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High-temperature stabilization of bulk amorphous Al_2O_3

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ABSTRACT

We present a method for high temperature stabilization of bulk amorphous aluminium oxide. The stabilization is achieved by dispersing polysilane dendritic molecules in aluminium hydroxide gel, which upon thermal treatment gives amorphous aluminium oxide stable up to 900 °C. The dispersed macromolecules covalently bind to the alumina matrix and induce homogeneously distributed strain fields that keep the alumina amorphous. The thermal conversion of the precursor system was followed by thermogravimetry with an evolved gas analysis, infrared spectroscopy and ^{29}Si NMR. The amorphous structure of aluminium oxide was confirmed with an X-ray and electron diffraction. Additionally, the amorphous state was supported by presence of penta-coordinated aluminium detected by ^{27}Al NMR and a low bandgap measured by a UV–visible absorption spectroscopy.

1. Introduction

In contrast with a variety of aluminium oxide crystalline polymorphs, an amorphous form possesses some special properties, originating from the non-crystalline nature. The structural disorder contributes to a much lower band gap [1, 2], photoluminescence [3–5], ferromagnetism [6] and higher thermal conductivity [7]. A lot of attention has been given to the amorphous aluminium oxide (am-Al_2O_3) for coating applications. The uniform amorphous matrix contributes to the excellent mechanical and optical properties. Although hardness of the amorphous material is lower than that of the polycrystalline alumina, a wear resistance is extremely high [8–12]. The amorphous coatings experience an adhesive failure. Above the critical load, buckling of the material at an edge of deformation occurs. In contrast, the nanocrystalline coatings experience a cohesive failure that results in a plastic deformation already at much lower load. An absence of voids and crystallite boundaries makes am-Al_2O_3 transparent in the visible light range [12–16]. In addition, with a refractive index similar to glass [17–19] it is perfect for glass coatings. In contrast with the hydrophilic polycrystalline alumina, the amorphous form is hydrophobic (contact angle > 100°) [8] making it a great catalyst support for anti-fouling and self-cleaning applications. It has been used as a gate insulator in transistors [20, 21], for corrosion protection [8, 22–24], enhancement of a thermal conductivity of nanofluids [7, 25], as a catalyst for biodiesel conversion [26] and for fluoride removal [27].

All the above-mentioned properties and applications are limited by the am-Al_2O_3 thermodynamic stability, which is preserved only till the onset of crystallization at temperatures as low as 400 °C [28]. The amorphous structure can be stabilized by introducing an additional disorder in its structure. Tavakoli et al. [29] demonstrated that, compared with α- and γ- crystalline polymorphs, a lower surface energy of am-Al_2O_3 nanoparticles with a size under 6.5 nm prevails over crystallization enthalpy and thus helps stabilizing the amorphous state. In the case of an interface between a metal and aluminium oxide the interface energy for am-Al_2O_3 is lower than for the crystalline state. For this reason, am-Al_2O_3 thin films remain amorphous up to 7 nm thickness, depending on crystallographic face of aluminium metal [30]. In some cases, the structural disorder can be introduced by doping (e.g. with P^{5+} [31], Y^{3+} [26, 32], Er^{3+} [33], La^{3+} [34], Si^{4+} [35], Fe^{3+} [36] or Cr^{3+} [33, 36]).

Based on the described mechanism for the stabilization of the amorphous alumina state, it is clear why am-Al_2O_3 was successfully synthesized only in a thin film or nanoparticle form, mainly by PVD (physical vapour deposition) [37] and CVD (chemical vapour deposition) or by electrochemical aluminium oxidation [3–5]. It is worth noticing that the films prepared from a gas phase are usually AlOOH up to 420 °C and crystallize above 650 °C [15, 38–40]. More convenient up-scalable techniques, as for example sol-gel methods, have been considered but have remained limited to nanoparticles production [14, 41–43].

Here we present a first method for high-temperature stabilization of bulk am-Al_2O_3. We show that a molecular dispersion of polysilane (PS)

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macromolecules in am-Al_2O_3 can stabilize it up to 900 °C. A similar technique has already been applied by our group for wear resistant glass coatings [12] but we have now extended it to the bulk.

