

# Corrosion of Structural Ceramics Under Subcritical Conditions in Aqueous Sodium Chloride Solution and in Deionized Water. Part I: **Dissolution of Si<sub>3</sub>N<sub>4</sub>-Based Ceramics**

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The results presented in this paper compare the behavior of silicon nitride prepared with the addition of yttria as sintering additive, and of a sialon ceramic in contact with an aqueous solution of sodium chloride (NaCl) at  $T \leq 290^{\circ}$ C. Both studied ceramics dissolved by preferential attack of Si–N bonds in the matrix accompanied by the release of ammonia and formation of protective, mostly oxide layer of corrosion products at the surface. Increase of dissolution rate of sialon in aqueous NaCl solution at 290°C was observed in comparison to dissolution in deionized water, achieving the value 27 mmol  $\cdot$  (m<sup>2</sup>  $\cdot$  h)<sup>-1</sup>. Penetration of chloride anions through protective layer of corrosion products is proposed to contribute to destruction of the passivation layer and renewal of the exposure of vulnerable material surface to corrosion medium.

#### I. Introduction

Some particularly advantageous, especially mechanic, proper-ties predestine nonoxide ceramics for various applications, such as reciprocating engine components, ball bearings, cutting tools, nonautomotive wear components, and gas turbine engines. However, high fracture strength, toughness, light weight, or some other mechanical properties are sometimes insufficient, if an excellent resistance to attack by the environment plays a key role and may, in some cases, be the prime reason for the selection of a particular material or a limiting factor of its use. Practically all nonoxide ceramics are in nonequilibrium state, thus reacting with environment in almost every application. In spite of this, they still remain valuable and demanding materials from the point of view of their corrosion resistance.

Chemistry and microstructure of a particular material as well as the variability of actual chemical environment are crucial for the evaluation of corrosion behaviour. Detailed understanding of corrosion mechanisms and kinetics of the processes is inevitable for prevention of active degradation of material, which results in decrease of its lifetime performance.

Recent studies on the corrosion behavior of nonoxide ceramic materials in acidic and basic aqueous solutions showed that both the corrosion rate and the corrosion mechanism strongly depend on the concentration and the temperature of the solution and on the composition of the grain-boundary phase.<sup>1-4</sup> Nickel and Seipel<sup>5</sup> studied the corrosion behavior of silicon nitride  $(Si_3N_4)$  ceramics in hot aqueous fluids, e.g. sulphuric acid. All methods he applied for monitoring of corrosion indicate partial or complete removal of the grain-boundary phase to be the main corrosion mechanism. They conclude deliberately used additives (e.g., sintering aids) or impurities makes advanced ceramics vulnerable to corrosion by hot aqueous fluids. Jacobson<sup>6</sup> studied corrosion of silicon (Si)-based ceramics in combustion environment. Five main types of corrosive degradation have been identified: passive oxidation, deposit-induced corrosion, active oxidation, scale/substrate interactions, and scale volatility. Additionally, nonoxide ceramics were discussed as promising materials for reactors for supercritical water oxidation units (SCWO reactors).7-11

Surprisingly, under these conditions the highest corrosion rates were not found at the highest temperatures, where the density of corrosion media (water vapour) was low, but at subcritical temperatures  $<470^{\circ}$ C with water of high density (above  $200-300 \text{ kg/m}^3$ ).<sup>12</sup> At these temperatures, the concentrations of both H<sup>+</sup> and OH<sup>-</sup> are about three orders of magnitude above their values in ambient water, so that water can be considered to be both acidic and alkaline. It was reported that the solubility of inorganic compounds under these conditions is high (subcritical like): practically all nonoxide ceramics are converted into their oxides or dissolve rapidly.<sup>13</sup>

The results presented in this paper compare the behavior of Si<sub>3</sub>N<sub>4</sub> prepared with the addition of yttria as sintering additive, and of a sialon ceramic in contact with an aqueous solution of sodium chloride (NaCl) under conditions close to, or within the subcritical region  $(150^{\circ}-300^{\circ}C)$ .<sup>14</sup> NaCl is a common by product of the treatment of chlorinated wastes in SCWO process units and is known as an aggressive corrosive agent of car parts due to winter road maintenance, or in pumps for hot high-salinity solutions used in units for desalination of seawater. The number of prospective applications of water-based fluids is not final, and has been appreciably growing, because supercritical water as the reaction medium<sup>15</sup> is an attractive solvent in view of the availability, ecological cleanliness, and practical safety.

Reported experimental work employed static and quasidynamic test procedures developed to evaluate the chemical durability and to determine dissolution rates of tested ceramic materials. Corrosion in deionized water as the reference corrosion medium was carried out simultaneously in order to reveal potential influence of the ionic strength.

