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Chemical stability of carbon-based inorganic materials for *in situ* x-ray investigations of ammonothermal crystal growth of nitrides

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ABSTRACT

The chemical stability of diamond, silicon carbide, vitreous carbon, and boron carbide in supercritical ammonia containing different mineralizers was investigated. The materials were found to show good corrosion resistance in the presence of selective or all tested mineralizers.

Diamond was found to be virtually inert in both ammonoacidic and ammonobasic reaction media.

Silicon carbide showed good chemical stability in varying ammonothermal reaction media.

The chemical stability of vitreous carbon was found to depend on its manufacturing temperature.

Corrosion of boron carbide strongly depends on the mineralizer used as well as on applied mechanical stress.

Based on their chemical stability and mechanical properties, the applicability of the materials in the respective ammonothermal reaction media as construction materials is evaluated. Additionally, the applicability of the materials as a window material for both high energy *in situ* x-ray imaging and low energy *in situ* x-ray diffraction is discussed.

1. Introduction

Ammonothermal synthesis is a promising technological approach for the growth of nitrides such as GaN [1,2] in excellent crystalline quality [3–5] as well as for the synthesis of novel nitrides and related materials [1,6]. In ammonothermal crystal growth research, direct insight into ammonothermal high-pressure autoclaves is very desirable but rarely available due to the challenging process conditions such as high pressure and high temperature. In addition, supercritical ammonia containing mineralizers is a reaction medium that is very corrosive to most suitable construction materials [7]. Recently, sapphire has been applied successfully as a window material for *in situ* x-ray imaging of nitrides under ammonothermal conditions using high energy x-rays [8]. The chemical stability of some ceramic materials has previously been investigated, including their applicability as liner material (in combination with sapphire windows) in high energy *in situ* x-ray imaging [9]. However, penetrating these ceramics (*e.g.* Si_3N_4) with x-rays requires rather high photon energy (*e.g.* 100 keV). In order to extend the possibilities of *in situ* x-ray measurements towards studies of the evolution of crystal quality during growth, applying lower energy x-rays (using *e.g.* Mo or Ag anode, about 20 keV) is necessary for achieving high angular resolution in diffraction experiments. Thus, a window material with lower absorption for low energy x-rays is required.

In this work, we investigate the chemical stability of materials with low x-ray absorption that enable high resolution *in situ* x-ray diffraction using low photon energy. Carbon-based inorganic materials are promising candidates as they may combine good chemical stability under ammonothermal conditions with good mechanical stability as well as low x-ray absorption. Therefore, the chemical stability of diamond, silicon carbide, vitreous carbon, and boron carbide in ammonothermal reaction media are evaluated and the applicability of the investigated materials in the respective ammonothermal reaction media is discussed.

2. Materials and methods

2.1. Selection of investigated materials

For the application as a construction material in high pressure

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vessels, sufficient mechanical properties are required and need to be maintained at operating conditions. The investigated materials represent potential construction or coating materials consisting of the lightest elements possible in order to minimize the absorption especially of low energy x-rays. Mass attenuation coefficients of the respective elements and compounds are depicted in Fig. 1. The photon energy of low energy x-rays of a Mo and a Ag x-ray tube are marked in the graph, as well as the photon energy of tungsten Kα1 which corresponds approximately to the average photon energy in previous experiments using sapphire windows and white light W x-ray tube for imaging (for details see [8,9]).

The transmission in the application is not only determined by the mass attenuation coefficients but also by the density of the respective material and the window thickness required to withstand the mechanical stress (typically 5–12 mm). Calculated data for the x-ray transmission for application in an autoclave for pressures up to 300 MPa (optical cell as used in [8]) are given in Fig. 2. According to the calculation, vitreous carbon and boron carbide provide substantially better transmission, especially of low energy x-rays, compared to the conventional sapphire windows or silicon carbide bulk material. The transmission for diamond is not calculated since the material is not available in sufficient thickness to be applied as bulk window material. Nevertheless, it is promising as a coating material. Silicon carbide is also investigated rather as a coating material since it does not provide sufficient transmission if applied as bulk construction material. However, it may be applicable as bulk material if low energy x-ray transmission is not needed, *e.g.* as liner or crucible material.

Vitreous carbon [11] has the lowest x-ray absorption of all investigated potential construction materials. In addition, it is a promising window material for diffraction studies since the material does not exhibit a crystalline structure and therefore does not contribute to the diffraction signal. The material is known to have good corrosion resistance towards various acids including hydrofluoric acid [12] as well as oxidation resistance up to about 600 °C according to the manufacturer. The latter is especially relevant to the window outside which is exposed to ambient air.