2. Experimental

A precursor solution was synthesized by an electrochemical method that was in details described in Ref. [44]. Shortly, an electrochemical cell consisted of two Al electrodes. A mixture of acetonitrile (J.T. Baker, Phillipsburg, NJ) and anhydrous $AlCl_3$ (Acros Organics, Geel, Belgium) was used as an electrolyte. Methyltrichlorosilane (Alfa Aesar, Karlsruhe, Germany) monomer was reduced at the electrode with a constant current of 0.5 A. After the electrolysis the acetonitrile solvent was changed for tetrahydrofuran (THF) (Aldrich, Steinheim, Germany). Polymethylchlorosilane was reduced by the addition of $LiAlH_4$ (Aldrich, Steinheim, Germany) to give dendritic polymethylsilane (PS, characterized in Ref. [44]). We were using two different amounts of anhydrous $AlCl_3$ that served as an electrolyte and a source of aluminium, to give a final $AlCl_3$:PS ratio of 6:1 and 2:1 (abbreviated as AlO-LO and AlO-HI, respectively). The resulting mixture was hydrolysed by slow addition of 50 mL of deionised water and dried under vacuum to give an orange-brown pastes. The pastes were heat treated at 300 °C for 2 h in air to obtain the brown powders. At this point the powders were repeatedly washed with deionised water to remove chloride; the presence of chloride in wash water was monitored with 0.01 M $AgNO_3$. The washed powders were heat treated at 400, 500, 600, 700, 800, 900, 1000, 1100 and 1500 °C.

A thermal analysis was performed on a TGA/DSC 2 (Mettler Toledo) thermal analyser coupled with a mass spectrometer Thermostar300 (Vacuum Pfeifer) for an evolved gas analysis. The samples were heated from 40 °C to 300 °C at 2 °C/min and then again from 40 °C to 1200 °C at 10 °C/min in static air atmosphere. The reported curves are buoyancy corrected. Furrier-transform infrared spectroscopy (FTIR) measurements were performed on a Perkin Elmer Spectrum 100 spectrometer with a PIKE Gladi attenuated total reflectance (ATR) module from 400 to 4000 cm^{-1}.

^{27}Al and ^{29}Si MAS NMR (magic-angle spinning nuclear magnetic resonance) spectra were recorded on a 600 MHz Varian NMR system equipped with a 3.2 mm Varian HX MAS probe. Larmor frequencies for the ^{27}Al and ^{29}Si nuclei were 156.21 and 119.11 MHz, respectively. For the ^{27}Al MAS experiments the samples were rotated at 20 kHz, a 20° excitation pulse with duration of 0.8 μs was employed, repetition delay was 1 s, and number of scans 2000. For the ^{29}Si MAS experiments the samples were rotated at 16 kHz, a 90° excitation pulse with duration of 2.8 μs was employed, repetition delay was 60 s, and number of scans 2800. The ^{27}Al frequency axis was referenced to a signal of 1 M solution of $AlCl_3$ in water and ^{29}Si frequency axis was referenced to a signal of tetramethylsilane. Decomposition of ^{27}Al spectra into individual contributions was carried out using DMFIT [45].

X-ray diffraction (XRD) analyses of the resulting powders were taken by a Rigaku Mini Flex 600 with a D/teX Ultra detector and CuKα (1.54059 Å) source from 10° to 90° (2θ), with a speed of 10°/min. The morphology was studied with scanning electron microscope (SEM) JEOL JSM 7001 at 5 kV. The powders were dispersed on a carbon tape and coated with 8–10 nm of carbon using a precision etching coating system (Model 682, Gatan). The morphology and crystallographic state were studied with a transmission electron microscope (TEM) JEOL JEM 2100F) at 200 and 100 keV in TEM and scanning transmission electron microscopy (STEM) mode with spot size 0.7 nm. For TEM observations, the nanocomposite powders were mechanically ground, dispersed in ethanol and deposited on a lacy C-coated Cu TEM grids (SPI, West Chester, PA). The observations were done on thinner parts of the particles deposited on the grid. Alternatively, the powders were mixed with epoxy resin. The cross-section of the particles was prepared by means of a standard mechanical sample preparation process and finalized by Ar^+ ion-milling and polishing (PIPS, GATAN) at grazing incidence (< 5°).

