

# Hot-Corrosion Behaviour of Silica and Silica-Formers: External *versus* Internal Control

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## Abstract

*Hot corrosion of silica and silica-formers was investigated in powder experiments and using Na<sub>2</sub>SO<sub>4</sub>-pellets on polished samples in air or oxygen. While silica reacts only mildly, silica-formers show strong gas-producing reactions. Worm-like textures of Na-silicate glasses appear on the surface. The texture is seen as due to the interaction of two immiscible liquids, where the bottom one (Na-silicate) has a higher surface energy than the top one (Na-sulfate). The dynamic nature of this interaction does not only account for the distribution of bubbles and provides sites for pit formation, it also promotes the enhancement of the main difference between silica and silica-formers: the latter act as reducing agents, either directly or via an oxygen gradient in the oxide layer, decomposing the sulfate with pressures of SO<sub>2</sub> > 1 bar. Only after a critical thickness is reached a closed Na-silicate layer exists and external parameters such as the p(SO<sub>3</sub>) of the external atmosphere play a key role. Hot corrosion of silica-formers consists thus of a rapid, internally controlled initial reaction, followed by external control. The strong initial reaction with its interplay of chemical and physical process is a major factor preconditioning the mode and strength of attack.*  
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## 1 Introduction

The hot corrosion behaviour of structural materials is a key issue for their application in a number of combustion environments. Although Si and Si-based non-oxide ceramics have been studied for years, the exact mechanisms and the differences between

the corrosion behaviour of the non-oxides (Si, Si<sub>3</sub>N<sub>4</sub>, SiC) and the oxide SiO<sub>2</sub> are still not completely understood.

To gain a better understanding of the processes taking place, some basic experiments have been performed in the laboratory. The experiments were conducted in air or oxygen, thus in atmospheres which are not identical to combustion atmospheres. Nonetheless we can show that they give valuable insights into the problem as some of the basic features of the hot corrosion of silica-formers seem to be controlled by internal parameters and to less extent by external parameters.

## 2 Experiments

All experiments were carried out in flowing air in a specially developed vertical tube furnace,<sup>1</sup> which allowed a rapid heating of the samples and a subsequent quenching to room temperature at the end of the runs. The samples were subjected to temperatures between 900 and 1150°C for times between 10 min and 24 h.

Powder experiments were conducted using fine powders of SiO<sub>2</sub> (fumed, Aldrich), α-Si<sub>3</sub>N<sub>4</sub> (LC-12N, HC-Starck) and Si (ground from a single crystal wafer). They were carried out in high-purity Al<sub>2</sub>O<sub>3</sub> crucibles by pouring the powder as a bottom layer and adding solid high-purity Na<sub>2</sub>SO<sub>4</sub> powder (Aldrich) on top.

After the powder experiments were complete the crucibles were cut in half to obtain two specimens. One of the pieces was then treated with water to dissolve the unreacted Na<sub>2</sub>SO<sub>4</sub>. Even though some Na-silicates are water soluble, most of those of interest here cannot be removed by water, hot or cold,<sup>2</sup> and will thus remain as part of the sample. To determine the phase content, crushed fragments of the samples were examined using XRD-techniques.

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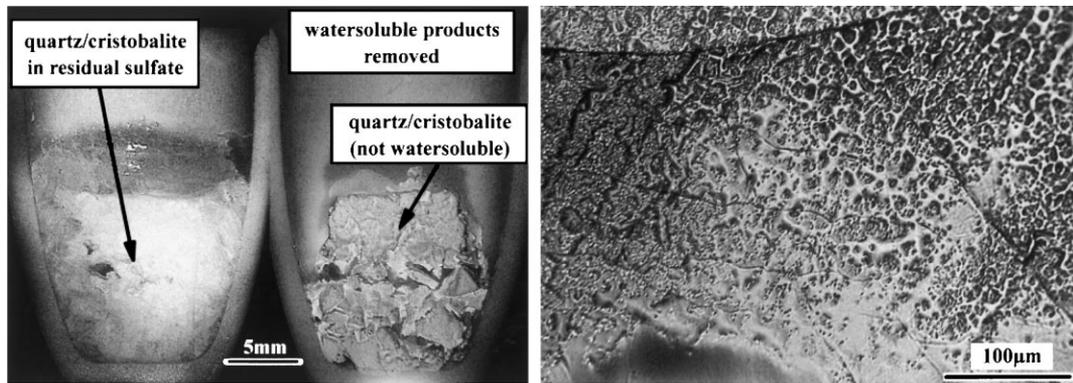


Fig. 1. Left:  $\text{SiO}_2$ -powder +  $\text{Na}_2\text{SO}_4$  after 24 h at  $900^\circ\text{C}$ ; Right: single crystal of quartz +  $\text{Na}_2\text{SO}_4$ , after 10 min at  $1150^\circ\text{C}$ , surface view.