In works published previously by other authors the extent of corrosion was monitored applying numerous techniques, relying mostly on determination of weight loss or weight gain of corroded specimen, followed by complementary measurement of the corrosion layer thickness and composition with various microscopy techniques. In this work the emphasis was put on

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the analysis of specific elements released from the material into the corrosion medium rather than on determination of the weight change alone, with complementary detailed study of the corrosion layer composition (phase and chemical). By combination of all mentioned techniques a set of data were obtained, which facilitated determination of the kinetic parameters of corrosion, together with broad analysis of corroded material and formed secondary products.

#### **II. Experimental Procedure**

#### (1) Materials

Two materials, Si<sub>3</sub>N<sub>4</sub> (S) and sialon (SA) were selected to study the corrosion behavior of nonoxide, Si<sub>3</sub>N<sub>4</sub>-based materials. The compositions are given in Table I. The Si<sub>3</sub>N<sub>4</sub> specimens were prepared from the powder SN-E10 (UBE Industries Ltd., Tokyo, Japan) with Y<sub>2</sub>O<sub>3</sub> (4N label, Pacific Industrial Development Corporation, Ann Arbor, MI) as the sintering aid. For preparation of sialon with the nominal composition Si<sub>2</sub>Al<sub>4</sub>O<sub>4</sub>N<sub>4</sub> the following commercial powders were used: a-Al<sub>2</sub>O<sub>3</sub> (Martoxide PS-6, Martinswerk GmbH, Bergheim, Germany);  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>/ LC12-S (H.C. Starck, Goslar, Germany); and AlN/grade C (H.C. Starck). The powder batch was attrition milled in isopropanol for 4 h. The powders were dried under infrared lamp and sieved, respectively, through a 25 and 71 µm sieve to prepare Si<sub>3</sub>N<sub>4</sub> and sialon powders with required granulometry, blocks with dimensions of 50 mm  $\times$  50 mm  $\times$  5 mm prepared by hot pressing at 1750°C and pressure 30 MPa under nitrogen (N) pressure of 0.1 MPa were cut and ground into rectangular bars 3 mm  $\times$  4 mm  $\times$  50 mm, their faces polished, and edges chamfered. The bars were then ultrasonically cleaned in acetone for 15 min, rinsed with distilled water, and dried for 3 h at 110°C.

## (2) Corrosion Experiments Under Static Conditions

Deionized water (conductivity  $25 \pm 5 \ 10^{-4} \ \text{S/m}$ ) used as the reference medium was prepared in the reverse osmosis purification system (CHEZAR, Bratislava, Slovak Republic). The 0.5 mol/L NaCl solution was prepared by dissolving  $29.96 \pm 0.03$  g of NaCl (MERCK, Darmstadt, Germany) in 1000 mL of deionized water. The bars were placed in teflon-lined pressure corrosion reactors with the inside volume 26 cm<sup>3</sup> filled with corrosion liquid and heated in laboratory drying oven. Both static and quasi-dynamic tests were carried out at the temperature of 290°C with maximum duration of the test 480 h. Additional static tests at temperatures 150° and 200°C were applied in order to obtain the data for determination of kinetic parameters, and for calculation of the activation energies. The ratio between the sample surface and the volume of corrosive liquid (S/V) was held constant at  $0.7 \pm 0.03$  cm<sup>-1</sup>. For determination of each experimental data point two specimens were placed in one reactor with 20 mL of the liquid medium. The tests were carried out in three reactors in parallel, i.e. six specimens were tested under identical conditions. Fresh specimens were used for each test. After the test the samples were removed from the reactors, rinsed with distilled water, dried, and weighed. In parallel, the tests without the ceramic specimens were carried out for given time interval, providing the eluate labelled as a *blank*. The concentration of the particular element detected in the blank was subtracted from the concentration determined in the eluates taken after the corrosion tests with the ceramic material.

### (3) Quasi-Dynamic Test

To avoid oversaturation of solution with regard to precipitation of corrosion products, which could act as a passivation layer,

 Table I.
 Starting Compositions of Tested Materials

	Composition of studied materials in wt%							
	${\rm Si_3N_4}$	$Y_2O_3$		$\alpha - Al_2O_3$	$Si_3N_4$	AlN		
Si <sub>3</sub> N <sub>4</sub> (S)	95	5	Sialon (SA)	47.9	32.9	19.2		

quasi-dynamic test conditions were also applied. Due to high temperatures used, typical flow-through experiment with fresh corrosion medium continuously flowing around the tested material could not be performed. Therefore an alternative arrangement has been used, where every 22 h the reactors were cooled down, the corrosive solution was removed and fresh solution was added to the reactor. The test was carried out in two reactors in parallel at the temperature of 290°C, and with the same specimens for the whole duration of test. The *S*/*V* ratio was identical to the static tests. The content of released elements including the total concentration of ammonia (NH<sub>3</sub>)-bound N (both in ionized and in molecular form) were determined in each eluate.

