Nanostructuring of Aluminium and Synthesis of Porous Aluminium Membranes by Anodising

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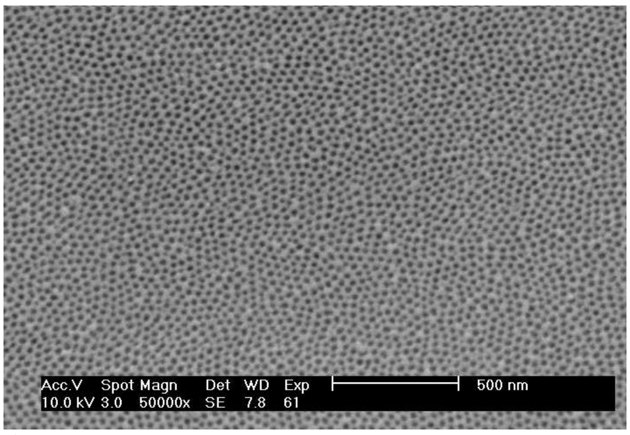
Recently controlled anodization of aluminium in aqueous acids was applied to achieve of a nm-scale porous structure with closed packed cells. Hexagonal patterns with extended long-range order was obtained by cycles of anodization and successive removal of the porous oxide (multi-step anodising process).

Nanostructures were produced on industrial aluminium foils by one-, two-, or three-step anodising in sulphuric acid at cell potentials between 15 and 25 V. A well-ordered hexagonal structure was obtained by a two-step anodising process (Fig.1a).. A high-density array of pores with a controlled pore diameter, inter-pore distance, and depth of pores was obtained. Some defects in the hexagonal arrangement of pores are noticeable at the boundaries between domains. The Fourier transform of SEM images of alumina layers as well as defects maps known as Delaunay triangulations [1] showed that for the two-step procedure ordering degree is independent of the cell potential [2]. Recently two-step anodising at 10 V was performed and resulted too in relatively well-ordered nanostructure at the top as well as at the bottom of anodic porous alumina layer. The pore diameter and the inter-pore distance after a second anodising step at different cell potentials vary in the range of 13 to 33 and 29 to 69 nm respectively. The dependencies vs. cell potential are linear and in very good agreement with literature data. No broadening effect of the pores with increasing length of pores was observed. Ordered porous alumina layers obtained after anodising in sulphuric acid, exhibit nanohole arrays with finer dimensions than those obtained in oxalic or phosphoric acid solutions.

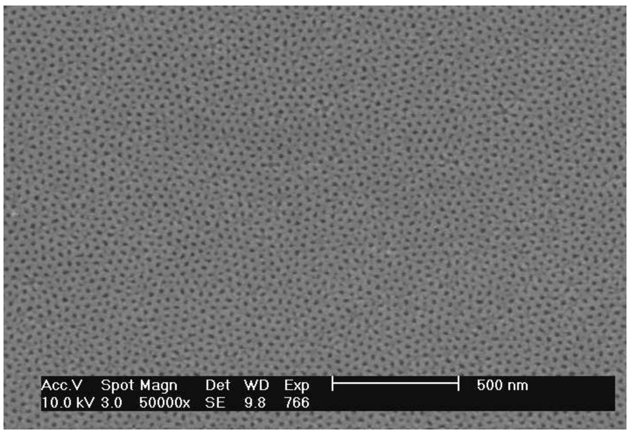
Fine membranes with a controlled size of pores and a high aspect ratio were manufactured by a two-step anodising of aluminium in sulphuric acid (Fig.1b). The bottoms of pores are also hexagonally arranged in the µm-size domains. The opening pore procedure results in showing defects up in the ordered structure. The aspect ratio of membranes formed at the cell potential of 23 and 15 V can be more than 3 800 and 6 700 respectively.

The channel structure of holes was observed by transmitting a He^+ ion beam vertically through the membrane. The dissipation of the beam after the membrane transmission was analysed (Fig.2). The relatively narrow high peak obtained confirmed that channels grow parallelly during anodization.

Effective growth rates of the oxide layer at different cell potentials were calculated from SEM taken on samples treated by two-step anodising procedures. The effective growth rate of the oxide layer on anodised aluminium achieved in our experimental conditions at 23 V, decrease exponentially with increasing anodising time. For the case of an anodising potential of 15 V, the dependence is linear. The evolution of growth rates with anodising time during a second step of anodization at a given cell potential is similar to the variation of current density with time.



a)Top view



b) Bottom view of membrane

Fig. 1 SEM images of porous alumina layer formed at 15 V by a two-step anodising in 20 wt % H_2SO_4 at 1°C. The duration of the first and second anodising step was 10 and 1 240 min, respectively. The pore opening time was 25 min.

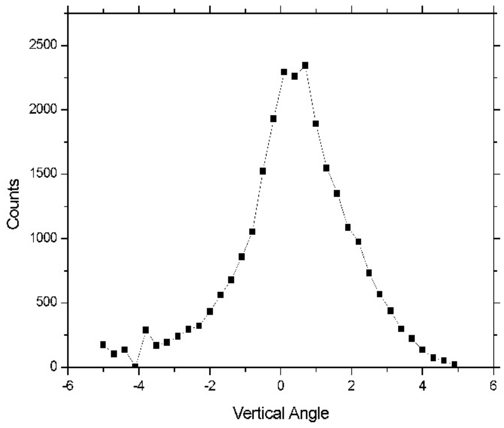


Fig. 2 Dissipation diagram of He^+ beam after transmission through sample anodised at 15 V. The thickness of membrane was about 28 µm.

[1] D.J. Bishop, P.L. Gammel, Ch.A Murray, in *The Vortex State*, N. Bontemps, Y. Bruynseraede, G. Deutshcer, A. Kapitulnik, Editors, Series C: Mathematical and Physical Sciences, Vol. 438, pp. 99 – 123, Kluwer, Dordrecht (1994).

[2] G.D. Sulka, S. Stroobants, V. Moshchalkov, G. Borghs, J-P. Celis, J. Electrochem. Soc., **149**(7), D97, (2002).