# Dissolution of Silicon Nitride in High Temperature Alkaline Solutions

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## ABSTRACT

The dissolution kinetics of $Si_3N_4$ in alkaline solutions were studied at temperatures ranging from 333 to 573 K. The results show that there is little dissolution of $Si_3N_4$ below 373 K. Above 373 K, there is release of the major constituents of silicon nitride into solution. The release rate of silicon follows zero order reaction kinetics $\frac{d[Si]}{dt} = k$ and that of nitrogen (as $[NH_4^+]$) follows the power law $[NH_4^+] = k\, t^{\alpha}$, where $\alpha$ has a value between 1.1 and 1.2. These release rates increase with increasing temperature. At 573 K, release of aluminum, a minor component of the $Si_3N_4$ studied, is also observed and follows first order reaction kinetics.

## 1       INTRODUCTION

[60]Co is a major contributor to external dose in nuclear power stations because of its long half-life (5.27 years) and high energy gamma emissions (1.17 and 1.33 MeV). It is produced from neutron activation of [59]Co, the stable isotope present in high cobalt alloys such as Stellite-6 used in some specialized components of many water-cooled nuclear reactors. Dissolved or particulate [59]Co can be transported to the reactor core and activated to [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 of nuclear workers. Reducing the use of Stellite in critical components would therefore improve nuclear worker safety.

Silicon nitride is being considered as a candidate material to replace high cobalt content alloys for some applications because of its strength, excellent wear resistance and good fracture toughness properties. It has been used in a number of industrial applications such as engine components, bearings and cutting tools. However, its hydrothermal stability under the water chemistry conditions of water-cooled nuclear reactors has not been fully investigated. This paper presents the results of a study of the dissolution kinetics of silicon nitride determined at temperatures ranging from 333 to 573 K in alkaline solutions. The results will be used to identify if silicon nitride ball can be used in water cooled nuclear reactors.

## 2    EXPERIMENTAL

### 2.1    Materials

The commercial silicon nitride balls used in this study had diameters around 8.7 mm, and were black with a shiny and smooth surface.  The chemical analysis of the material provided by the manufacturer is shown in Table 1. The results showed that silicon and nitrogen are the major elements corresponding to 88% of weight and other elements are minor in the tested silicon nitride balls.

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

| Element | Si | N | Al | Y | Ti | O | C | Mg | Ca | Fe |
|---------|-----|------|-----|-----|------|-----|-------|-------|-------|-------|
| Weight% | 52.74 | 35.07 | 3.4 | 3.4 | 0.78 | 4.5 | 0.088 | 0.010 | 0.012 | 0.004 |

### 2.2    Dissolution Tests

The dissolution rate of silicon nitride in dilute LiOH solutions at 333 K 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 was maintained during the test to minimize 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 K.  When the temperature of the solutions reached 333 K, a nylon mesh containing seven silicon nitride balls was inserted into the test solution to start the dissolution 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 333 K and different pHs were conducted to quantify possible leaching of silicon and other impurities from the glass flasks without nylon mesh.

A 'refreshed' test was carried out at pH 10.5 and 333 K 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 333 K, a test was performed at pH 9.5 in which air was slowly bubbled into solution maintained during the test to keep the dissolved $O_2$ saturated1. An acidic gas absorbent was installed to remove trace amounts of acidic gases before the airflow entered the test solutions. The dissolved $O_2$ concentrations were monitored using the indigo carmine method and a V-2000 photometer purchased from CHEMtrics, Inc.

The dissolution tests at 373, 473 and 573 K were performed in Hastelloy C autoclaves with a nominal volume of 2000 mL, similar to those used in previous studies [1].  The temperature of the solutions in the autoclaves was measured to within an uncertainty of ±2 K 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 of lithium hydroxide solution at pH

9.5 was added to the autoclaves and no 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 to 34 days. The pH and conductivity of each sampled solution were measured at 298 K. The concentrations of the samples were determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with a precision of 5%. The concentration of ammonia was quantified using ion chromatography, with a detection limit of 1.1μmol/kg.