(A)  $NL_i$  value calculations: The amount of an element released into solution was expressed in terms of the value  $NL_i$  in  $(g/m^2)$  according to the Eq. 1, which is often applied in studies of chemical durability of glasses<sup>16</sup>

$$NL_{i} = \frac{c_{i}}{w_{i}\frac{S}{V}}$$
(1)

where  $c_i$  is the concentration of an element (i) in solution in (mg/L), S is the surface of the ceramic material in contact with corrosive solution in (m<sup>2</sup>), V is the volume of the corrosive solution in (m<sup>3</sup>), and  $w_i$  is the mass fraction of the element (i) in the ceramic material. This way the amount of the element released into the solution is normalized with respect to its content in corroded material. Identical  $NL_i$  values of all elements indicate congruent dissolution of the material. The variation of the  $NL_i$  values indicates either preferential dissolution and release of some elements, or precipitation of corrosion products and depletion of the solution of some elements.

Data acquired from the *quasi*-dynamic tests at the respective time of corrosion t were recalculated according to the following equation:

$$\mathbf{NL}_{i}^{t} = \frac{c_{i}}{w_{i}\frac{S}{V}} + \mathbf{NL}_{i}^{t-\Delta t}$$
(2)

The Eq. 2 includes cumulative effect of the amount of dissolved elements in the studied time interval  $\Delta t$ .

#### (4) Methods of Analysis

The contents of metallic elements (Si, Al, Y) released into the solution were determined with the use of the Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP AES, Vista MPX, Varian Australia Pty Ltd., Mulgrave, Australia) with radial viewing, equipped with V-groove nebuliser and Sturman–Masters spray chamber. The presence of high concentrations of metallic ions in the corrosion solution, such as Na<sup>+</sup>, might significantly disturb the analysis.<sup>17,18</sup> A simple internal standard-ization technique with beryllium as an internal standard was therefore utilized for multielement analysis of the eluate solutions containing 0.5 mol/L NaCl, to eliminate possible errors introduced by the solution with high-salt content.<sup>19</sup>

 $Si_3N_4$  is known to react, under the conditions similar to that of the corrosion test, with water, yielding silica, and  $NH_3$  according to the following reaction<sup>5</sup>:

$$Si_3N_4 + 6H_2O \Rightarrow 3SiO_2 + 4NH_3 \tag{3}$$

 $NH_3$  dissolves in water until equilibrium between  $NH_3$  gas and ammonium ions is established. Not all of the dissolved  $NH_3$ reacts with water to form ammonium ions. A substantial fraction remains in the solution in molecular form. For quantification of the total  $NH_3$  nitrogen (both in ionized and molecular form) in eluates the spectrophotometric method with sodium nitroprusside (UV-VIS-NIR spectrometer Cary 2300, Varian Techtron Pty Ltd., Mulgrave, Australia) was employed according to the standard STN ISO 7150-1. Corrosion surfaces and polished cross sections of corroded specimens were examined by scanning electron microscopy (SEM/EDX, Carl Zeiss SMT GmBH, model EVO 40 HV, Jena, Germany) at accelerating beam voltage 20 kV. Corrosion products formed at exposed surfaces were investigated with the use of X-ray diffractometer (XRD, Bruker AXS Inc., Madison, WI) specially designed for measurement of thin layers, in the  $2\theta$  interval  $20^{\circ}$ – $80^{\circ}$  using CuK $\alpha$  radiation.

#### III. Results

#### (1) Microstructure

Characteristic microstructure of specimen of the material S consists predominantly of elongated homogeneously distributed  $\beta$ -Si<sub>3</sub>N<sub>4</sub> grains (dark gray areas) with low aspect ratio and grainboundary phases (lighter areas), as illustrated in Fig. 1(a). The Si<sub>3</sub>N<sub>4</sub> grain size ranges between 150 and 500 nm with randomly scattered grains with diameter up to 2 µm. Some residual pores in the range between 0.1 and 1.0 µm are present in the material. The main phase is  $\beta$ -Si<sub>3</sub>N<sub>4</sub>, with small amount of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>. Some additional crystalline phases have been also detected, such as YSiO<sub>2</sub>N and Y<sub>2</sub>Si<sub>3</sub>O<sub>3</sub>N<sub>4</sub>.

Microstructure of the sialon (SA) is relatively fine grained, and characteristic for this type of nonoxide ceramics (Fig. 2(b)). The grain size ranges usually from 1 to 1.5  $\mu$ m, with small fraction of randomly scattered grains with the size up to 10  $\mu$ m. The material is also characterized by the presence of residual porosity up to 3%, and phase inhomogeneities comprising mainly small fraction of unreacted  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, slightly above the detection limit of the XRD.

## (2) Static Experiments

(A) Corrosion in Deionized Water: The time dependences of the weight change normalized with respect to the corroded surface area for the tests carried out in deionized water at  $150^{\circ}$ ,  $200^{\circ}$ , and  $290^{\circ}$ C are summarized in Figs. 2(a) and (b). At



Fig. 1. Microstructure of the material S (a) and of the material SA (b).



Fig. 2. Weight loss measured for S and SA specimens in deionized water at  $150^{\circ}$  and  $200^{\circ}$ C (a) and at  $290^{\circ}$ C (b).

