



Improving the corrosion resistance of sol-gel-derived aluminoborosilicate glass coatings by nitridation



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ABSTRACT

The resistance to chemical corrosion, in particular, alkali attack, remains a major challenge in the design of oxide glass compositions. Using a sol-gel-derived aluminoborosilicate glass as a model system, here, we report on the effect of thermal nitridation on corrosion of oxide glasses. Nitridation of thin-film glasses is achieved by reactive treatment in a hot ammonia gas flow. Surface chemical analyses reveal the incorporation of nitrogen anions into the glass structure. Due to the increase in bond density, this results in increasing surface hardness of the nitrated region, but also in a significantly reduced corrosion rate for treatment in alkaline solutions. It is found that the improvement in the alkali resistance seems to depend on the silica content of the parent glass due to the preferences of nitrogen for Si–N bonds. As the silicon content is higher (~21 at.%) than in previously studied aluminoborosilicate glasses, a stronger slow-down of the corrosion kinetics upon nitridation is observed.

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1. Introduction

Since the pioneering studies of Elmer and Nordberg in the late 60ies [1], it has been recognized that oxynitride glasses can be prepared – besides direct deposition from nitridic melts – through nitriding of initially nitrogen-free glasses using a hot NH₃ gas flow. Due to kinetic limitations on the underlying diffusion processes this technique seems particularly suitable for porous glasses and thin glass coatings where the surface-to-volume ratio can be maximized. The sol-gel route can readily be employed for preparation of such materials, in a two step process leading to nitridic thin film glasses. In the first step, syntheses may be conducted by the acid or base-catalyzed hydrolysis of tetraethylorthosilicate (TEOS) [2,3], trimethyl borate (TMOB) [4], titanium-isopropoxide (TTIP) [5] and tetra-n-butyl titanate (TBT) [6] in alcohol and suitable complexing agents to form silica-, boron oxide- and titania-bearing xerogels, respectively. In the second step, the oxidic gels are partially nitrided in a hot NH₃ gas flow [2–6]. Other studies similarly reported on the use of liquid ammonia [7] and liquid ammonium hydroxide [4,8] to partly ammonolyze the precursor solution before gelation. The NH₃ gas treatment leads to a nitrogen content of a few atomic percent in compact layers, and of up to 25 wt% in highly-dispersed aerogels [9].

The grand promise of oxynitride glasses are their superior physical properties, in particular, higher glass transition temperature, higher viscosity, higher Young's modulus and higher hardness. Details have been reported in numerous studies [10–13]. In addition the high flexibility in the incorporable amount of nitrogen of up to ca. 70 equivalent percent allows for adjusting desirable glass properties in wide ranges [14–18]. The improvements of the thermal and mechanical properties are understood on the basis of a modified glass structure, resulting from the incorporation of nitrogen atoms. In particular, the substitution of oxygen atoms by nitrogen atoms converts non-bridging sites and generates new bridging sites. The latter reaction, i.e., the exchange of 2-fold coordinated oxygen anions by 3-fold coordinated nitrogen atoms introduces additional bonds into the network structure, which increase the degree of cross-linking [19]. Even through the Si–N bond strength is somewhat lower than that of Si–O, due to the higher bond density, also the local bond energy density increases which contracts and rigidifies the network [11,13,20]. For most glass systems linear relationships between the degree of anion exchange (nitrogen-to-oxygen ratio) and the improvement of mechanical properties have been established [21], at least for low or moderate degrees of anion substitution. In consequence, hardening of glass surfaces by nitridation has been proposed for materials in electronic [22], energy-related [23,24] or transparent armor [25] applications.

In contrast to the mechanical properties the effect of nitriding on the chemical durability has been studied to a much lesser extent. In particular, its variation between different glass systems remains largely

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unexplored. On the other hand, while most of the above noted advantages of nitridation cannot be made use of in real-world applications due to the very low penetration depth of a typical anion exchange process, even very thin layers may prove highly effective for altering the chemical properties of surfaces or, for example, for avoiding subcritical crack growth [26]. In the cases of phosphate and alkali silicate glasses the incorporation of nitrogen into the network increases the acid-, water- and alkali resistance [27–31] while almost no improvement has been seen in nitriding calcium aluminosilicate glasses [28] and magnesium aluminosilicate glasses [32]. Instead, the unusual behavior of the aluminium-bearing silicate glasses led to a transition in corrosion rates with increasing nitrogen content. Thus, nitrided sodium silicate glasses showed a higher alkali resistance than corresponding nitrided calcium aluminosilicate glasses [11]. This observation came as a negative surprise because due to the high relevance of aluminosilicate glasses for a broad variety of specialty applications, where improving the chemical resistance through a comparably simple gas treatment would have been highly desirable.

Against that background, the question arises whether the incorporation of boron oxide into the aluminosilicate glass structure, i.e., an aluminoborosilicate composition would enable the combination of the higher mechanical resistance of aluminosilicate glasses with the higher chemical resistance – induced by nitridation – of silicate glasses. The present study follows this question. The mechano-chemical performance of an aluminoborosilicate glass coating derived from sol-gel and subsequently nitrided in flowing ammonia gas are studied, adopting the molar ratio of the network formers $\text{Al}_2\text{O}_3\cdot\text{B}_2\text{O}_3\cdot\text{SiO}_2 = 2:3:14$ in the parent glass to model commercial aluminoborosilicate glasses, such as Schott AF45 and Corning Eagle.