The silicon nitride balls were rinsed using deionized water and then dried with methanol to determine the mass change. A portion of the dried balls was descaled using ultrasound to remove the corrosion film and determine the mass loss and corrosion rate. The descaling solutions were acidified and sent for elemental analysis using ICP-MS or ICP-AES. Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX) were used to examine the morphology and chemical composition of the corrosion products.

## 3   RESULTS AND DISCUSSIONS

### 3.1   Weight Change and Visual Appearance

There was no obvious difference in the visual appearance of the balls tested at 333 and 373 K after 20 days. The balls tested at 333 K and pH 7 appeared slightly more greyish in color than those tested at pH 9.5 and 10.5. The slightly greyish material on the balls in the test at pH 7 may have been a very thin film of a silicate species released by dissolution of the flask and subsequently deposited on the balls. Weight measurements showed no mass change after testing at temperatures equal to and below 373 K. Three balls from each test at 333 K and one ball from the 373 K test were placed in an ultrasonic bath for 30 minutes after testing to attempt to remove any corrosion film from the ball surfaces. The surfaces of the balls at pH 7 were shiny after ultrasonication, while the surfaces of the balls from the other tests showed no changes. All the balls tested showed no mass change before and after ultrasonic cleaning, which shows that the dissolution of silicon nitride at temperatures equal to and below 373 K is insignificant under the test conditions. As there was no obvious difference in the appearance and mass of the balls tested at 333 and 373 K, only the data from the balls tested at 373 K are shown in Table 2.

The balls tested at 473 K for 34 days and at 573 K for 20 days were found to be covered with a layer of loose white power and the data measured for one ball at each temperature were listed in Table 2. Weight measurements of the balls after testing showed a significant mass loss at these temperatures. After ultrasonic cleaning for 30 minutes, the loose layer was removed and the surfaces of the balls appeared black and dull. The corrosion rate (Table 2) of silicon nitride balls increases rapidly with increasing temperature. For comparison, reported values of the release rate of cobalt

from Stellite in high temperature water range from 0.2-2 mg/dm$^2$day [2]. Based on the corrosion rate in Table 2, a silicon nitride ball would completely dissolve in 4882 days (13.4 year) at 473 K and 212 days (0.58 year) at 573 K.

**Table 2 Mass of Silicon Nitride Balls Before and After Testing**

| T(K) | Mass before testing (g) | Mass after testing (g) | Test duration (days) | Mass after ultrasonic cleaning (g) | Mass change (g) | Corrosion rate (mg/dm$^2$/day) | Corrosion rate (mass% day$^{-1}$) |
|------|------|------|------|------|------|------|------|
| 373 | 0.8479 | 0.8479 | 30 | 0.8479 | 0.0000 | 0.0 | 0.0 |
| 473 | 0.8480 | 0.8438 | 38 | 0.8414 | -0.0066 | 29.3 | 0.02048 |
| 573 | 0.8479 | 0.7753 | 20 | 07677 | -0.0801 | 674 | 0.4724 |

## 3.2 Chemistry Data

### 3.2.1 Test at 333 K

The major dissolved elements detected at 333 K in the solutions were lithium, silicon, aluminum and calcium. However, after subtracting the concentrations of the elements detected in the blank solutions, it was found that the net concentrations of most elements were negative, indicating these elements were released from the flask and externally added solutions, not the silicon nitride. Similar results were also found from the conductivity measurements. The only exception was calcium, which is a minor component in the silicon nitride balls (0.012% weight in Table 1). The concentrations of calcium in the solutions at pH 7 and pH 9.5 increased with increasing time (Figure1a). It should be noted that the calcium concentrations in Figure 1 were also corrected for the initial calcium concentrations (at $t = 0$ $h$) because the dissolved calcium concentration in deionized water can change daily.

