

Porous anodic oxides are of increasing interest for nanotechnological applications, such as photonic crystals, sensors and solar cells, as well as of continuing importance for protection and functionalization of metal surfaces, eg of aluminium in aerospace, architectural, packaging and electronic sectors, where energy reduction and environmental compliance of processes are critical considerations. Despite significant previous research, the understanding of porous oxide growth is still subject of much debate. The present programme has enabled in-depth probing of the mechanism of porous oxide growth involving collaboration between the University of Manchester (U.K.) and the University of Paris (France), combining complementary expertise in respectively high-resolution electron microscopy and ion beam analysis. Key experiments have involved the use of ^{18}O as a tracer species in the study the transport of oxygen in the growing oxide films. Since the film morphology changes significantly as the film evolves from an initial non-porous oxide to a fully porous oxide, microscopy of the oxide at the various stages of film growth is vital to the interpretation of the tracer data. A further key feature of the study is the use of multispectrum analysis to provide confidence in quantification of nuclear data, using SPACES, SIMNRA and RUMP softwares, with analyses of oxides by non-resonant and resonant nuclear reactions and elastic scattering, the latter including RBS and MEIS (at Daresbury Laboratory U.K.). The overall experimental methodology was developed from extensive studies of anodizing of aluminium in phosphoric acid electrolyte (PAE). The first studies explored the optimum conditions for carrying out ^{18}O tracer experiments, in terms of ^{18}O concentration in the electrolyte, thickness of oxide and conditions of anodizing (cell type, current density). The preferred method involved formation of a thin non-porous oxide in ^{18}O -enriched electrolyte, followed by various times of anodizing in non-enriched electrolyte. The findings revealed a major re-distribution of the ^{18}O as the porous film evolves, which correlated with the evolution of the porous structure (Fig.1.a,b). The latter initially comprised a region of high porosity (60%), with a pore morphology related to the texture of the original surface of the aluminium, followed by emerging of the major pores, of low porosity (10%) with a size related to the anodizing voltage. The ^{18}O was distributed during film growth between the highly porous material, which remained at the film surface, the walls of the major pores, and also the thin layer of non-porous oxide that remains at the base of the film (Fig.2.a). Notably, the dependence of the oxygen contents of the films and the film thickness on the time of anodizing indicated increasing efficiencies of film growth and rates of film growth as the film progresses from the initial non-porous type to the fully porous morphology. The major pores appear to be generated by flow of anodic oxide. However, it is possible that the initial pores develop by a differing mechanism, which is currently being explored by using a tungsten tracer to distinguish whether flow of oxide or dissolution of oxide is the principle cause. Following successful establishment of

the methodology with PAE, other anodizing electrolytes were investigated (chromic acid, sulphuric acid, borax), which reveal significant differences in film formation compared with PAE in terms of distribution of ^{18}O and kinetics of oxide growth. For instance, in the case of chromic acid, the films reveal relatively constant rates of film growth and a constant growth efficiency, which is lower than that in PAE. The films also have large differences in the pore morphologies, with feathered pores formed in chromic acid and smooth-sided pores formed in sulphuric acid and PAE (Fig.1.c-e). Further, the ^{18}O remains at the outer part of the film, contrasting with the presence of ^{18}O in the inner regions of films formed PAE (Fig.2). Assessment of the growth mechanism of these other oxides awaits the full analysis of the extensive data that have been accumulated. Notably, however, the ^{18}O appears to be retained in the film during anodizing in all of the investigated electrolytes, which is contrary to a simple dissolution mechanism of pore formation.

In parallel with the studies of aluminium, work has been carried out on porous oxide formation on titanium, tantalum and zirconium, using organic-based, fluoride containing electrolytes, which are used extensively for generation of nanotubes on these materials. Here interest lies in whether pore generation occurs by a different mechanism to that in anodic alumina, and the transition between a nanoporous oxide and a nanotubular oxide. In the case of zirconium, the effect of water content in the electrolyte on the formation of the nanotubes has been explored, with ^{18}O tracer experiments and RBS being used to determine the composition of the oxides and the source of oxygen in the oxides, whether from the organic constituent or water. The finding revealed films containing significant amounts of fluoride in addition to oxide, with the water being the major source of the oxygen in the oxide. Ion beam analytical studies have also been carried out on formation of porous oxides on stainless steel, using an ac polarization method to produce oxides of up to 100 nm thick, which are being investigated to prevent fouling of surfaces. The studies are complemented by surface analysis by other methods, such as TEM and GDOES. Finally, a limited amount of work has been done on formation of porous oxides by plasma electrolytic oxidation, although the oxides proved too thick and non-uniform for nuclear reaction analysis of ^{18}O . However, success in obtaining ^{18}O distributions of sequentially formed oxides was achieved by imaging SIMS, which has not been reported previously for this type of oxide. The findings revealed the transport of oxygen to the inner part of the oxide by a short-circuit mechanism.

