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Effect of atomic layer deposited aluminium oxide on mechanical properties of porous silicon carbide

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Abstract

Silicon carbide nanopowder was coated with amorphous alumina by atomic layer deposition (ALD), using trimethylaluminium $Al(CH_3)_3$ (TMA) and water as precursors. The ALD experiments were carried out at 300 °C, using variable cycle count or changing pulse times at constant cycle count. Depending on deposition conditions, hardness averaging at 14.8 GPa and corresponding reduced elastic modulus of 114 GPa were measured. Maximum hardness values and reduced moduli of elasticity reached 25–30 and 134–202 GPa, respectively, improving the mechanical properties of composites. Increased precursor flow had positive effect on mechanical properties – maximum values of hardness and elastic module reached 35–45 and 218–261 GPa, respectively. In the composites, the mechanical properties were improved compared to pure alumina films or silicon carbide and the brittleness characteristic of SiC particle tablets was decreased.

Keywords: Nanocomposite; Nanoindentation; Atomic layer deposition

1. Introduction

Nowadays ceramic materials find a wide range of applications in all industrial areas. Multi-structured ceramic based composites and hybrids offer an unprecedented potential to realize functionalities well beyond the limits of the well-known "classical" materials. Mixing the components is the usual method for producing multicomponent composites. However, the composites for specific applications require a precise control of the amount and distribution of the constituents, which could be achieved by using different methods such as chemical vapour deposition [1], physical vapour deposition [1,2] and atomic layer deposition (ALD) [3,4].

ALD is a chemical deposition method based on saturated surface reactions. The unique feature of ALD is the subsequent pulsing of precursor vapours (elements or compounds) onto the substrate, one at a time. Between reactant pulses the reactor is purged with an inert gas. Suitable adjustment of the conditions, *i.e.* substrate temperature, reactant doses and lengths of pulse and purge sequences, a (sub-) monolayer of the first reactant will be chemisorbed and retained on the substrate after the purge sequence. This chemisorbed monolayer reacts subsequently with the other precursor dosed onto the substrate resulting in a solid film and volatile by-products. By repeating the deposition cycle the film will grow layer-by-layer. The film thickness is, nevertheless, only a function of the number of deposition cycles repeated. As a result, the growth is said to be self-controlled or self-limited [5,6]. Besides low growth temperature, other major advantages of ALD are precise film thickness control, uniformity and conformity of the deposited layer over irregular substrates [7].

Aluminium oxide (Al_2O_3) is one of the most widely used ceramic materials with significant technological importance for several applications, because of combination of high melting point, chemical stability and good mechanical properties [8]. Silicon carbide is one of the hardest materials known [9] and both alumina and silicon carbide can thus be used due to their hardness [10–13].

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ALD of aluminium oxide from trimethylaluminium (TMA) and water has been intensively studied [14]. The process is also suited for mechanical reinforcement of, for example, polymeric 3D cellular structures [15] and can be applied for the treatment of powders [16,17]. ALD can preliminarily be conducted at lower temperatures compared to those usually needed for sintering of ceramics [18] and may result in the production of conformal crystalline or amorphous thin films [19]. So far ALD of alumina has mainly been used for electronic applications to deposit insulating layers [20–22]. In addition, drill bits hard facing material has been deposited using ALD [23].

The aim of the present work was to evaluate the effect of ALD alumina carried out on SiC nanoparticles compacted to a porous tablet, to address the effect of cycle length and count of film deposition to mechanical properties of resultant composite structure. The work reports the results of investigations on penetration depth of ALD films in porous substrate and its primary influence on the hardness and modulus of elasticity of the formed composite material.

2. Materials and methods

2.1. Materials

The SiC nanopowder was produced by induction plasma synthesis as described by Leparoux et al. [24], possessing mostly spherically shaped particles with average size between 30 and 40 nm. SiC powder amounting to 0.01–0.03 g was used to form green bodies with dimensions 11 mm in diameter and 50–250 μm in thickness. A hydraulic press was used to compress the powder in a die up to 170 MPa. Other treatments (*e.g.* sintering) were not applied. The tablet samples were placed in an aluminium object holder with rabbets on their edges, so that the ALD precursors could adsorb and diffuse into the tablets from both sides (Fig. 1).