The calcium concentration released in the tests at pH 9.5 purged with Ar appeared to be higher than that in the tests at pH 9.5 saturated with dissolved $O_2$ (6 ppm). The blank calibrated calcium concentrations at pH 7 and pH 9.5 show that calcium is leached out of silicon nitride balls more easily than other elements.
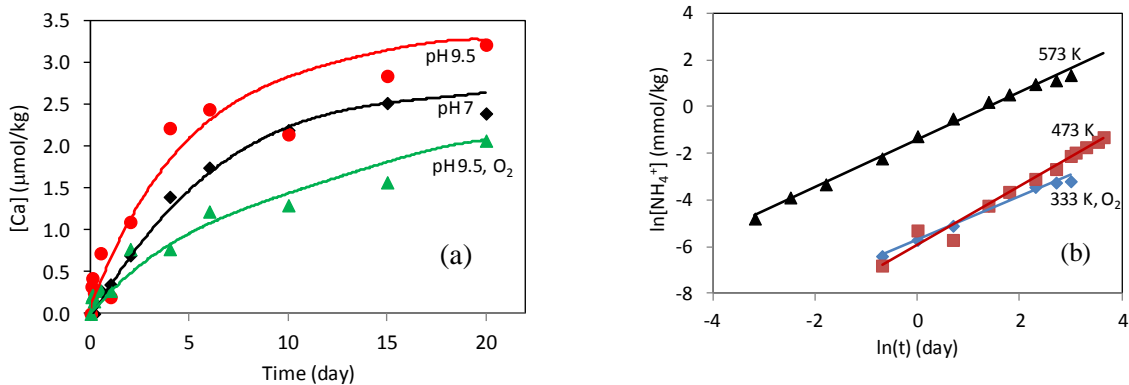


**Figure 1: (a) Calcium concentration at pH 7 and pH 9.5 as a function of time; (b): logarithm of measured ammonium concentration as a function of logarithm of time at pH 9.5.**

For the tests at pH 10.5, including the refreshed test, the dissolved calcium concentrations after subtraction of the blank solution results were zero, indicating reduced release in high pH alkaline solution. It should be noted, however, that about

50% of the total dissolved calcium at pH 7 and pH 9.5 was released from the flasks, leading to a significant uncertainty in the estimated calcium concentration released from the silicon nitride.

### 3.2.2 Tests at and Above 373 K

The pH and conductivity of the solution as a function of time at 373 K in autoclave were shown in Figure 2a and 2b. The low conductivity in solution shows that the concentration of dissolved ionic species from silicon nitride at 373 K is very low under the experimental conditions. The elements released to the solution at 373 K and pH 9.5 mainly are Ca and Si. In general, the concentrations of the dissolved species in the autoclave were below 2.5 µmol/kg and did not change much over the 30-day test duration, similar to those in the tests below 373 K, indicating that the corrosion of the silicon nitride balls was insignificant under these conditions.
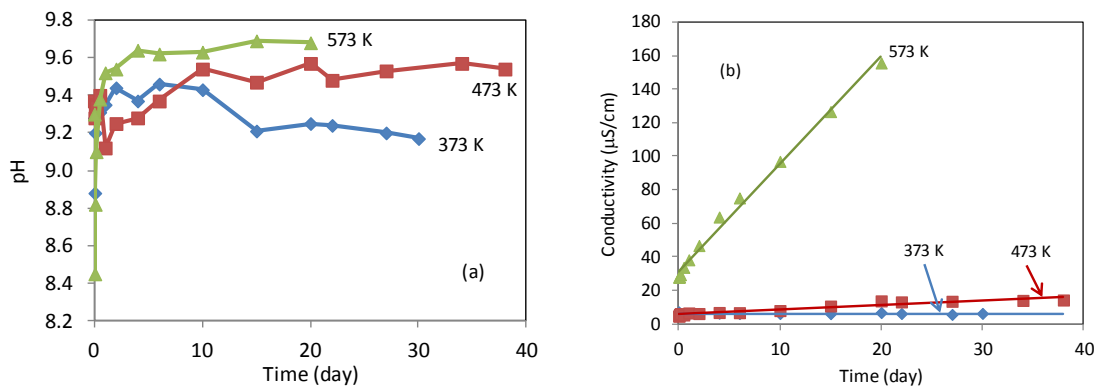


