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# Corrosion of silicon nitride in high temperature alkaline solutions

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ABSTRACT

The corrosion of silicon nitride ($Si_3N_4$) in alkaline solutions was studied at temperatures from 60 to 300 °C. $Si_3N_4$ experienced significant corrosion above 100 °C. The release rates of silicon and nitrogen follow zero order reaction kinetics and increase with increasing temperature. The molar ratio of dissolved silicon and nitrogen species in the high temperature solutions is the same as that in the solid phase (congruent dissolution). The activation energy for silicon and nitrogen release rates is 75 kJ/mol which agrees well with that of silica dissolution. At 300 °C, the release of aluminum is observed and follows first order reaction kinetics while other minor constituents including Ti and Y are highly enriched on the corrosion films due to the low solubility of their oxides.

## 1. Introduction

Cobalt-based alloys such as the Stellites are used for hard facings and ball bearings of fuelling machines in water-cooled nuclear reactors (WCRs) because of their high resistance to wear and galling over a wide range of temperature. Nevertheless, a small amount of cobalt will be released from these alloys by wear and corrosion, and can be transported to the reactor core in the high temperature coolant, where it is adsorbed and neutron activated to $^{60}$Co ($^{59}$Co(n, γ)$^{60}$Co). If released from in-core surfaces, radioactive $^{60}$Co can then be transported to, and deposited on, out-of-core surfaces, which results in increasing radiation exposure to nuclear workers. $^{60}$Co has been a major contributor to external dose in WCR power stations because of its relatively long half-life (5.27 years) and high energy gamma emissions (1.17 and 1.33 MeV) [1]. To reduce $^{60}$Co radiation fields, it is necessary to reduce its source terms. Although cobalt is present as a trace impurity in other alloys (such as carbon steels and stainless steels) of the heat transport system components of WCRs, the cobalt-based alloy Stellite is a major source term for $^{60}$Co, which contributes to radiation fields around piping at nuclear reactors. Reducing the use of Stellite in critical components would therefore reduce radiation protection costs and significantly improve nuclear worker safety.

Silicon nitride has been considered as a candidate material to replace high cobalt-content alloys for some applications in WCRs because of its excellent wear resistance and high fracture strength properties. It has been used in a number of industrial applications such as engine components, bearings and cutting tools [2]. However, before this material can be used in WCRs, an assessment of its corrosion rate and the release rates of its constituents under the relevant water chemistry conditions is required.

The corrosion of silicon nitride has been studied in different media and at a range of temperatures [3–9]. Experimental results [10–13] show that the corrosion rate under hydrothermal conditions can follow different rate laws (e.g. parabolic, linear) depending on the composition and manufacturing process of the silicon nitride. The corrosion rate of silicon nitride increases with increasing temperature and has an activation energy of 74–110 kJ/mol depending on the material processing and the chemical composition of the silicon nitride [12,14,15]. It has been argued that such a high activation energy indicates a chemical reaction on the surface and therefore corrosion of silicon nitride is a chemical reaction controlled process [14,16]. However, as the activity energy is also similar to that of water diffusion in amorphous silica, it was suggested that the corrosion of silicon nitride is controlled by water diffusion into an amorphous silica layer [7,17]. Hence, more experimental and theoretical studies are required to understand the corrosion mechanism of silicon nitride.

Additives can significantly affect the corrosion rate of silicon

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nitride in high temperature aqueous solutions. Typical additives in $Si_3N_4$ are $Al_2O_3$, $Y_2O_5$, $TiO_2$ and MgO, all with concentrations less than 10 wt percent. Experimental results [18,19] show that $Si_3N_4$ with added $Al_2O_3$ and $Y_2O_5$ has the lowest corrosion rate followed by $Si_3N_4$ with added MgO and pure-$Si_3N_4$. The formation of a hydrated yttrium aluminosilicate on the surface of $Si_3N_4$ improves its corrosion resistance compared to the formation of silicon oxide while the formation of a hydrated magnesium silicate on the surface of $Si_3N_4$ imparts much less corrosion resistance, probably due to the lower solubility of yttrium aluminosilicate than that of magnesium silicate. For hot-isostatically-pressed sintered $Si_3N_4$ (HIP–$Si_3N_4$) without additives, no protective layer is formed on the surface and the dissolution is faster than those of $Si_3N_4$ with additives [18].

Most corrosion studies of $Si_3N_4$ have been performed in neutral water and concentrated alkaline and acidic solutions, and the corrosion rates were found to depend on the material processing and composition [5,6,12,16]. Although the overall corrosion rate of silicon nitride has often been reported, the elemental release rates, especially those of additives in silicon nitride, are rarely reported. Moreover, the corrosion behaviour and release kinetics of silicon nitride, and its additives in weakly alkaline solutions under hydrothermal conditions, especially under chemistry conditions relevant to WCRs have not been reported. These data are required to assess the potential application of silicon nitride in WCRs and particularly the potential neutron activation of the released elements from silicon nitride to reduce activity transport in the heat transport system of nuclear reactors. Furthermore, the corrosion mechanism of silicon nitride under hydrothermal conditions was also not understood well as discussed above. This paper addresses these issues and reports on experimental studies of corrosion rates of a commercial silicon nitride, and the release kinetics of its components at temperatures ranging from 60 to 300 °C in alkaline solutions relevant to nuclear reactor water chemistry.