The overall findings of the studies contribute significantly to understanding of porous oxide growth by anodizing, which will be of benefit to future development of improved porous oxides for a range of new applications that are currently being researched, as well as underpinning the use of the oxide in more traditional areas where more economic and environmentally friendly processes are sought, as well as enhanced film performance.

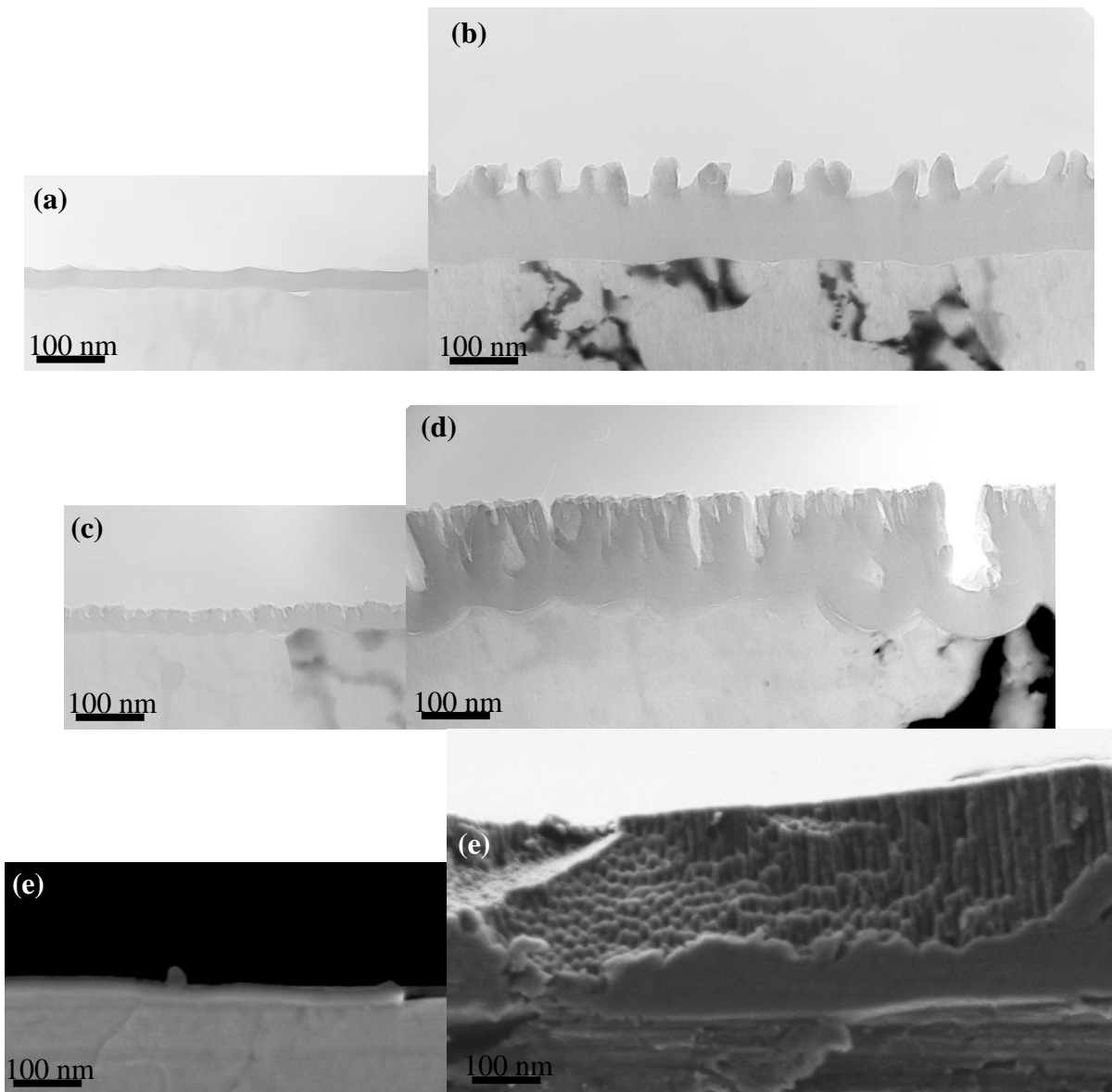