**Figure 2: (a) pH as a function of time; (b) Conductivity as a function of time.**

At 473 K, the conductivity of solutions (Figure 2b) and the concentrations of silicon and ammonium increased with testing time (Figure 1b and 3a) while the concentrations of other minor elements in silicon nitride were relatively stable. Unlike the tests at temperatures equal to and below 373 K where the corrosion rate of silicon nitride was found to be very low, the corrosion rate at 473 K was relatively high and proceeds according to:

$$Si_3N_4 + 6\,H_2O = 3SiO_2 + 4NH_3 \qquad\qquad (1)$$

$$SiO_2 + OH^- + H_2O = H_3SiO_4^- \qquad\qquad (2)$$
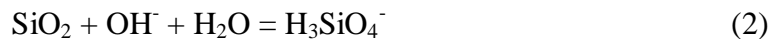
The dissolution of silicon nitride produces silicon dioxide, which can be dissolved in alkaline solutions and reduce the pH of the solution; however, the $NH_3$ produced by equation (1) compensates for the reduced $OH^-$ concentration and keeps the pH of the solution relatively stable after initial days of testing.

At 573 K, the depression of the pH over the first few hours of the corrosion test of silicon nitride was significant, but the pH rapidly recovered as more and more ammonium was released to the solution (Figure 2a). In general, the results at 573 K were similar to those obtained at 473 K, although the pH increased more rapidly at 573 K compared to 473 K, especially over the first few days, as a result of the much

higher dissolution rate of silicon nitride at 573 K. The solution conductivity also increased much faster at 573 K than at 473 K, and showed a linear dependence with time (Figure 2b).

### 3.2.3 Dissolution Kinetics of Silicon and Nitrogen

The weight change and chemistry data presented in the previous sections show that, as the temperature increases above 373 K, the dissolution of silicon nitride starts to become significant. At 473 and 573 K, silicon is a dominant species in solution and the measured concentration of silicon in solution increases linearly with increasing time (Figure 3a). A similar result was reported for the dissolution kinetics of silicon nitride containing different additives in neutral water at 573 K and 8.6 MPa [3].

The linear correlation coefficient at 373 K is poor because of the relatively low measured silicon concentrations and large experimental uncertainty. It should be noted that the dissolved silicon concentrations under the test conditions were still below the solubilities of quartz (8.2 mmol/kg at 473 K and 21.7 mmol/kg at 573 K) and amorphous silica (32.4 mmol/kg at 473 K and 53.4 mmol/kg at 573 K) in pure water [4], i.e., the solutions were not saturated with respect to silicon dioxide. The solubilities of quartz and amorphous silica in alkaline solutions are expected to be greater than those in pure water because of the role of OH$^-$ in the dissolution process (Equation (2)).

The observed linear relationship between silicon concentration and elapsed time shows that silicon release from silicon nitride follows zero order reaction kinetics.

$$\frac{d[Si]}{dt} = k \tag{3}$$

where $k$ is the zero order reaction constant and follows an Arrhenius equation between 373 and 573 K:

$$log_{10}k = -\frac{3911}{T} + 8.99. \tag{4}$$

The linear relationship between log$k$ versus 1/$T$ is shown in Figure 3b and an activation energy of 74.7 kJ/mol was obtained from the slope, which agrees with that obtained in deionized water and sodium chloride solution [5].
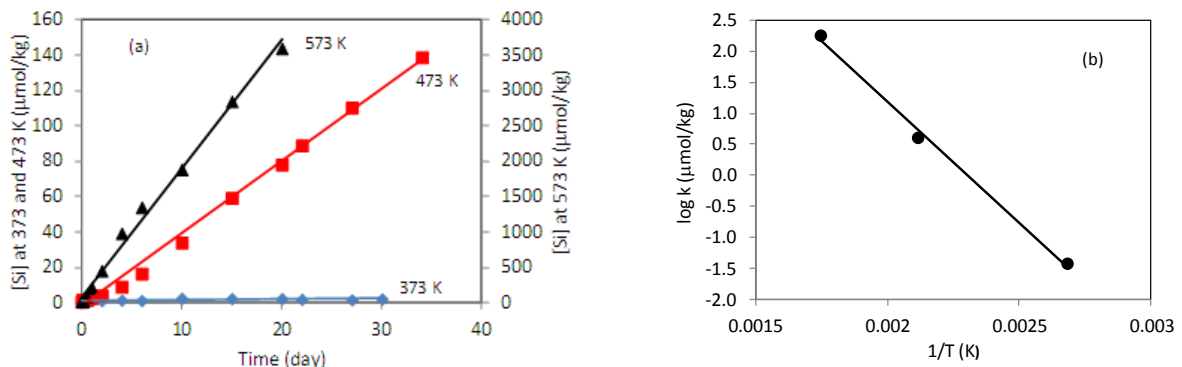


**Figure 3: (a) Silicon concentration as a function of time; (b) logarithm of dissolution rate constant of Si$_3$N$_4$ as a function of temperature.**

The relationship between the ammonium concentration and elapsed time (Figure 1b) can be expressed as

$$[NH_4^+] = k\,t^\alpha \tag{5}$$

where $k$ is the release rate constant; $t$ is the release time (days); and $\alpha$ has a value between 1.1 and 1.2 under the present experimental conditions. Since the value of $\alpha$ is close to 1, the release kinetics of ammonium is approximately a zero order of chemical reaction, similar to that of silicon discussed previously. The value of $\alpha$ for ammonium release is about 2 times that for typical alloy corrosion such as stainless steel [6]. At 333 K, the ammonium concentrations for times shorter than 1 day were the same as those of blank solutions, and these data were not used in the fitting in Figure 1b. In general, the released nitrogen concentrations in solutions are about 30% (molar scale) greater than those of silicon, matching the molar ratio in $Si_3N_4$ and showing the dissolution is congruent, i.e., the molar ratio of dissolved species in solution is the same as that in the solid phase.

### 3.2.4 Release of Minor Constituents

A small amount of aluminum (3.4%) is used in the manufacture of silicon nitride. The concentrations of aluminum measured in the test solutions were generally below 0.37 µmol/kg at temperatures less than 473 K, similar to the concentrations in the water blanks. At 573 K, the aluminum concentration increased significantly with elapsed time (Figure 4a). The kinetics of the aluminum release ([Al] versus time) can be expressed as

$$[Al] = [Al]_\infty(1 - e^{-kt}) \tag{6}$$

which shows that the release rate of aluminum follows first order kinetics (Figure 4):

$$\frac{d[Al]}{dt} = k[Al] \tag{7}$$

where $k$ is the first order reaction constant and $[Al]_\infty$ is the dissolved aluminum concentration in solution at dissolution equilibrium. The plot of $\ln(1-[Al]/[Al]_\infty)$ versus $t$ should be a straight line (Figure 4b).
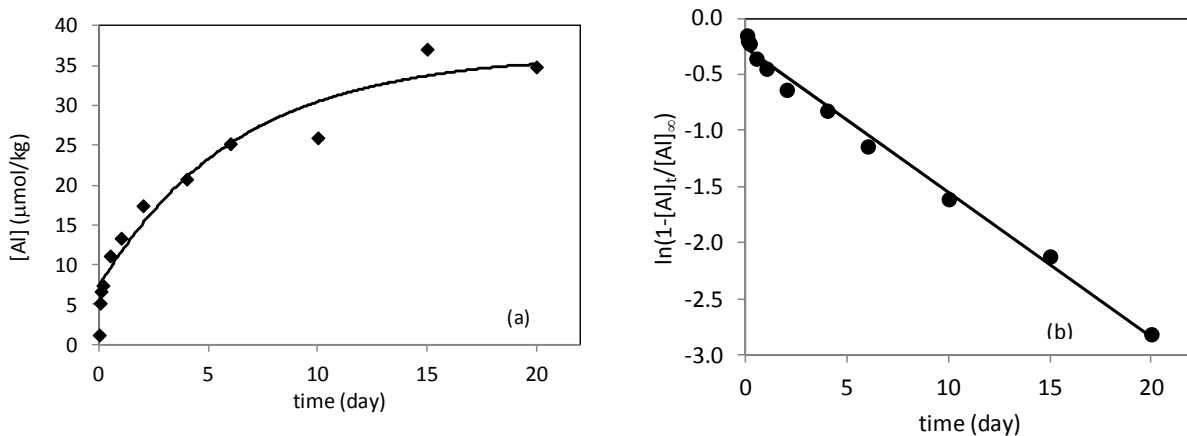