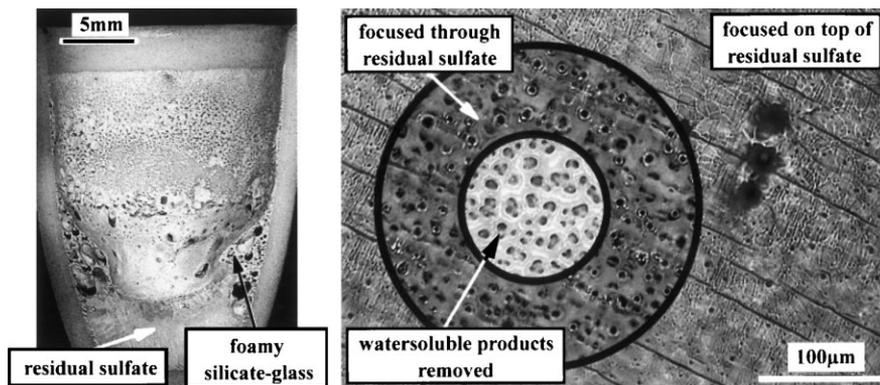


Fig. 2. Left:  $\text{Si}_3\text{N}_4$ -powder +  $\text{Na}_2\text{SO}_4$  after 24 h at  $900^\circ\text{C}$  for 10 min; Right: HP- $\text{Si}_3\text{N}_4$  (NC 132) at  $1150^\circ\text{C}$ , surface view.

Corrosion experiments using a quartz-crystal and two types of  $\text{Si}_3\text{N}_4$  ceramics (Kyocera SN 220M, Norton NC 132) were executed by placing  $\text{Na}_2\text{SO}_4$  pellets on the polished surfaces of the samples. After these experiments samples were investigated directly in a second step after water treatment for  $\text{Na}_2\text{SO}_4$  removal.

### 3 Results

In the temperature range between 900 and  $1150^\circ\text{C}$  the reaction between  $\text{SiO}_2$  and  $\text{Na}_2\text{SO}_4$  was slow, resulting in the formation of small amounts of glass (Fig. 1). The silica-powder turned into blocky crystalline agglomerates of quartz and cristobalite.

In contrast, all non-oxides showed a rather violent gas producing reaction with the formation of large amounts of a foamy glass. In the case of the Si-powder elementary sulfur could be found. A strong smell of  $\text{H}_2\text{S}$  indicated reactions between the sulfur or sulfides and the humidity of air.<sup>3</sup> Fig. 2 shows examples for  $\text{Si}_3\text{N}_4$ .

Optical investigations of the surface of the polished  $\text{Si}_3\text{N}_4$ -ceramic (SN 220M, Kyocera) after the corrosive treatment with the  $\text{Na}_2\text{SO}_4$  melt at  $900^\circ\text{C}$  in air for 22 h revealed worm-like structures (Fig. 3). The same structures were observed during corrosion experiments using the quartz single

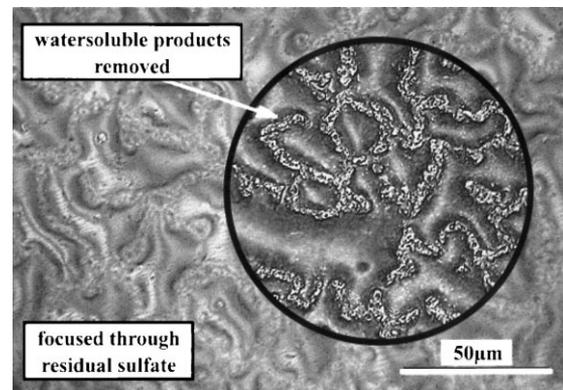


Fig. 3. Worm-like features on the surface of  $\text{Na}_2\text{SO}_4$ -treated  $\text{Si}_3\text{N}_4$  (SN 220M) after 22 h at  $900^\circ\text{C}$ .