## 2. Experimental

### 2.1. Materials

The silicon nitride balls used in this study were purchased from Toshiba Materials Co. Ltd., and had diameters of approximately 7.93 mm with a black, shiny and smooth surface. These balls are prepared by sintering and then hot isostatic pressing (HIP). The balls have a density of 3.24 g/cm$^3$ (using Archimedes' method) with a rupture strength of 1203 MPa (using 3-point bending test) and a Vicker's hardness 1494 HV20 (using 196 N load and holding for 30 s) as provided by the manufacturer.

The chemical composition (Table 1) of $Si_3N_4$ (Lot number A86224) was specified by the manufacturer as measured using Atomic Adsorption Spectroscopy (AAS). The composition was checked using Energy Dispersive X-ray Spectroscopy (EDX) on 10 different spots of the silicon nitride surface. Considering the relatively large uncertainty of EDX (±10% for Si and N), the concentrations of elements measured using EDX agreed well with those obtained from AAS. It should be noted that the large uncertainties from EDX are mostly related to the non-uniform distribution of elements in the silicon nitride. Silicon and nitrogen are the major elements, accounting for 88% of the weight with the remainder being made up of Al, Y, Ti, Ca and Mg.

### 2.2. Corrosion tests

The corrosion rate of silicon nitride in dilute LiOH solutions at 60 °C was investigated in a 5000 mL 3-necked glass flask equipped with a condenser to minimize evaporation losses. A low flow rate of ultra-purified Ar (0.2 L/min) was maintained during the test to minimize the uptake of oxygen and carbon dioxide from the air. A calibrated thermocouple connected to a temperature controller was used to control the temperature of the test solution to within ±1 °C. When the temperature of the solutions reached 60 °C, a nylon mesh containing seven silicon nitride balls was inserted into the test solution to start the corrosion test, and the ratio of silicon nitride ball surface area to the volume of solution was kept at $3.43 \times 10^{-4}$ m$^2$/L. Blank tests at 60 °C and different pHs were conducted to quantify possible leaching of silicon and other impurities from the glass flasks without nylon mesh. The pHs of solutions were measured at 25 °C.

A 'refreshed' test was carried out at pH 10.5 and 60 °C to determine if the release rates were higher when the test solution was replaced after each sampling with fresh LiOH solution at pH 10.5. The same silicon nitride balls remained throughout the duration of the test.

To study the effect of dissolved $O_2$ on the dissolution of silicon nitride at 60 °C, a test was performed at pH 9.5 in which pressurized air from a cylinder was slowly bubbled (0.2 L/min) into the solution to saturate it with dissolved $O_2$ around 6 ppm. An acidic gas absorbent was installed to remove trace amounts of acidic gases before the airflow entered the test solutions. The dissolved $O_2$ concentration was monitored using the indigo carmine method and a V-2000 photometer purchased from CHEMtrics, Inc.

The corrosion tests at 100, 200 and 300 °C were performed in Hastelloy C autoclaves with a nominal volume of 2000 mL, similar to those used in previous studies [20]. The temperature of the solutions in the autoclaves was measured to within an uncertainty of ±2 °C using calibrated type-K thermocouples, connected to temperature controllers. A platinum mesh containing three $Si_3N_4$ balls was suspended from the thermal well on the autoclave lid using Teflon tape as an insulator to avoid galvanic coupling between the platinum and the thermal well. The required volume (1.4 L) of lithium hydroxide solution at pH 9.5 was added to the autoclaves, and no further pH adjustment was carried out during the experiment. The system was then heated to the target temperature and allowed to stabilize before the first 10 mL sample was taken. Samples were obtained through a condenser line directly into a syringe, and then passed through a 0.22 μm filter and into a plastic sample bottle.

In all of the tests (flask and autoclave), samples were taken at various times over a period of 20–38 days depending on the corrosion rate of silicon nitride. The pH and conductivity of each sampled solution were measured at 25 °C. The concentrations of the elements released into solution were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and

**Table 1**
Elemental composition of $Si_3N_4$ balls.

| Element | Si | N | Al | Y | Ti | O | Mg | Ca | Fe |
|---|---|---|---|---|---|---|---|---|---|
| AAS[a] | 53 ± 1 | 35 ± 1 | 3.4 ± 0.5 | 3.4 ± 0.6 | 0.8 ± 0.2 | 5 ± 1 | 0.01 ± 0.05 | 0.01 ± 0.02 | 0.004 ± 0.025 |
| EDX[a] | 54 ± 3 | 41 ± 3 | N/D[b] | 5.3 ± 0.3 | 0.4 ± 0.3 | N/D[b] | N/D[b] | N/D[b] | N/D[b] |

[a] The total percentage might be not equal to 100% because of rounding off the redundant digits.
[b] N/D: not determined.