**Figure 4: (a) Dissolved aluminum concentration as a function of time; (b) first order kinetics of aluminum release at 573 K.**

Theoretically, the value of $[Al]_\infty$ should be the solubility of aluminum hydroxide or oxide under the test conditions. If the initial phase of the aluminum corrosion product from silicon nitride is boehmite, a thermodynamically less stable phase than gibbsite, the value of $[Al]_\infty$ should be the solubility of boehmite, 41.8 μmol/kg at pH 9.5 and 573 K, calculated from thermodynamic equilibrium constants [7], while the fitted value of $[Al]_\infty$ using Equation (7) is 35.4 μmol/kg. The measured aluminum concentration was 34.8 μmol/kg on Day 20, indicating the aluminum in the solution was close to, but not at, saturation with respect to the solubility of boehmite.

Yttrium is used as a medium to support the formation of the structure of silicon nitride and was present in the material at a concentration of 3.4 % (Table 1). The concentration of dissolved yttrium in the test solutions were generally below the detection limit of ICP-MS (0.04 μmol/kg). High concentrations of yttrium were observed in the corrosion film formed on the load ball surfaces in three autoclave tests (Table 3), showing that there is little release of yttrium from the silicon nitride ball material due to its very low solubility in alkaline solutions [8].

Titanium is present at a concentration of 0.78 wt% in the silicon nitride ball material. The concentration of titanium in the test solutions was generally below the detection limit (2 ppb) of ICP-MS. Like yttrium, high concentrations of titanium were found in the corrosion film formed on the ball surfaces (Table 3).

High concentrations of calcium, magnesium and aluminum were also found in the corrosion films removed from the surfaces of the silicon nitride balls by ultrasonic cleaning after the tests (Table 3). The low concentrations of these elements in the test solutions (with the possible exception of calcium), but high concentrations in the corrosion film formed on the surfaces of the silicon nitride balls are due to the low solubilities of the oxides of these elements in alkaline solutions. The chemistry data show that there is preferential release of the major constituents of the silicon nitride ball material (Si and N) into water under the experimental conditions, with low but detectable releases of Ca, and high releases of aluminum at 573 K.

**Table 3 Elemental Concentrations (μmol/kg) in the Ultrasonic Bath Cleaning Aqueous Solutions**

| T(K) | Ca | Mg | Si | Al | Ti | Y | Fe |
|------|------|------|------|------|------|------|------|
| 373 | 0.70 | 0.12 | 2.10 | 0.11 | 0.04 | 0.67 | 0.54 |
| 473 | 11.0 | 0.50 | 42.7 | 15.6 | 3.55 | 21.4 | 0.25 |
| 573 | 14.5 | 0.28 | 33.8 | 8.92 | 0.75 | 15.7 | 0.72 |

\* The solution after ultrasonic cleaning for the test at 573 K was filtered while the solutions for the tests at 373 and 473 K were not filtered.

### 3.2.5 SEM Surface Analysis of Corrosion

Surface analysis was performed on randomly selected silicon nitride balls using SEM/EDX. For tests at and below 373 K, the SEM images of the surfaces before and after testing did not show significant differences, confirming that the corrosion is insignificant under these conditions. At 473 and 573 K, evidence of significant corrosion was observed (Figure 5). The surface of the sample tested at 573 K was rougher than that tested at 473 K and shows 'pitting', indicating that significant silicon nitride has been dissolved from these areas.