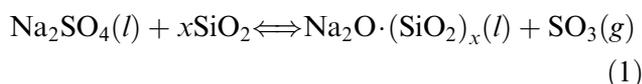
crystal [cp. Fig. 1(b)] and similar features were described by Lawson *et al.*<sup>4</sup> for silica.

From Fig. 3 it is evident that those structures are not an artifact produced by the water treatment as they were visible through the sulfate and simply remained after the removal of the water-soluble components.

### 4 The Chemical Mechanism

These observations allow modification of the models used so far to describe the rather strong reaction during the hot-corrosion of Si-bearing

materials which was ultimately explained by the hot corrosion of  $\text{SiO}_2$ . In these models, a reaction of the  $\text{Na}_2\text{SO}_4$  melt with the  $\text{SiO}_2$ -scale formed on the surface of non-oxide ceramics is proposed which leads to the formation of a Na-silicate melt according to reaction (1).



A solid  $\text{SiO}_2$  layer changes thus into a liquid silicate melt with an increased gas permeability and hence leads to significantly accelerated oxidation.

The precondition for reaction (1) is the decomposition of the sulfate according to



The  $\text{Na}_2\text{O}$  activity required for the silicate-formation [reaction (1)] is hence directly dependent upon the partial pressure of  $\text{SO}_3$ . In other words, the externally applied pressure of  $\text{SO}_3$ , e.g. by a combustion process, should be the prime control for the hot corrosion process. This aspect has been described in detail by Jacobson and co-workers in a number of publications.<sup>5-8</sup>

If there is no applied external  $p(\text{SO}_3)$ , as would be the case for treatments in air or oxygen, we may calculate a natural decomposition for  $\text{Na}_2\text{SO}_4$ . For  $900^\circ\text{C}$  in pure oxygen such calculations using CHEMSAGE<sup>9</sup> give  $\text{Na}_2\text{O}$ -activities of approximately  $8 \times 10^{-8}$ .

The calculation of the activity of  $\text{Na}_2\text{O}$  for  $\text{Na}_2\text{SO}_4$  in  $\text{O}_2$  above is in fair agreement to values quoted by Lawson *et al.*<sup>4</sup> However, there is a discrepancy to the measured values of Jacobson.<sup>10</sup> While calculations using CHEMSAGE give an agreement within one magnitude of power with the measured values for conditions with external supply of  $\text{SO}_3$ , the  $\text{O}_2$  treatment data differ strongly from our calculation ( $10^{-12}$  instead of  $10^{-8}$ ). The value of  $10^{-12}$  for the activity of  $\text{Na}_2\text{O}$  would however exclude any reaction with silica as it is in the range of coexisting  $\text{Na}_2\text{SO}_4 + \text{SiO}_2$  (Fig. 4). Reactions are observed in the experiments and thus we assume that there are unknown problems in the determination of the activity of  $\text{Na}_2\text{O}$  in  $\text{Na}_2\text{SO}_4$ . The calculated values are high and correspond to the coexistence of  $\text{Na}_2\text{SiO}_3$  and  $\text{Na}_2\text{SO}_4$ , as can be seen from Fig. 4.

As a consequence, the conditions are basic for  $\text{SiO}_2$  and it must react towards a sodium silicate. However, the formed Na silicate should be  $\text{Na}_2\text{SiO}_3$ , which is crystalline at  $900^\circ\text{C}$ . There is no equilibrium between this silicate and the  $\text{SiO}_2$  substrate. Thus more  $\text{SiO}_2$  has to be dissolved, shifting the composition towards  $\text{Na}_2\text{Si}_2\text{O}_5$ , which is liquid at  $900^\circ\text{C}$ .

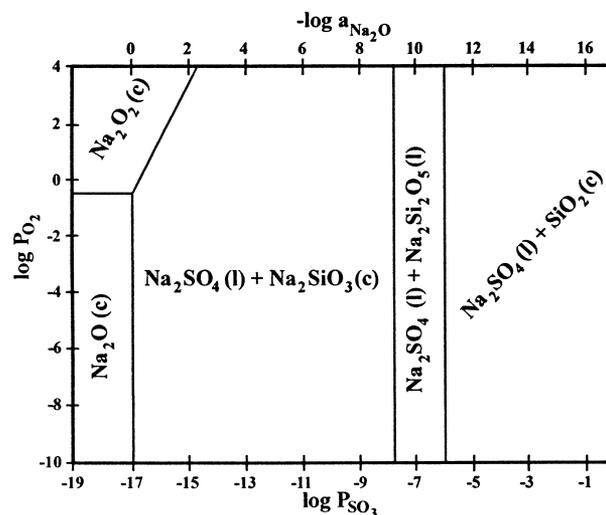


Fig. 4. Stability diagram at  $900^\circ\text{C}$  in the system Na-Si-S-O after Shi *et al.*<sup>11</sup>