2. Experimental

2.1. Sol-gel synthesis and preparation of glass coatings

The preparation of aluminoborosilicate glasses by the sol-gel route followed the protocol developed by Dislich [33], which requires three different precursor solutions (Fig. 1). These were prepared from dissolving 4.92 g aluminium-tri-sec-butoxide (ATSB), 2.06 g trimethylborate (TMB) and 2.08 g tetraethoxysilane (TEOS) in isopropyl alcohol (IPA, filled up to 24 g solution each) as aluminium, boron and silicon source, respectively. The ATSB solution was modified with 2.6 g ethyl acetoacetate (EAA) as a chelating agent while 0.4 g water and 0.4 g HNO_3 were used to initiate and catalyze the TEOS hydrolysis. The three solutions were stirred and finally mixed at 20 °C to adjust the molar ratio 2:3:14 for ATSB:TMB:TEOS.

Cleaned silica glass plates (type II, GVB, Herzogenrath, Germany) of size $50 \times 30 \times 1 \text{ mm}^3$ were dipped into the sol and pulled upward using a withdrawal speed of 2 mm s^{-1} . Before dipping, the silica glass plates were cleaned using de-ionised water and acetone. Depending on target thickness, each plate was coated 10–13 times, dried in air for 30 min and cured at 350 °C for 1 h between successive coatings (preheated box furnace lined with silica glass).

2.2. Nitridation

Glasses were nitrided in flowing NH_3 gas at temperatures in the range of 500 to 700 °C for up to 30 h. To meet the safety regulation for handling ammonia gas at elevated temperatures, the set-up was flushed with nitrogen during heating and cooling (5 K min^{-1}) while NH_3 gas was exclusively used for dwelling (flow rate 5 L h^{-1}). Plates of the coated silica glass were mounted on a silica stage in a silica glass lined tube furnace (80 mm diameter and 5 L volume). In order to cover pure thermal effects, control samples were heat-treated in the same time-temperature regime, but using regular air-flow for ramping and dwelling. After gas-flow treatment the glass coatings were X-ray amorphous. Samples were labeled accordingly with a tripartite code which identifies

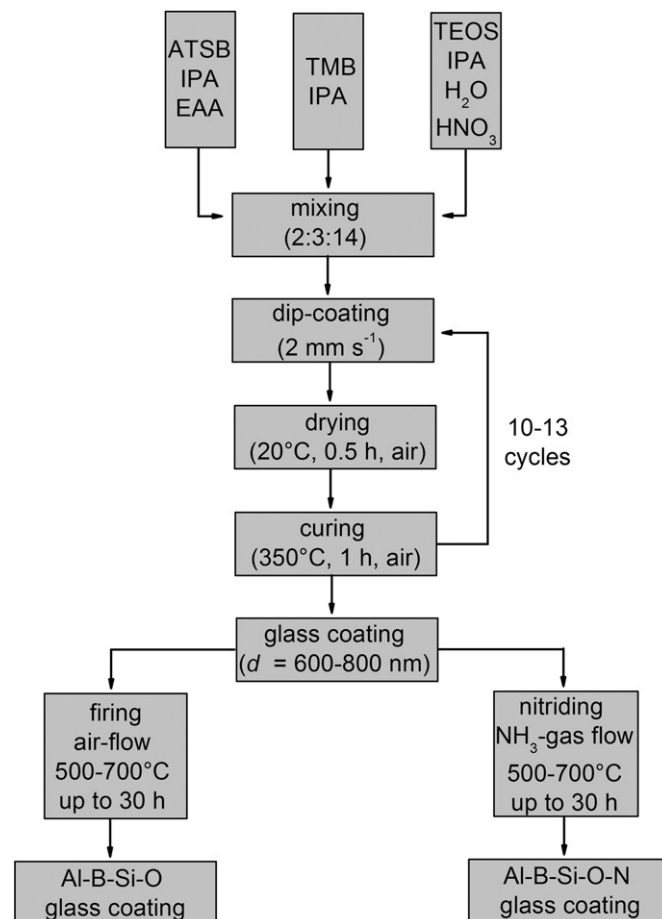


Fig. 1. Flow chart of the preparation of aluminoborosilica oxynitride (Al-B-Si-O-N) glass coatings and nitrogen-free aluminoborosilica oxide (Al-B-Si-O) glass coatings using three different starting solutions as Al_2O_3 , B_2O_3 and SiO_2 sources, respectively.

dwell temperature (in °C), dwell time (in h) and the nature of gas (n = NH_3 , a = air), listed in Table 1.

2.3. Glass composition

X-ray photoelectron spectroscopy (XPS, Omicron NanoSAM, Taunusstein, Germany) was applied as a surface-sensitive quantitative technique to provide evidence for the quantity of nitrogen atoms incorporated into the glass structure. The spectrometer was equipped with a hemispherical energy analyzer using Al $K\alpha$ rays (pass energy = 20 eV). Spectra were scanned with a step-width of 0.2 eV and a dwell time of 2 s. Ratios of atomic fractions were calculated from the XPS data by using a procedure described by Seah [34]. Herein, the area of the XPS peaks is calculated after subtraction of a Shirley type background. The different excitation probability of different atomic levels in this evaluation is considered by applying the concept of atomic sensitivity factors. Quotients of peak areas which have been divided by the sensitivity factors are equal to the ratios of the atomic fractions of these elements.

For analysis of the nitridation depth, an electron-gas secondary neutral mass (SNMS) spectroscope (INA-X Specs, Berlin, Germany) was used. The analyzed area had a diameter of 5 mm and was sputtered using Kr^+ plasma with an energy of 500 eV in a high frequency mode, HF (1000 kHz). Ionization probability factors of standard materials were used to convert intensity signals to atom fractions of each element (mass). The time-dependence of the sputter profiles was converted into depth-dependence by measuring the depth and flatness of the sputtered crater using a white-light interferometer with a vertical resolution of 10 nm (FRT WLI-PL, Bergisch-Gladbach, Germany). For the sol-

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