To further characterize the corrosion films formed on the silicon nitride balls, elemental analysis was performed using EDX, which provides a semi-quantitative measurement of the elemental composition of "newer" surface region. For silicon nitride balls tested at 333 K and pH 9.5, the EDX data show that the elemental compositions before and after ultrasonic cleaning are almost the same, consistent with the data presented previously showing no significant corrosion of the silicon nitride ball material. For silicon nitride balls tested at 473 K, the EDX analysis shows slightly enriched concentrations of Al, Y, and Ti, and lower concentrations of N and Si in the corrosion films compared to the bulk material. Similar results are also observed for the corrosion products from the 573 K tests, but with much more enriched concentrations of O, Y, Ti and less N compared with those at 473 K. These results show that the major corrosion products on the surface of silicon nitride balls are the oxides of Si and Y, with lesser amounts of Al and Ti oxides. Calcium and magnesium were found in the chemical analysis of the corrosion film but was not detected probably due to less sensitivity of EDX to these elements and their relatively low concentrations. In general the results from EDX were similar to those obtained from ICP-MS/AES analysis of the corrosion film.
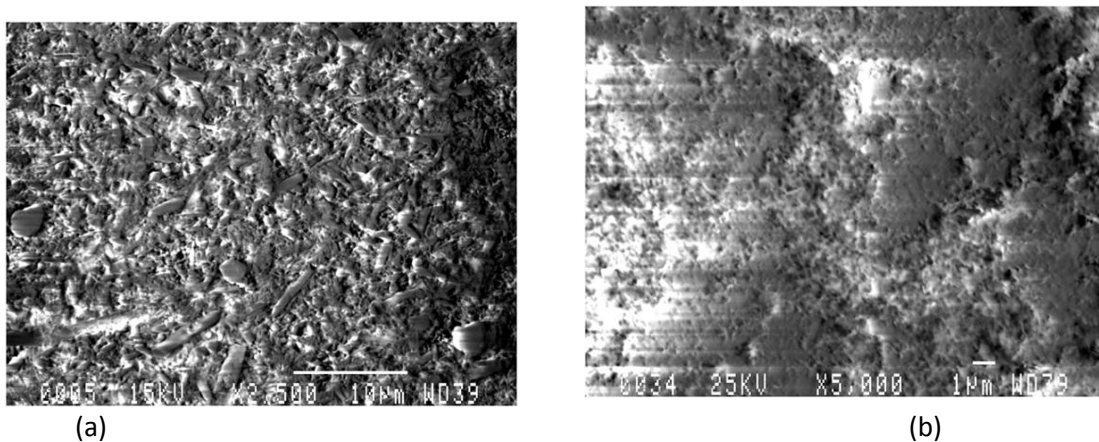


(a)                                                                    (b)

**Figure 5. Secondary electron image of the surface of a silicon nitride ball after 38 days exposed at 473 K (a) and (b) at 573 K at pH 9.5.**

## 4    SUMMARY

The data presented above (weight change, chemical analysis, surface analysis) lead to a consistent picture of the behaviour of silicon nitride under mildly alkaline conditions. Below 373 K, there was little corrosion of silicon nitride under any of the conditions tested. Above 373 K, some corrosion and elemental release into solution were detected. The corrosion rate and amount of elements released increase with increasing temperature. There is preferential release of Si and N into solution at temperatures equal to and below 573 K and their release rates follow zero order kinetics. Most of the other minor constituents of the silicon nitride remain in the loose corrosion film on the ball surface because of the low solubilities of the relevant oxides in alkaline water. Such a corrosion film is not corrosion protective and can be easily removed from the surface of silicon nitride balls. At 573 K, aluminum release is also observed and the release rate follows first order kinetics. Based on the dissolution tests, silicon nitride is safe to use at and below 373 K to replace cobalt alloys in water cooled nuclear reactors.

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