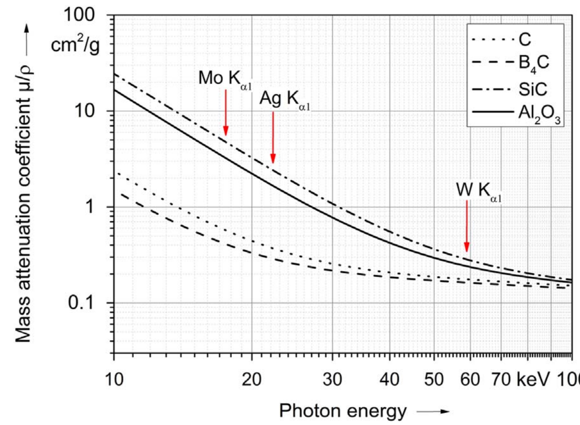

Fig. 1. Calculated mass attenuation coefficients of investigated materials according to NIST database [10].

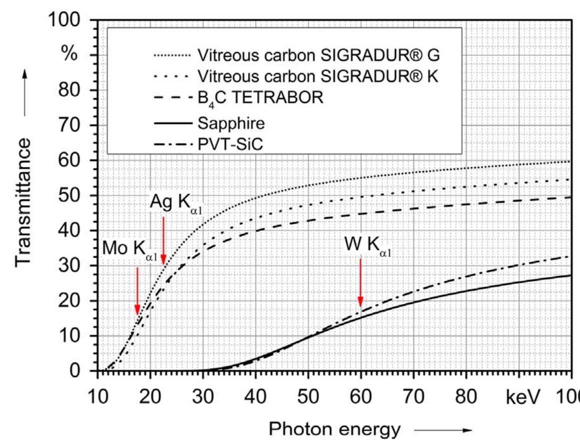

Fig. 2. Calculated transmission of window materials in application in optical cell for ammonothermal experiments up to 300 MPa.

2.2. Corrosion experiments

Experiments were carried out in custom made ammonothermal reactors made of alloy 718. The reactors were unlined, unless otherwise stated. Head parts such as fittings, tubes or rupture disk made of stainless steel (e. g. 1.4571 or 1.4435) were used (SITEC-Sieber Engineering AG, Switzerland). For corrosion tests without mechanical stress, the samples were exposed simultaneously to ammonia (Linde, 99.999%) with different mineralizers as additives. Corrosion interactions of the co-loaded samples were neglected as a working hypothesis. Ammonium chloride (Sigma-Aldrich, 99.99% based on trace metals basis), ammonium fluoride (Sigma-Aldrich, 98.0%, ACS reagent) or NaN_3 (Carl Roth GmbH +Co KG, 99.0% p.a.) were added in a molar amount of about 40.5 mmol. The mineralizer was placed in a small crucible made of alloy 718 at the bottom of the autoclave. The samples were prevented from lying directly on top of each other using Inconel wires to ensure free access of the reaction medium to all sample surfaces. All samples (for details see Table 1) were placed in the bottom part of the autoclave in order to minimize deviation of temperature between different samples. After the autoclave was closed, it was evacuated and purged with nitrogen three times to remove oxygen originating from loading at air. Finally, the autoclave was filled with ammonia to reach the respective fill level for obtaining varying supercritical conditions. The autoclave was heated using a custom made heating sleeve (Winkler GmbH) to the desired final temperature for the respective reaction time. The pressure was monitored using a pressure transmitter (P2VA1, Hottinger Baldwin Messtechnik GmbH). After the desired reaction time, the autoclave was cooled down to room temperature, ammonia was released and the autoclave was purged with nitrogen and evacuated three times to remove ammonia. The samples were cleaned with distilled water using an ultrasonic cleaner.

Between the ammonoacidic and ammonobasic series of experiments, possible contamination of the autoclave was minimized by a one day run with pure ammonia at 176 MPa and 500 °C. The full amount of mineralizer used in a single experiment is usually completely dissolved during the experiment, thus, its residuals can be assumed to dissolve within one cleaning run as well.

In order to first investigate the general stability in presence of the reaction medium, most experiments were performed without addition of the material to be synthesized in the application. However, any additional material may influence the formation of soluble species and thus may influence the chemical stability of the window material. Thus, selective experiments were performed with pieces of HVPE-grown GaN crystals present in the reaction vessel to ensure transferability to the application in GaN crystallization.

Specific details of experimental data of individual experiments are given in the following tables: Table 2 for experiments with NH_4F as mineralizer, Table 3 for experiments using NH_4Cl mineralizer, and Table 4 for experiments with NaN_3 mineralizer.

In addition to the chemical stability experiments described above, boron carbide samples were mounted as autoclave