Calculations in this work and those of Shi *et al.*<sup>11</sup> are based on available thermodynamic data, which usually contain data for stoichiometric compounds. At  $900^\circ\text{C}$  the liquid composition for an equilibrium with crystalline  $\text{SiO}_2$  would rather be  $\text{Na}_2\text{O} \cdot 3.3 \text{SiO}_2$  according to the phase diagram of the  $\text{Na}_2\text{O}-\text{SiO}_2$  system.<sup>12</sup>

A calculation, which would include these true compositional data would end up with even lower  $\text{Na}_2\text{O}$  activities for the boundary  $\text{SiO}_2/\text{Na}$  silicate melt. The calculation thus predicts that Na silicate melt will form between  $\text{Na}_2\text{SO}_4$  and  $\text{SiO}_2$  with a concentration gradient with relatively high  $\text{SiO}_2$  contents and lower  $\text{Na}_2\text{O}$  activities towards the silica and relatively low  $\text{SiO}_2$  and high  $\text{Na}_2\text{O}$  activities towards the sulfate in order to satisfy both the equilibrium with substrate at the layer bottom and the sulfate melt at the top. This layer should have protective character, and any further reaction would then be controlled by the diffusion of  $\text{Na}_2\text{O}$  through the Na silicate-layer as Na diffusion is much faster than  $\text{O}_2$  diffusion in silicate glasses.<sup>13,14</sup>

This is consistent with our experiments, which show that the reaction between  $\text{SiO}_2$  and the sulfate melt proceeds fairly slow. The most notable effect is the nucleation and growth of crystalline  $\text{SiO}_2$  modifications from the fumed silica with its high starting surface area. It is well known that  $\text{Na}_2\text{O}$  can be incorporated into  $\text{SiO}_2$  modifications, namely tridymite, but also into cristobalite and fosters their crystallisation.<sup>15,16</sup> The crystal growth reduces the effective surface area and slows down reaction speed.

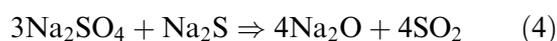
Thus the  $\text{SiO}_2-\text{Na}_2\text{SO}_4$  interaction alone cannot be responsible for the strong reactions observed during the hot corrosion of Si-based non-oxide ceramics in our laboratory experiments. The difference in the behaviour of  $\text{SiO}_2$  and the non-oxides

may be better understood considering the rectification of industrial glasses. Here residual gases, which are dissolved in the glass melt are removed by adding  $\text{Na}_2\text{SO}_4$  as rectifying agent<sup>17</sup> together with sulfides like  $\text{BaS}$ ,  $\text{Na}_2\text{S}$ ,  $\text{ZnS}$  or, in the simplest case, carbon.<sup>18</sup> These act as reducing agents which promote a complete dissociation of the added  $\text{Na}_2\text{SO}_4$ .

Thermodynamic calculations show that at  $900^\circ\text{C}$  the sulfate is not stable under reducing conditions and that a formation of  $\text{Na}_2\text{S}$  takes place at a  $p(\text{O}_2)$  below  $\approx 10^{-14}$  bar according to



Thus the addition of sulfides will act likewise to remove excess  $\text{Na}_2\text{SO}_4$  by the net reaction



The increase of the  $\text{Na}_2\text{O}$  activity in a  $\text{Na}_2\text{SO}_4$  melt at  $1000^\circ\text{C}$  by addition of free carbon described by Jacobson *et al.*<sup>7</sup> is based upon the same principle.

Strong gas production in our experiments with  $\text{SiO}_2$  formers and thus it is self-evident that those may act as reducing agents. All silica formers have native oxide scales even at room temperature and the equilibria between them and  $\text{SiO}_2$  require extremely low  $p(\text{O}_2)$  levels, at  $900^\circ\text{C} < < 10^{-14}$  bar). The observation of an oxynitride sub-layer at the interface between layer and pure  $\text{Si}_3\text{N}_4$ <sup>19</sup> is an experiment evidence for a very low  $p(\text{O}_2)$ .

