whether oxygen or chlorine was evolved. Acidic solutions, especially sulphuric acid, attacked strongly: the graphite and non-porous GC electrodes were worn by etching, but the porous GC electrodes were crumbled into pieces, in many cases during the first electrolysis day. The durability of all electrodes in alkaline solutions was markedly better.

From our experiments we conclude that in electrolytic durability, non-porous glassy carbon is as good as or, because of its good mechanical properties, in some cases even better than graphite. However, pores make the durability of glassy carbon distinctly worse.

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Fourier transform–infra-red spectra of phosphate coatings on Armco iron

The commercial application of phosphate coatings for protecting metal surfaces has steadily increased [1], but their chemical composition and structure are not yet fully understood [2]. The development of interferometric absorption–reflection techniques has in recent years, greatly improved the possibilities of utilization of infra-red spectroscopy for the study of thin coatings on metal surfaces [3, 4].

Absorption-reflection spectra of phosphate coatings on Armco iron were recorded in the range 400 to 3800 cm^{-1} with a FTS-14V Digilab Fourier Transform Spectrometer, using a Harrick reflectance attachment. The angle between sample plate and light beam was 30°. The measurement parameters were: resolution 4 cm^{-1}, sampling interval 1, number of scans 100. The Fourier transform was calculated with double precision, using 32-bit words. Thin phosphate coatings can be formed by application of phosphoric acid solution alone, i.e. not containing metallic phosphates, to an iron surface.

Fig. 1a shows the spectrum of coatings obtained using H_3PO_4 0.1 N solution at 25° C. This spectrum corresponds to iron phosphate [5]: its structure does not depend significantly on the time of immersion.

The spectra are more complicated for coatings obtained using zinc phosphating solutions, which are mostly employed. Fig. 1b and c show typical spectra obtained for different times of immersion in a standard solution (H_3PO_4 68.7 g + H_2O 41.7 g + ZnO 15.0 g; diluted before use as follows: solution 8 cm^3, H_2O 90 cm^3, 20% $NaNO_2$ 2 cm^3) at 25° C. There is an evident evolution of the spectra, whose main features will be briefly discussed.

At the very first stage of reaction, the spectrum looks similar to that of Fig. 1a. Iron phosphate is, therefore, also formed first in zinc phosphating solution. With increasing time of immersion (Fig. 1b), a progressive splitting of bands corresponding both to $\nu_3(F_2)$ P–O stretching vibrations

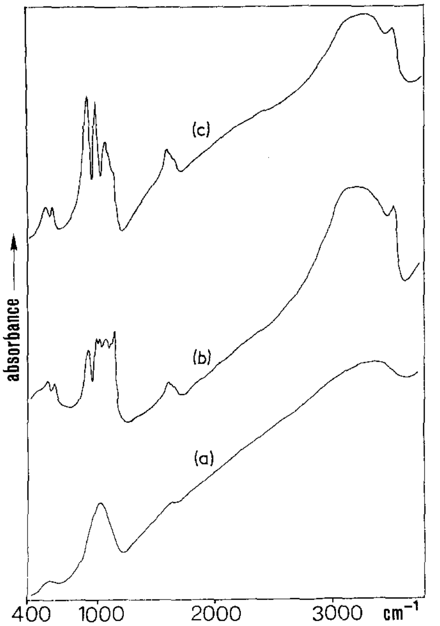

Figure 1 Fourier transform absorption–reflection infrared spectra between 400 and 3800 cm^{-1} of phosphate coatings on Armco iron. (a) H_3PO_4 0.1 N solution (30 min); (b) zinc phosphating solution (30 sec); (c) same solution as (b) (30 min).

(900 to 1200 cm^{-1}) and to $\nu_4(F_2)$ O–P–O bending vibrations (500 to 700 cm^{-1}) can be observed, ending in a complete loss of degeneration after prolonged immersion (Fig. 1c). The final spectrum is characteristic of crystalline hydrated zinc phosphate [5, 6], both pure or mixed with iron phosphate.

Further information is also given by the higher frequency region. The sharp band centred near 3580 cm^{-1}, corresponding to a free hydroxyl stretching vibration, suggests that hydrated zinc phosphate formed on the surface, although probably near to hopeite $Zn_3(PO_4)_2 \cdot 4H_2O$ crystal structure [7], may contain free hydroxyl groups. This high-frequency band disappears after heating the sample at 160° C. Under these conditions the main absorptions due to stretching (3000 to 3400 cm^{-1}) and bending (1600 to 1700 cm^{-1}) vibrations of associated water molecules also modify their structure, thus showing the existence of at least two different kinds of molecular water in the crystalline layer.

Water plays an important role, as it has been observed [8] that zinc phosphate coatings heated in the absence of air lose their corrosion resistance at temperatures between 150 and 163° C. Structural modifications connected with loss of water probably result in a volume decrease of the coating which causes voids and thereby lowers the corrosion resistance. Further experiments are now in progress in order to obtain quantitative information on the influence of various parameters on composition and morphology of phosphate and chromate coatings.

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