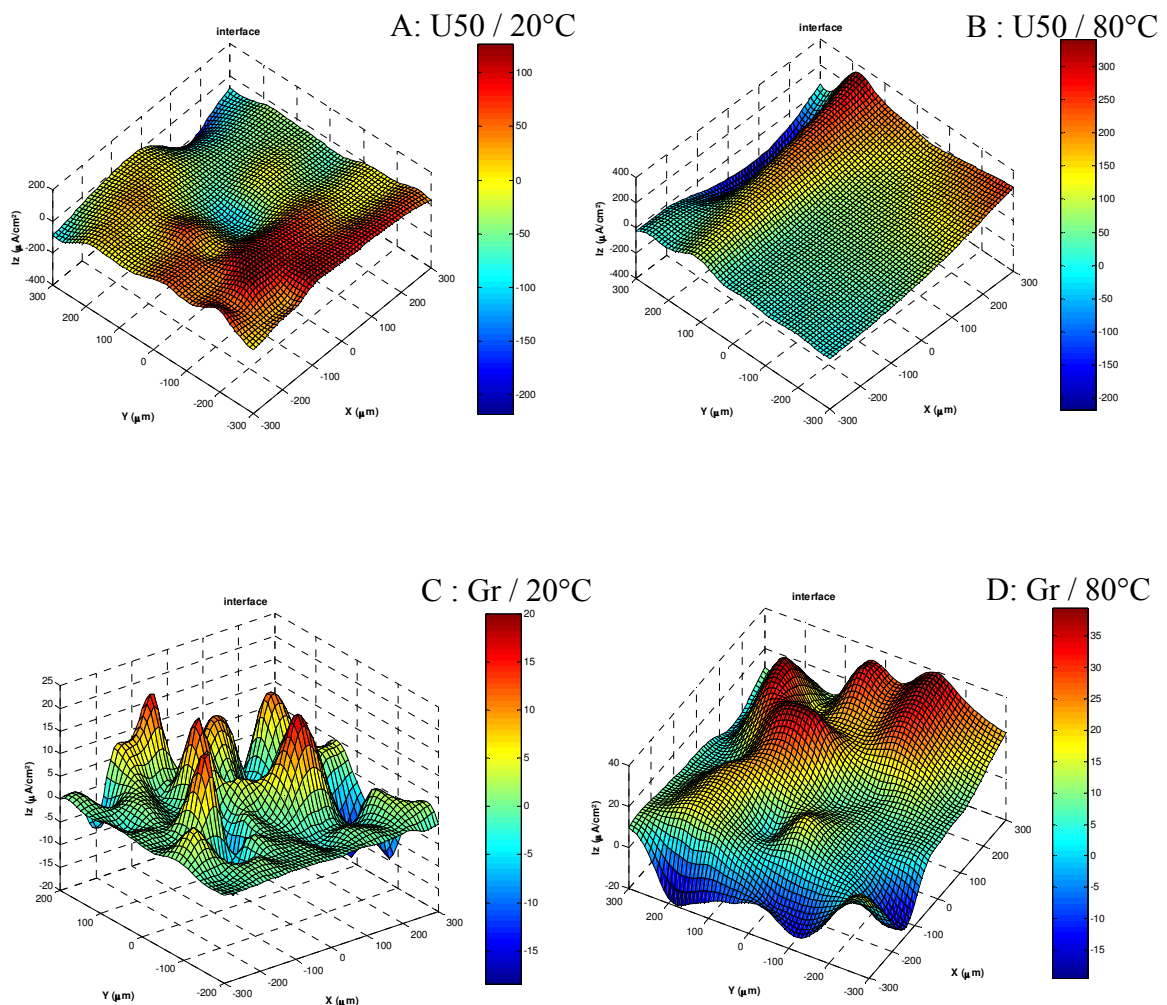


Figure 5: The SVET maps

Conclusion:

The aim of this study was to investigate the corrosion resistance of graphite in polluted phosphoric acid at different temperatures. Graphite remained very resistant even if the temperature increased to 80°C. Graphite kept its resistive properties, and the recorded rate of corrosion remained always low, even if the active sites became more numerous. This effect may be due to the electro-adsorption of ions on the active sites on the surface of the graphite electrode, certainly activated by the increase of temperature.

Compared to stainless steels, graphite material was more resistant with a low corrosion rate. SVET proved to be a good technique to compare corrosion behaviour of different materials. The SVET analysis indicated that the corrosion which occurred on graphite was generalised corrosion and for stainless steel it was localized corrosion.

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