There is an ongoing debate about the oxygen concentration profile in an  $\text{SiO}_2$  scale on  $\text{Si}$ ,  $\text{Si}_3\text{N}_4$  or  $\text{SiC}$ . A high concentration of  $\text{O}_2$  at the substrate/scale interface is only conceivable if  $\text{SiO}_2$ -formation is governed by reaction control, which would be plausible considering the very high  $\Delta G$ -Values for those reactions. This would lead to linear oxidation kinetics. However, the oxidation of  $\text{SiO}_2$  formers is very well described by parabolic laws,<sup>20,21</sup> which is evidence for diffusional control.

It is clear that even a parabolic behaviour requires the presence of an initial  $\text{SiO}_2$  layer and that there is an initial period of time, in which the behaviour is basically linear.<sup>22</sup> During this period reaction speed or transport in the gas phase is the rate-limiting step. The thickness of the initial layer is in the order of a few tens of Angström, the times of the linear behaviour are of considerable lengths at low temperatures, but at  $900^\circ\text{C}$  they are well below an hour.

The hypothesis to satisfy the contradiction put forward by Luthra ('mixed control'<sup>23,24</sup>), is more or less based on this interplay between linear and parabolic behaviour. Even if this model would describe the process accurately there is still a very low  $p(\text{O}_2)$  in the vicinity of the interface.

The starting supply of  $\text{SiO}_2$  to form Na silicates comes from the pre-existing scale. Depending on the choice of model for the gradient profile, the depth, at which a low  $p(\text{O}_2)$  is encountered will vary. But invariably the initial consumption of a thin  $\text{SiO}_2$  scale will meet those conditions very quickly.

The 'reaction control' model would not make the situation any better: the sulfate melt could then consume the whole layer only to see a bare surface of  $\text{Si}$ ,  $\text{Si}_3\text{N}_4$  or  $\text{SiC}$ . The latter would then turn directly into the reducing agents and establish the extremely low  $p(\text{O}_2)$  at the interface to the silicate melt.

In any case Na silicate formation has to be considered from a different point of view, i.e. its dependence on oxygen potential. The equilibrium between sulfate, silica and silicates [eqn. (1)] may be rewritten as



This formulation is preferred to the usual formulation with  $\text{SO}_3$  as a product gas because  $\text{SO}_2$  will always be the main species, particularly under reducing conditions. For  $900^\circ\text{C}$  a partial pressure of 1 bar  $\text{SO}_2$  is reached at a  $p(\text{O}_2)$  of approximately  $10^{-12}$  bar. At the condition of sulfide formation, i.e.  $p(\text{O}_2) \approx 10^{-14}$  bar it would already exceed 10 bars.

The calculation is for a stoichiometric melt of  $\text{Na}_2\text{Si}_2\text{O}_5$ . Similar calculations with a composition of  $\text{Na}_2\text{SiO}_3$  with its higher  $\text{Na}_2\text{O}$  activity gives lower values for  $p(\text{SO}_2)$ . As discussed above the true composition of the melt in equilibrium with  $\text{SiO}_2$  should be  $\text{Na}_2\text{O} \cdot 3.3\text{SiO}_2$ . Thus with this composition we have a  $\text{Na}_2\text{O}$  activity, which is lower than  $\text{Na}_2\text{Si}_2\text{O}_5$ . Consequently even higher pressure of  $p(\text{SO}_2)$  would result, if thermodynamic data for the correct  $\text{SiO}_2$  rich Na silicate melt composition at the  $\text{SiO}_2$  silicate interface were available.

Thus the consumption of  $\text{SiO}_2$  in a low  $p(\text{O}_2)$  environment will result in very high pressures of  $\text{SO}_2$  even before the condition of sulfide formation is met. Indeed we have no evidence for  $\text{Na}_2\text{S}$  in the scales. The elementary S observed in Si-powder experiments is attributed to the condensation from gaseous  $\text{S}_2$  during quenching. The value of  $p(\text{S}_2)$  in the gas phase will also be high under reducing conditions.

Whether this condition leads to violet bubble formation or transport through the scale by other paths is probably governed by temperature and other parameters such as the layer thickness at the time of encountering the low- $p(\text{O}_2)$  conditions.