 $150^{\circ}$  and  $200^{\circ}$ C similar weight losses were measured for both materials exposed to deionized water. Unlike for sialon specimens, rapid loss of weight of Si<sub>3</sub>N<sub>4</sub> specimens was observed at the temperature of  $290^{\circ}$ C up to 48 h of the test later followed by a steady state until the end of the experiment. Irrespective of the temperature, nearly no weight change was observed during the dissolution of sialon ceramics (Figs. 2(a) and (b)). This might indicate either the temperature independence of dissolution of the sialon material, or that the state of saturation was achieved soon after the exposure to deionized water.

However, various factors, especially inhomogeneous dissolution in some places (pitting corrosion) with simultaneous precipitation of reaction products and formation of passivation layer at others, or random cracking and peeling off the passivation layer might influence the weight loss-time dependences significantly. We therefore do not consider the weight loss to be a correct parameter for evaluation of corrosion rates and mechanisms, as will be discussed later.

Although the preliminary considerations based on weight loss measurements could classify sialon as promising and chemically resistant material, which could be applied under studied conditions and in the studied temperature interval. The chemical analysis of eluates did not support the expectations.

Reaction of  $Si_3N_4$  with water proceeds according to the Eq. 3 yielding NH<sub>3</sub> and silicon dioxide as the reaction products. No specific influence of the selected corrosion media on dissolution of  $Si_3N_4$  ceramics could be observed, irrespective of the temperature (Fig. 3). However, higher *NL*(N) values were detected for dissolution of sialon in NaCl solution at 290°C, which was nearly eight times higher than for dissolution in deionized water (Fig. 4) at the same temperature. Corrosion tests with sialon in 0.5*M* NaCl were carried out only for temperature 290°C.



Fig. 3. Time dependence of NL(N) values obtained for S specimens dissolved under static conditions at all temperatures in both corrosion media.

NH<sub>3</sub> determined in eluates after corrosion of S specimens at 290°C was recalculated to the normalized amount of N and compared with the amount of dissolved Si (Fig. 5(a)). Comparable amounts of N and Si were leached from Si<sub>3</sub>N<sub>4</sub> ceramics to the solutions at all applied temperatures under static conditions. The NL values of N and Si determined in the corrosion medium were identical, in other words the dissolution of Si<sub>3</sub>N<sub>4</sub> proceeds congruently indicating preferential degradation of Si<sub>3</sub>N<sub>4</sub> matrix grains. Yttrium was not considered because concentrations in both deionized water and NaCl solution are near the limits of detection (0.01 mg/L) for applied analytical method. In the time interval up to 48 h the time-concentration dependence of both elements Si and N, is approximately linear, then the rate of the dissolution reaction slows down as the equilibrium is approached, and a layer of passivating precipitates is formed at the surface. The XRD analysis confirmed the presence of cristobalite (PDF 76-941) at corroded surfaces.

 $NH_3$  was quantified also in the eluates from the corrosion of sialon ceramics in deionized water (Fig. 5(b)). Already in the first hours of dissolution significantly lower *NL* values of dissolved Si were measured in comparison to *NL* values of  $NH_3$  nitrogen and with very low *NL* of aluminum, ranging from only 0.05 to 0.1 g/m<sup>2</sup>. This indicates that the saturation with respect to Si and Al was attained already in the early stage of the dissolution reaction as will be discussed in more detail below.

The SEM analysis of the specimen S corroded for 288 h at 290°C (Fig. 6(a)) indicates the presence of newly formed  $SiO_2$ 



**Fig.4.** Comparison of NL(N) values obtained under static conditions for SA specimens dissolved in 0.5*M* NaCl at 290°C, and in deionized water at 150°, 200°, and 290°C.



**Fig. 5.** Normalized amount of nitrogen and silicon as a function of corrosion time for  $Si_3N_4$  (a) and sialon (b) specimens, in deionized water at 290°C. The *NL*(Al) values (b) are included for the sialon.

phase, cristobalite. The layer of precipitates was found to form already after 48 h of the test, remaining compact during whole time interval studied. The examination of the surface of sialon ceramics corroded under the same conditions (Fig. 6(b)) revealed the presence of unidentified phase, with crystal-like morphology, similar to that observed by Nagae et al.<sup>20</sup> However, based on the XRD analysis these authors had obtained no evidence of the compounds other than sialon at corroded surfaces. In our case the XRD analysis of corrosion products removed from the specimen's surface revealed the presence of  $\alpha$ -aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) (PDF 89–7717) together with the Si<sub>2</sub>Al<sub>4</sub>O<sub>4</sub>N<sub>4</sub> (PDF 48–1617) sialon: both phases were identical to that detected by XRD in the underlying uncorroded matrix. High background at the XRD diffraction pattern implies the presence of significant amount of an amorphous phase of unknown composition (Fig. 6(c)), possibly aluminum hydroxides, hydrated silica or amorphous aluminosilicates of variable composition. The EDX analysis of the amorphous layer confirmed the presence of Si, Al, O, and N. However, due to small thickness of the precipitated layer the analysis was likely to be strongly influenced by the underlying substrate, and is therefore not considered as a suitable indication of the true composition of the precipitates. The presence of unidentified layer covering completely the surface of sialon specimens explains the retardation of the rate of dissolution in an early stage of the corrosion process in deionized water (Fig. 5(b)), as well as negligible weight change as seen in Fig. 2(b).