2.2. Atomic layer deposition process

Trimethylaluminium (Strem Chemicals, 98%) and distilled water were used as ALD precursors. The deposition of amorphous alumina was carried out in a flow-type in-house built hot-wall ALD reactor [25] onto SiC green bodies and, complementarily, on two-dimensional reference Si pieces cut out of a silicon wafer. The temperature in the reaction chamber was held at 300 ± 6 °C.

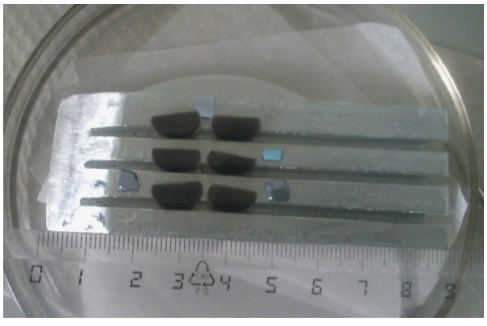

Fig. 1. Pieces of silicon wafer and SiC samples (tablets) in holder rabbets prepared for ALD.

Nitrogen was used as a carrier gas while the reactor pressure was around 250 Pa.

It should be considered that the SiC tablets were porous in the beginning of the ALD process and it takes time for precursors to diffuse into the tablets. Precursor diffusion, and thus also the film deposition depth, are, expectedly, limited by the exposure time of the tablets to the precursor flow, *i.e.* by the pulse length. Precursor pulse lengths varied from 2 s up to 20 s.

In order to conveniently follow the possible development of thickness profile along the gas flow direction, pieces of silicon reference wafers Si(100) were placed in front, back and mid, related to the sample, along the substrate length. That also allowed the verification of the correlation between separate experiments.

2.3. Characterization

Crystallographic structure of the samples was examined by X-ray measurements, performed at room temperature on a X-ray diffractometer SmartLab (Rigaku™) using CuKα radiation from a 9 kW rotating anode.

Uncoated powder compacts were vizualized with atomic force microscope (AFM) in tapping mode (Park Scientific Instruments) using silicon tip. Image editing was done using Gwyddion 2.38.

Plan-view and cross-sectional scanning electron microscopy (SEM) images of films grown on 3D substrates were obtained from selected samples using Dual Beam® equipment Helios Nanolab 600 with focused ion beam cutting capability (FEI Company). SEM was also used to determine the particle size and in combination with energy dispersive X-ray spectroscopy (EDX) to study the elemental composition.

Spectroscopic ellipsometer (Semilab Sopra GES-5E) was used to measure the film thickness, using 365 and 633 nm wavelengths at an angle of 75° on Si reference substrates. The fitting was performed using Cauchy approximation [26].

Nanoindentation measurements [27,28] were conducted with a NanoTest (Micro Materials Ltd) testing system. The tests were load-controlled and conducted at room temperature using a triboscope nanoindenter system with diamond Berkovich tip. The calibration range covered indentation depths up to 320 nm. The instrument was calibrated by using a standard fused silica sample (hardness 8 GPa, elastic modulus 72 GPa) prior to measuring the mechanical properties of the material. The drift rate was pre-set to 2.5 nN/s before the beginning of each indentation test. Thermal drift data collection time was 30 s and dwell period at maximum load was 10 s. Indentation count was set to 20. Results were calculated by 2nd order polynomial function, using data from unloading curves maximum value down to 20% of that. The fit mean square errors were below 4% in all separate measurements.

3. Results and discussion

3.1. Atomic force microscopy of a compact body

Atomic force microscopy (AFM) was used to characterize the green-body surfaces, in order to evaluate the morphology and