## 5 To Make Things Worse: Surface Stresses

As shown above [Figs 1(b) and 3] the hot corrosion process leads to peculiar worm-like textures which are growing with time (Fig. 6 after 30 min, Fig. 3 after 22 h). In the glass industry similar structures are known to be the result of the interaction of completely or partial immiscible liquids during the melting of glasses (Fig. 5).<sup>25,26</sup>

These textures are usually observed on a small scale. But looking closely onto the surface of hot corroded  $\text{Si}_3\text{N}_4$  (Fig. 6) it is apparent that the valleys between the 'worms' of Na silicate melt are filled with equally worm-like textures on a small scale. There is thus a fractal character of these textures on different size levels, the initial structure may well be comparable to Fig. 5. It is therefore likely that the observed worm-like structures are the result of immiscibility-related phenomena during the hot-corrosion process.

As can be seen from Figs 1–3 there are two coexisting melts present during the corrosive attack: a  $\text{Na}_2\text{SO}_4$  melt on the top and the newly formed Na silicate melt at the interface to the substrate. This silicate melt is  $\text{SiO}_2$ -rich because it is not soluble even in hot water.<sup>2</sup> Reference to phase diagrams<sup>27,28</sup> confirms the liquid immiscibility at those compositions, a complete miscibility only exists for  $\text{Na}_2\text{O}$ -rich compositions.

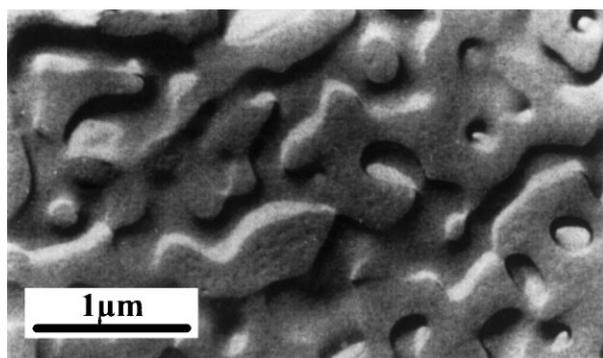


Fig. 5. Immiscibility-derived textures in the system  $\text{BeF}_2\text{-LiF}$ .<sup>26</sup>

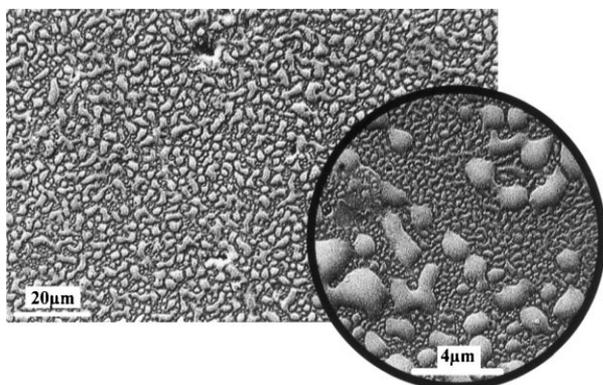


Fig. 6. SEM-surface view of a  $\text{Si}_3\text{N}_4$  (NC 132) after 30 min of  $\text{Na}_2\text{SO}_4$  treatment at  $900^\circ\text{C}$ .

The surface tensions of  $\text{SiO}_2$ -rich silicate melts and  $\text{Na}_2\text{SO}_4$  melts at  $900^\circ\text{C}$  have values of about 300 and 190 mN/m, respectively.<sup>13,29,30</sup> The tendency of a liquid with higher surface energy to form droplets in a liquid with lower surface energy is well known: it is the very base of every emulsion. Jebsen-Marwedel and Brückner studied the details of the behaviour of glass and salt melts.<sup>31–33</sup> They showed that eddies at the interface between the liquids will form and support the persistence of isolated areas of two liquids, even if they come from an initial two-layer situation.

In the hot-corrosion experiments of this study, the density of the silicate-melt is higher ( $> 2.2 \text{ g cm}^{-3}$ ) than the density of the sulfate melt ( $2.104 \text{ g cm}^{-3}$ ). Therefore, the new formed silicate melt will tend to remain at the interface to the substrate in the shape of the observed worm-like structures. The consequences of this behaviour are outlined in our model below.

## 6 External and Internal Control

In the case of  $\text{SiO}_2$  (Fig. 7) a Na silicate melt is formed at the interface  $\text{Na}_2\text{SO}_4\text{-SiO}_2$  by the reaction of  $\text{SiO}_2$  with the basic sulfate melt ( $a_{\text{Na}_2\text{O}} > 1 \times 10^{-11}$  at  $900^\circ\text{C}$ ). This melt is enriched in  $\text{SiO}_2$  from the substrate, and so develops a gradient with a composition towards the equilibrium with condensed  $\text{SiO}_2$ . This composition may be read from the phase diagram.