(B) Corrosion in an Aqueous NaCl Solution: In the first 96 h of dissolution in 0.5 mol/L NaCl solution at 290°C both materials exhibited similar decrease of weight (Fig. 7). However, unlike dissolution in deionized water the steady state was not



Fig.6. SEM image of the surface of specimen S (a) corroded in deionized water 288 h at 290°C and SA (b) after 24 h in deionized water. X-ray diffraction pattern of corrosion products removed from surface of SA specimen, corroded 480 h in deionized water (c).

achieved. After 96 h further rapid change was observed on the weight loss-time dependence of the material S, while in the case of SA approximately linear trend was preserved in the whole studied time interval. The normalized amounts of Si and N in eluates from S specimens corroded in 0.5M NaCl solution do not significantly differ from those measured in deionized water eluates, indicating similar mechanism of congruent dissolution of the Si<sub>3</sub>N<sub>4</sub> matrix in both media (Fig. 8(a)). The retardation of the corrosion process in the latter hours of the test observed in deionized water was not recorded in this case. The surface of Si<sub>3</sub>N<sub>4</sub> ceramics was covered with a layer of corrosion products, morphologically, and from the point of view of their phase composition, identical to that found at the surface of S material corroded in deionized water. The XRD of corrosion products



**Fig.7.** Weight loss measured for S and SA specimens in aqueous sodium chloride solution at 290°C.

removed from the surface of the S specimen revealed the presence of crystalline cristobalite (PDF 76–941). The main difference observed when compared with corrosion in deionized water was extensive cracking and peeling off of the layer of precipitates (Fig. 8(b)). Delamination of the precipitated layer might prevent or delay the attainment of the steady state and may be also responsible for the abrupt weight loss observed after 96 h.

The amount of N released into the corrosion media was found to be one order of magnitude higher for SA than for the S ceramic (Fig. 9(a)). In principle sialon is, similarly to S, also expected to dissolve congruently, but the release of aluminum into the solution together with Si and Na<sup>+</sup> ions is believed to shift the equilibrium quickly toward the formation of corrosion products (Fig. 9(b)) other than those found in deionized water. This would explain lower concentrations of Si measured in NaCl solution than in deionized water as well as extremely low *NL*(Al) values determined in both corrosion media. Investigation of the corrosion products removed from the surface of corroded sialon ceramic by XRD (Fig. 10) revealed the presence of NaAl<sub>3</sub> Si<sub>3</sub>O<sub>10</sub>(OH)<sub>2</sub> (paragonite, PDF-24-1047) together with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (corundum, PDF-71-1123) and boehmite (PDF-1-1283).

Cracks and places with peeled off layer, on the Fig. 9(b) marked with arrows, are likely to be responsible for restarting and accelerating of dissolution process in NaCl solution.

## (3) Quasi-Dynamic Conditions

The formation of protective surface layer under static test conditions at 290°C influences, and in some cases, effectively prevents determination of kinetic parameters of the corrosion process. In order to avoid saturation of the solution with respect to the secondary phases formed at the surface of studied materials in the course of corrosion quasi-dynamic arrangement of the experiments was applied. The data were then used for determination of the initial dissolution rates at 290°C. The cumulative *NL* values of leached N and Si calculated according





**Fig.8.** Normalized amount of nitrogen and silicon as a function of corrosion time for  $Si_3N_4$  in 0.5 mol/L NaCl solution at all temperatures (a). SEM micrograph of corroded surface after 288 h at 290 °C (b). Cracks and places with the peeled off-layer are marked with arrows.

to Eq. (2) and their time dependences in deionized water and in 0.5 mol/L NaCl solution are, respectively, shown in Figs. 11(a) and (b).

Evaluation of experimental data obtained for the *S* ceramics from *quasi*-dynamic tests at 290°C showed only negligible influence of corrosion media on the dissolution process. Speaking in terms of the weight loss, the amount of *S* dissolved in deionized water and in 0.5*M* NaCl solution was 0.005 and 0.006 g/cm<sup>2</sup>, respectively, with the relative standard deviation (RSD) 7%. The S material dissolves congruently with similar *NL*(N, Si) values irrespective of the corrosion solution used. Analysis of the surface of *S* specimen corroded under *quasi*-dynamic conditions Figs. 12(a) and (b) revealed pitting corrosion. Higher magnification images of attacked places, Fig. 12(b), revealed needle-shaped imprints of dissolved Si<sub>3</sub>N<sub>4</sub> grains in residual glassy phase.