Fig. 1. Transmission electron micrographs (TEM) of aluminium anodized in 0.4 M phosphoric acid at 295 K to (a) 20 V (b) 100 V. TEM of aluminium anodized in 0.25 M chromic acid at 313 K to (c) 15 V (d) constant value of voltage. Scanning electron micrographs of aluminium anodized in 0.4 M sulphuric acid at 295 K to (a) 15 V (b) constant value of voltage.

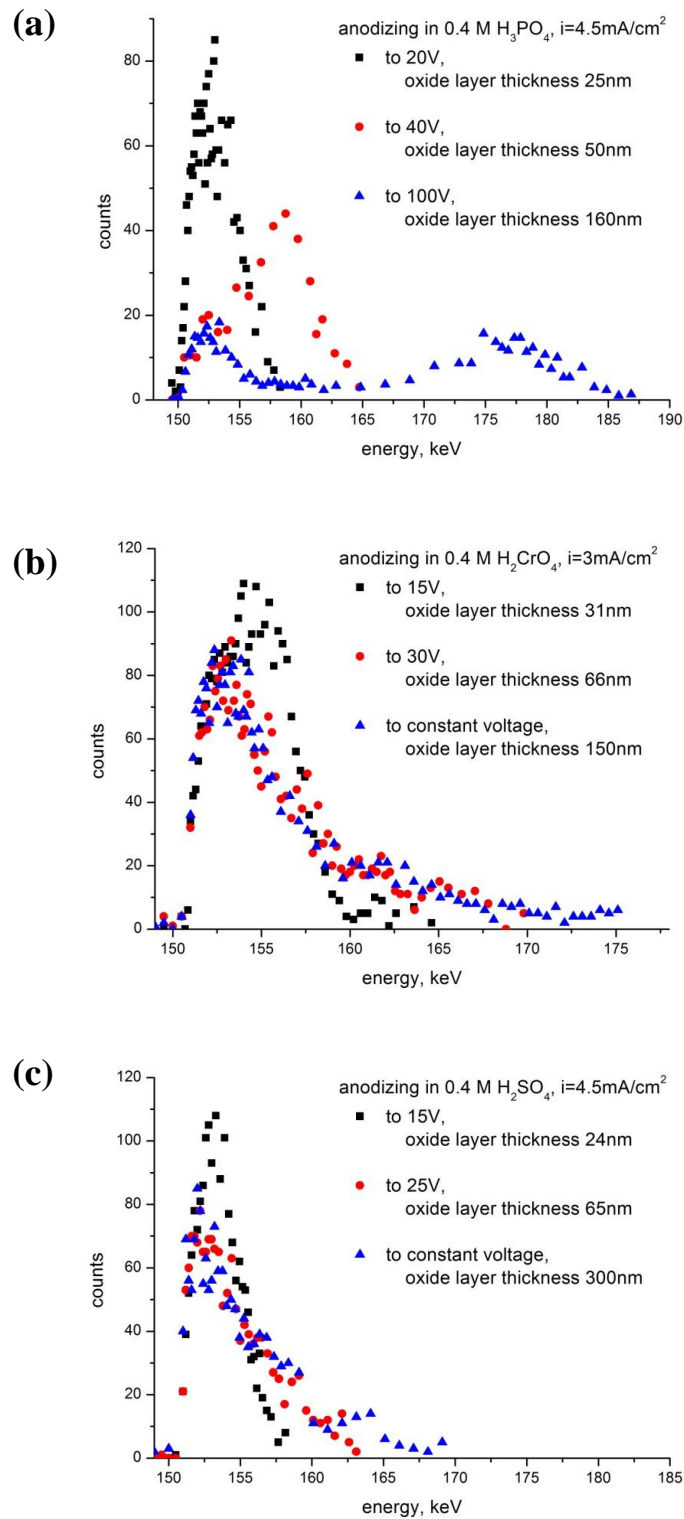


Fig.2. E excitation curves, determined using the resonance at 151 keV of the $^{18}O(p,\alpha)^{15}N$ reaction, for specimens (a) anodizing in phosphoric acid, (b) chromic acid, and (c) sulphuric acid.