Due to their different surface tensions and the turbulence effects at their interface local areas of the silicate melt will form hillocks on the surface of the  $\text{SiO}_2$ , dragging the silicate melt locally away from its point of origin. This produces new bare  $\text{SiO}_2$  surfaces, the renewed direct contact between the sulfate melt and the  $\text{SiO}_2$  again promotes the formation of Na silicate. As a consequence progressively larger melt areas form.

This reaction stops, when we have a force balance between the surface tension action and the mass and the viscosity of the silicate formed, i.e. there will be a critical point, when the silicate melt forms a closed layer. Alternatively the process stops when its cause is removed, i.e. when the  $\text{Na}_2\text{SO}_4$  is used up or evaporated.

At the interface to the substrate, the silicate melt is in contact with the  $\text{SiO}_2$ , which, if it is not already the starting phase, will turn into tridymite/cristobalite. Since these crystalline phases contain Na, they will be less reactive, slowing down the process. The corrosion rate is then only influenced by the  $\text{Na}_2\text{O}$  activity of the sulfate and the diffusion of  $\text{Na}_2\text{O}$  through the silicate layer and into the bulk  $\text{SiO}_2$ . The reaction speed will then be liable to

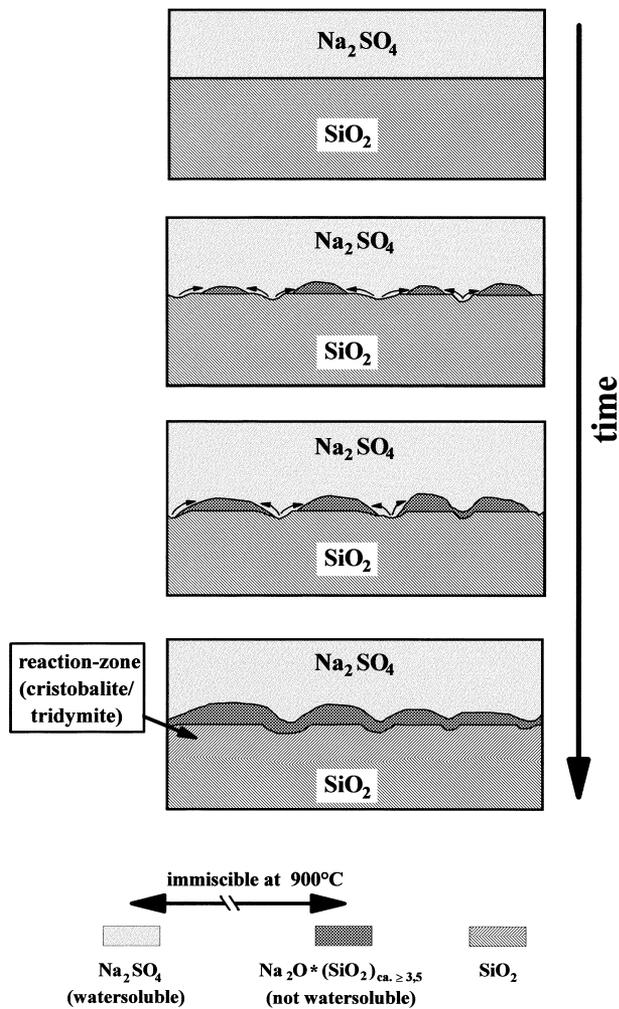


Fig. 7. Proposed schematic model of the hot corrosion attack on  $\text{SiO}_2$  (see text for details).

changes by variations of the  $\text{SO}_3$  vapour pressure of the outer atmosphere. Thus it is envisaged that after a short initial period, in which a wavy silicate layer is produced, external control is an effective control parameter.

Although the starting conditions for the corrosive attack of a  $\text{Na}_2\text{SO}_4$  melt on  $\text{Si}_3\text{N}_4$  are identical, the further reaction differs significantly as shown in Fig. 8. The thin passivating native  $\text{SiO}_2$  layer on the  $\text{Si}_3\text{N}_4$  ceramic starts to react with the basic sulfate melt in the same way as before to form Na silicate.