The EDX analysis revealed significantly decreased concentration of N in such places, which were at the same time markedly enriched by Y and O. These observations together with the chemical analysis of the eluate suggest that yttrium silicate oxynitride grain-boundary glass phase is, at least under the applied test conditions, resistant to attack by the used corrosion solutions.

Simultaneous congruent release of Si and N to deionized water was observed in eluates from corrosion tests of the sialon ceramics, while Al, detected in solution in significantly lower amounts, reprecipitates in the form of hydroxid-oxides (such as AlOOH) as confirmed by XRD where it was identified together with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (corundum) phase, likely originating as a residuum from the original, uncorroded material.

There is, nevertheless, no doubt about the influence of Na<sup>+</sup> and Cl<sup>-</sup> ions on dissolution of SA ceramics. The NL(N) values





**Fig. 9.** NL(Si) and NL(N) as a function of corrosion time for sialon specimens in 0.5 mol/L NaCl solution at 290°C (a). SEM image of corroded surface after 288 h at 290 °C (b). Cracks and the places with peeled off layer of corrosion products are marked with arrows.

were nearly three times higher comparing to NL(N) calculated for dissolution in deionized water, and can be in part related to increased ionic strength of the corrosion solution. In addition, formation of precipitation products, AlOOH and paragonite NaAl<sub>3</sub>Si<sub>3</sub>O<sub>10</sub>(OH)<sub>2</sub> different from those detected in deionized water, deplete the solution of Al and Si promoting further dissolution of sialon (Fig. 11(b)). A layer of secondary crystalline phases was found at the surface of SA specimen corroded in both corrosion solutions even under *quasi*-dynamic conditions at 290°C (Fig. 13).



**Fig. 10.** X-ray diffraction pattern of the corrosion products removed from the surface of SA specimen, corroded 480 h in 0.5M NaCl at 290°C.



Fig. 11. Time dependences of NL(N) and NL(Si) leached from S and SA specimen in deionized water (a) and in aqueous sodium chloride solution (b).

## (4) Corrosion Rate and Activation Energies

As shown by the results of static tests the dissolution processes of both studied ceramics are markedly influenced by the temperature of corrosion media. The interpretation of corrosion rates at temperatures above 150°C was influenced by saturation of solution, which is the problem encountered also by other authors.<sup>21</sup> The rate constants of dissolution at the temperature <290°C and at 290°C were determined from the linear parts of the experimental *NL*(N) (mol/m<sup>2</sup>) vs time dependences obtained from the analysis of the data acquired, respectively, from static and *quasi*-dynamic tests. The activation energies were obtained using the Arrhenius equation (Fig. 14)

$$\ln k = \ln A - E_{\rm a}/(RT) \tag{4}$$

The values of rate constants and the activation energies are summarized in Table II. The apparent activation energy of dissolution of Si<sub>3</sub>N<sub>4</sub> in deionized water and in 0.5*M* NaCl solution is 73.6±8 and 69.3±16 kJ/mol, respectively. Similar values of  $E_a$  (73–110 kJ/mol) were estimated by Sato *et al.*,<sup>22</sup> and Somiya,<sup>10</sup> who concluded that dissolution of Si<sub>3</sub>N<sub>4</sub> ceramics under hydrothermal conditions (below 300°C) is controlled by surface chemical reactions. In contrary Yoshimura concluded that the activation energies at the level 73–84 kJ/mol as determined in his work<sup>23</sup> correspond to diffusion of H<sub>2</sub>O in amorphous silica. Based on the literature data it is therefore not possible to make unambiguous conclusions on the controlling mechanism. Very low concentrations of yttrium determined in the corrosion medium suggest a high chemical durability of yttrium oxy-nitride





**Fig. 12.** SEM image of S specimen analyzed after corrosion in deionized water (a) and in aqueous sodium chloride solution (b) under *quasi*dynamic conditions at 290°C. Detail of a pit: the  $Si_3N_4$  grains etched away (b).

glassy phase in the tested  $Si_3N_4$  ceramics. The corrosion rate  $14.2 \pm 1 \text{ mmol} \cdot (m^2 \cdot h)^{-1}$  determined by Nickel *et al.*<sup>21</sup> for  $Si_3N_4$  powder corroded at 300°C show excellent agreement, within error levels, with the findings obtained in this study,  $15.0 \pm 0.2 \text{ mmol} \cdot (m^2 \cdot h)^{-1}$ .

Apparent activation energy of dissolution of sialon in deionized water was  $29.5 \pm 10 \text{ kJ/mol}$  and initial dissolution rate at  $290^{\circ}\text{C}$  was  $10.6 \text{ mmol} \cdot (\text{m}^2 \cdot \text{h})^{-1}$  which is comparable to dissolution rate determined for  $\text{Si}_3\text{N}_4$  ceramics. Nearly threefold increase of dissolution rate of sialon in aqueous NaCl solution at  $290^{\circ}\text{C}$  was observed in comparison to dissolution in deionized water, achieving the value  $27.0 \text{ mmol} \cdot (\text{m}^2 \cdot \text{h})^{-1}$ .



