ESRF	**Experiment title:** Structural and phase transitions of anodic alumina at high temperatures	**Experiment number**: MA-2696
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Shifts: 12	**Local contact(s)**: Carlotta Giacobbe	*Received at ESRF:*

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Diffraction experiments were carried out on four series of anodic aluminas, prepared by anodization of high purity aluminium in different acid electrolytes (0.3 M $H_2C_2O_4$, 0.3 M H_2SO_4 and 0.1 M H_3PO_4). To check phase formation during annealing, a set of pre-annealed specimens was measured, and a number of *in situ* experiments were conducted. For comparison, total scattering data were also collected for several chemically synthesized aluminas of various polymorphs.

It turned out that, no matter of acid used, all as-prepared anodic aluminas are amorphous (Fig. 1, left panel). All observed distances are in good agreement with those reported in literature [1], and are, namely Al-O bond in AlO_4 tetrahedra (1.82 Å), O-O bond along AlO_4 tetrahedra (2.95 Å), Al-Al bond from corner-sharing tetrahedra (3.21 Å). Distances of 4.17 and 4.49 Å correspond, either to third coordination sphere, or to inclusion of foreign atoms, as sulfur or phosphorous, into the amorphous structure.

The structure of oxides after annealing slightly above crystallization temperature, as determined by preliminary TGA/DSC measurements, was examined (Fig. 1, right panel). On a local scale, all crystallized anodic oxides are spinel-type γ-Al_2O_3. The difference in peaks intensities, starting from 10 Å, is caused by a different size of diffracting domains.

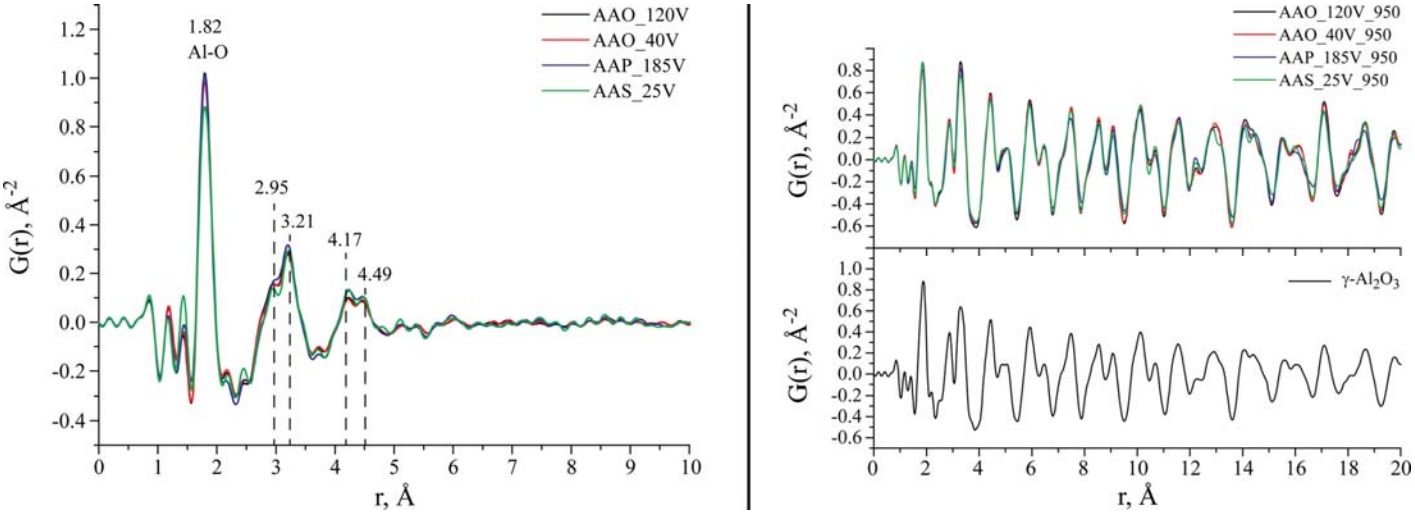

Fig. 1. PDFs of amorphous aluminas, prepared under different anodization conditions (left panel) and PDFs of the same aluminas after crystallization at 950 ºC (right panel, top) compared to PDF of chemically synthesized γ-Al_2O_3 (right panel, bottom). Anodic alumina prepared in phosphoric acid at 185 V is marked as AAP_185V, in sulfuric acid at 25 V as AAS_25V, in oxalic acid at 40 and 120 V as AAO_40V and AAO_120V, respectively.

Aluminas crystallization pathways were studied in a set of *in situ* experiments during isothermal annealing at 950 °C. An example for one of the samples, AAO_120V, is given in Fig. 2. Despite of multiple possibilities of low-temperature polymorph intermediates formation [2], no such phases were observed – all aluminas crystallized into spinel-type structure.

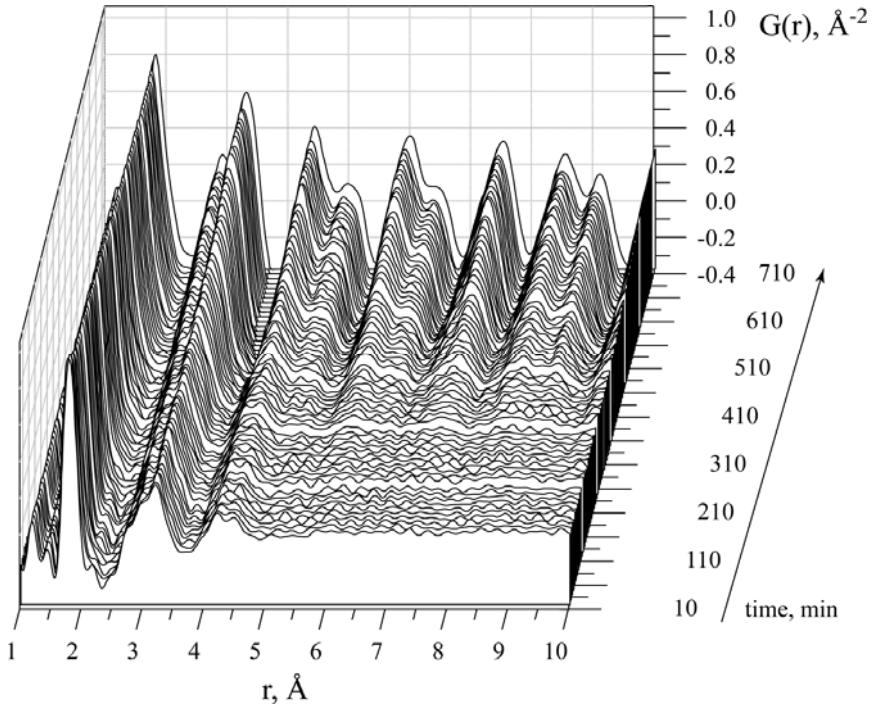

Fig. 2. A set of PDFs taken *in situ* for AAO_120V during isothermal annealing at 950 °C.

The high-temperature *in situ* experiments in mirror furnace were cancelled due to extremely intense and non-uniform contribution from platinum capillary, which was much stronger than the signal from alumina samples and does not allowed for correct substraction of its contribution during patterns normalization.

Finally we would like to thank Carlotta Giacobbe for her excellent support during the experiment.

References:

1. R. Kniep, P. Lamparter, S. Steeb, Structure of anodic oxide coatings on aluminum, Angew. Chem. Int. Ed. 28(7) (1989) 951.
2. G. Busca, Structural, surface, and catalytic properties of aluminas, in Advances in catalysis (F. Jentoft, Ed.), V. 57, Ch. 3, Amsterdam: Academic Press, 2014.