Diffuse reflectance measurements were performed on a Perkin Elmer Lambda 650S UV–Visible spectrometer equipped with an Integration sphere, in a range from 800 to 190 nm in comparison with Spectralon standard. The UV–visible absorbance spectra and the band gap energy were calculated by the Kubelka-Munk function.

3. Results and discussion

Hydration of aluminium chloride to yield sol-gel of aluminium hydroxides is a known low-temperature method for the synthesis of crystalline aluminium oxide in a bulk [28, 46] or thin film form [47]. The crystallization of α-Al_2O_3 can start at a temperature as low as 400 °C [28]. The low temperature crystallization is attributed to a compact structure of the concentrated sol that contains polycations as chains, layers, or tridimensional structures with edge-sheering AlO_6 octahedra [48]. Our system of hydrated aluminium chloride with dispersed polysilane molecules (with a diameter ~40 nm [44, 49]) after heat treatment yields bulk am-Al_2O_3 matrix that does not crystallize upon heating up to 900 °C. We confirmed this with an XRD analysis, TEM imaging and electron diffraction.

3.1. Formation studies

To follow formation of the stabilized am-Al_2O_3 from the synthesized gel we used thermogravimetry coupled with mass spectroscopy (TG-MS). During heating to 300 °C around 70% of mass is lost (Fig. 1a). Excess water is lost up to 120 °C. At around 130 °C, water (m/z = 17) and HCl (36,38) are lost. This can be attributed to hydroxylation reactions that are well studied [50]. The hydroxylation is accompanied with evolution of short silane oligomers (41,43), siloxane (73) fragments, THF (42) and CO_2 (44). At 250 °C another step can be observed. It is accompanied with an increase in silane fragments intensity showing on an onset of PS degradation. This step is accompanied with CO_2 evolution, showing that organic groups from the polymer are oxidised. THF (42) that was trapped into the polymer structure during the synthesis is also evolved. The difference between AlO-HI and AlO-LO is not in their degradation behaviour but in the mass loss. For AlO-HI the mass loss in hydroxylation step (140–200 °C) is much smaller than in polymer degradation step (above 250 °C) as a result of different ratio between alumina and polysilane. The samples continue to decompose on heating up to 1200 °C (Fig. 1b). Another 35% of mass is lost, giving approximately 20% overall yield. During this process some HCl is released and Al_2O_3 formed. CO_2 is present, which indicates on partial burning of the polymer to SiO_2 and CO_2. Above 600 °C HCl and silane fragments are not detected anymore. The mass loss slightly continues with the loss of methane (15) showing on the polymer degradation.

The PS degradation can be better understood from ^{29}Si MAS NMR spectra (Fig. 2). The samples after heat treatment in air at 600 °C show two resonances, one at −111 ppm and another at −82 ppm, corresponding to amorphous SiO_2 and Si in a local environment similar to mullite, respectively [51]. The mullite-like structures indicate on formation of an interface between the dispersed PS and am-Al_2O_3 matrix. With further heating at 900 °C the resonance for SiO_2 starts to vanish while the resonance for Si bonded to Al becomes more dominant showing on diffusion reaction between SiO_2 and Al_2O_3.

The FTIR spectra of AlO-HI, heat treated in air, give further important information on chemistry of this system (Fig. 3). PS is identified by vibrations of Si-CH_3 bond and CH_3 group at 1270 and 2971 cm^{-1}, respectively. An intensity of these vibrations diminishes from 300 °C to 500 °C and disappears at 600 °C. Si—H bond is identified at 300 °C with a few peaks between 2200 and 2000 cm^{-1}. These vibrations disappear at 400 °C as the Si—H bond is the first to thermally dissociate in PS. The hydration resulted in the presence of water (3600–2500 cm^{-1} and ~1640 cm^{-1}) and –OH groups on Al (~1110 cm^{-1}) and Si