**Fig. 13.** A layer of corrosion products observed by SEM on a SA specimen corroded in NaCl solution. The numbered places were analyzed by EDX.



Fig. 14. Arrhenius plot of  $\ln k$  vs 1000/T for sialon and Si<sub>3</sub>N<sub>4</sub>.

#### IV. Discussion

The Si-N-Si structure in Si<sub>3</sub>N<sub>4</sub>-based compounds is rendered rigid by the necessity of N forming three rather than two bonds unlike for flexible, adjustable Si-O-Si bridge bonds in silicon dioxide. Schott et al.<sup>24</sup> reviewed the mechanisms, which control kinetics of mineral dissolution and precipitation in aqueous solution. They concluded that water molecules coordinate to metal centers and dissociative chemisorptions occurs with formation of positively  $(-OH_2^+)$ , negatively  $(-O^-)$  charged and neutral hydroxyl groups (-OH) depending on pH of the solution. Thus in dissolution of the studied ceramic materials a series of adsorption and hydrolysis reaction steps affecting the bonds of SiN<sub>4</sub> tetrahedra might be involved. The bonding around the N atoms is somewhat  $sp^2$ -like: that is, three hybrids of s,  $p_x$ , and  $p_y$ form three bonds to Si atoms, with the  $p_z$  orbitals (sticking out of the plane) nonbonding.<sup>25</sup> The free electron pair of N under favorable condition of subcritical water is likely to react with H<sup>+</sup> ions along with chemisorptions of water molecules to Si atom center.

 $Si_3N_4$  ceramics then in a contact with aqueous environment dissolves as follows<sup>2</sup>:

$$Si_3N_4 + 3(n+2)H_2O + 4H^+ \rightarrow 3SiO_2 \cdot nH_2O + 4NH_4^+$$
 (5)

Based on the results shown above we propose that the Si–N bonds in Si<sub>3</sub>N<sub>4</sub> and both the Si–N and Al–N bonds in sialon are attacked preferentially under the conditions of the corrosion test. Successive adsorption and hydrolysis reactions affecting the Si–N bonds result in production of NH<sub>3</sub>, which dissolves in solution changing pH in our case from  $6.2\pm0.3$  to  $9.6\pm0.1$  while Si is gradually<sup>26</sup> released and in solution present in the

Table II. The Activation Energy of Dissolution of S and SA Ceramics and Rate Constants Measured for Corrosion in Deionized Water and 0.5*M* NaCl

	Deionized w	ater	0.5 mol/L NaCl					
Samples	$k \pmod{(\mathrm{mmol} \cdot (\mathrm{m}^2 \cdot \mathrm{h})^{-1})}$	E (kJ/mol)	$k \pmod{(\mathbf{mmol} \cdot (\mathbf{m}^2 \cdot \mathbf{h})^{-1})}$	E (kJ/mol)				
Si <sub>3</sub> N <sub>4</sub> /S/								
290°C	$15.0 \pm 0.2$	$73.6 \pm 8$	$20.1 \pm 0.7$	$69.3 \pm 16$				
200°C	$0.69 \pm 0.07$		$0.63 \pm 0.03$					
150°C	$0.11 \pm 0.01$		$0.16 \pm 0.01$					
Sialon/SA/								
290°C	$10.6 \pm 0.3$	$29.5 \pm 10$	$27.0 \pm 2$					
$200^{\circ}C$	$1.8 \pm 0.3$		_					
150°C	$1.4 \pm 0.2$							

-, not determined.

form of soluble silicic acid. Consequently, the equilibrium is reached and solution becomes saturated with respect to possible secondary phases, which precipitate at the surface of the material and form a passivation layer.

The mechanism of dissolution of sialon in aqueous solutions could not be established unambiguously, but based on the results obtained in this work the following reaction (Eq. 6) could possibly be proposed for the reaction process:

$$Si_{2}Al_{4}O_{4}N_{4} + 2(n+2)H_{2}O + 12H^{+}$$
  

$$\rightarrow 4Al^{3+} + 4OH^{-} + 2SiO_{2}nH_{2}O + 4NH_{4}^{+}$$
(6)

Ammonium detected in the eluates from sialon ceramics could originate not only from cleavage of Si–N but also of Al–N bonds. Exposure of AlN to water results in formation of aluminum hydroxides and hydroxid-oxides, according to the following reactions<sup>27,28</sup>:

$$-AlN - +2H_2O \rightarrow AlOOH(amorph) + NH_3$$
 (7)

$$AlOOH(amorph) + H_2O \rightarrow Al(OH)_3(crystal)$$
 (8)

Unlike for material S the presence of aluminum along with Si dissolved in solution as silicic acid is likely to shift the equilibrium resulting in the formation of insoluble aluminosilicate or hydroxyaluminosilicate phases at the very beginning of the dissolution process. The formation of hydroxyaluminosilicates requires the prior formation of  $Al(OH)_3$  solid. In aqueous environment formation of  $Al(OH)_3$  solids appears greatest at pH above 6.0.<sup>29</sup> The reaction between aluminum and silicic acid in solution can be then defined according to the following equation<sup>30</sup>:

$$Al^{3+} + Si(OH)_4 \Leftrightarrow AlOSi(OH)_3^{2+} + H^+$$
(9)

The protective layer of precipitates slows down the process so that further dissolution of S and SA ceramics is controlled either by diffusion of  $NH_3$  or water molecules through precipitated layer or by solubility of the primary corrosion products.

In both studied ceramics corroded in NaCl solution the destruction of surface layer of corrosion products appeared to contribute to more severe dissolution of the materials. Based on similar observations of the influence of various, especially halide, anions, on the corrosion of stainless steels and nickel-based alloys<sup>12,13</sup> one can speculate that the chloride anion, as an aggressive agent in aqueous NaCl solution promotes destruction of the protective oxide layer. Such local destruction of the layer enables direct access of water, which then reacts with freshly exposed surface of the material, thus enhancing severity of the attack.

The penetration of corrosion media through the precipitated layer then results in its cracking and peeling off (the places marked with arrows in the Figs. 8(b) and 9(b)). This would in turn restart the corrosion process at freshly exposed surface. Moreover, the sodium ions together with Al ions are believed to shift the equilibrium towards precipitation of sodium aluminosilicates, such as paragonite identified in precipitation layer. Dissolution restarts due to depletion of solution from precipitating elements. N is not incorporated into any secondary phase detected by XRD, and remains in solution in the form of dissolved ammonium ion.

### V. Conclusions

Two kinds of tests, both under static and *quasi*-dynamic conditions, were applied in order to understand dissolution mechanism of  $Si_3N_4$  and sialon ceramics under subcritical conditions in neutral aqueous solutions. The corrosion rates for both ceramics are increasing with temperature. The tests carried out under static conditions enabled identification of precipitated corrosion products after saturation was achieved under the conditions of most severe attack at 290°C. The corrosion tests performed under quasi-dynamic conditions facilitated determination of initial dissolution rates at 290°C and calculations of activation energies. Both studied ceramics dissolved by preferential attack of Si-N bonds in the matrix accompanied by the release of NH<sub>3</sub> and formation of protective, mostly oxide layer of corrosion products at the surface.

In Si<sub>3</sub>N<sub>4</sub> ceramics, the severity of corrosion attack increased with time and temperature of corrosion. Corrosion pits were formed at the surface in the initial stage of the process. Yttrium silicate oxynitride grain-boundary phase was found to be highly resistant in both tested media. The Si<sub>3</sub>N<sub>4</sub> ceramics thus corroded preferentially by congruent dissolution of Si<sub>3</sub>N<sub>4</sub> matrix grains irrespective of the used corrosion solution, with initial dissolution rates of 15.0 and 20.1 mmol  $(m^2 \cdot h)^{-1}$  in deionized water and NaCl solution, respectively, as determined at 290°C. The apparent activation energies in deionized water and in the NaCl solution were  $73.6\pm8$  and  $69.3\pm16$  kJ/mol, respectively, indicating the corrosion was controlled either by surface chemical reactions or by diffusion of H<sub>2</sub>O in protective silica layer. Mechanical destruction of protective SiO<sub>2</sub> layer in NaCl solution is considered as the main reason for renewal of dissolution of Si<sub>3</sub>N<sub>4</sub> at 290°C under static conditions.

The original assumption that the corrosion resistance of Si<sub>3</sub>N<sub>4</sub>-based materials can be enhanced by dissolution of alumina in the crystal structure, creating sialon in the process, was not confirmed. The likely mechanism of corrosion of sialon ceramics was preferential disruption of Si-N and Al-N bonds in (Si, Al)ON<sub>2</sub> tetrahedra, with aluminum released into solution precipitating in the form of insoluble hydroxyaluminosilicates once the saturation concentration was attained. Apparent activation energy of dissolution of sialon in deionized water was  $29.5 \pm 10$  kJ/mol and initial dissolution rate at  $290^{\circ}$ C was 10.6 mmol  $(m^2 \cdot h)^{-1}$  which is comparable to dissolution rate determined for Si<sub>3</sub>N<sub>4</sub> ceramics. Protective Al<sub>2</sub>O<sub>3</sub> layer was formed in early stage of interactions of material with deionized water. The presence of aluminum in aqueous NaCl solution together with Si and Na<sup>+</sup> ions resulted in early achievement of saturation with respect to formation of corrosion products, NaAl<sub>3</sub>Si<sub>3</sub>O<sub>10</sub>(OH)<sub>2</sub> and AlOOH. In addition, nearly threefold increase of dissolution rate of sialon in aqueous NaCl solution at 290°C was observed in comparison to dissolution in deionized water, achieving the value 27.0 mmol  $\cdot$  (m<sup>2</sup> · h)<sup>-1</sup>. Penetration of aggressive chloride anions through protective layer of corrosion products is proposed to contribute to destruction of the layer and renewal of the exposure of vulnerable material surface to corrosion medium.

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