By the time the reaction front reaches the level of low  $p(\text{O}_2)$  the sulfate will decompose according to eqn (5) and bubbles of  $\text{SO}_2$  may appear. The process is modulated by the action of surface stresses. In the same way as for silica the newly formed silicate melt concentrates in hillocks, exposing areas with even lower  $p(\text{O}_2)$ . The valleys between the hillocks are thus perfect sites for bubble formation.

This process may explain the bubble distribution. The hillocks and valleys form as a consequence of surface tensions even for initial planar layers and their distribution is therefore of random

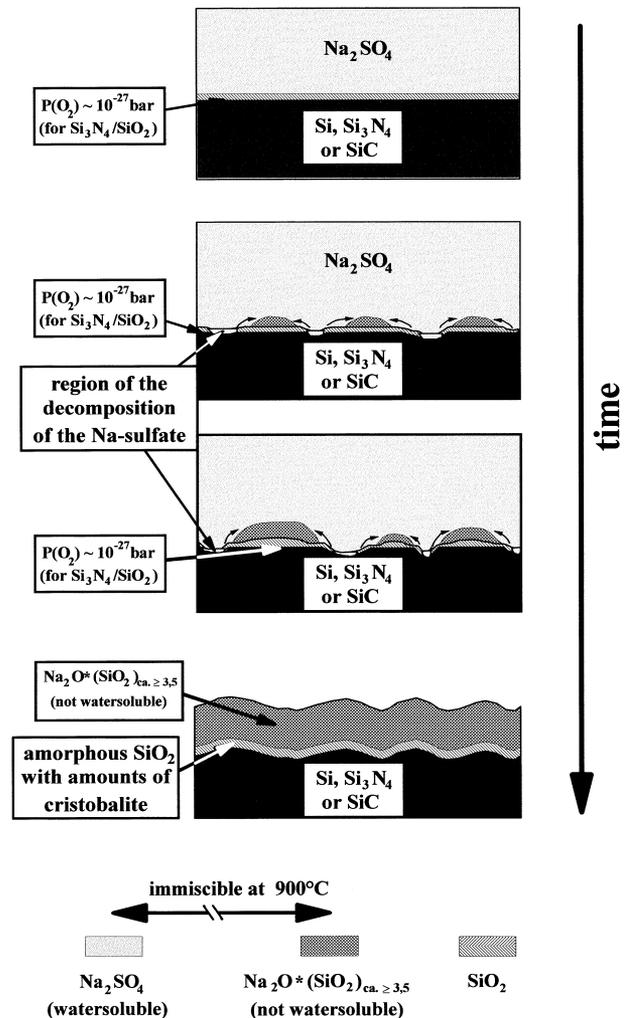


Fig. 8. Proposed schematic model of the hot corrosion attack on non-oxide Si-based ceramics (see text for details).

statistical nature. Their distribution may thus be completely unrelated to the microstructure of the substrate. A slight initial modulation is indicated for  $\text{Si}_3\text{N}_4$  substrates with their comparatively large areas of grain boundary phase, which may result in local chemistry changes of the silica consumed. However, the hillocks may move on the surface<sup>31</sup> and therefore the initial distribution pattern may vanish to yield a completely random pattern.

The location of the bubbles may precondition the paths for fast oxidation, if they burst or thin the sulfate melt. Thus pitting is a possible consequence, which is evidenced by the experimental study of Jacobson and Smialek<sup>34</sup> on SiC.

A few more consequences may be derived from this situation: depending on the details of oxygen gradients and oxidation kinetics one may hypothesise that bare  $\text{Si}_3\text{N}_4$  comes into contact with the sulfate melt. In this case it should react differently. According to calculations using the program CHEMSAGE<sup>9</sup> the main reaction is:



Since it involves an equilibrium between  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$  it will maintain the extremely low  $p(\text{O}_2)$ , for  $900^\circ\text{C} \approx 10^{-27}$  bar. Thus here  $\text{N}_2$  production along with sulfide formation would take place. From this situation again a gradient in oxygen would develop, so that the  $\text{SiO}_2 + \text{Na}_2\text{S}$  layer is topped by a layer of Na silicates with or without silica, which is in turn capped by the sulfate.

So far no direct evidence for this behaviour, has been observed, but investigations are continuing.

Again, only when a sufficiently thick closed silicate layer has formed or all the sulfate has been consumed, the process will turn into a diffusional problem. However, since the process here involves strong gas formation and thereby causes much greater disruptions, it is envisaged that the dynamic situation will persist for much greater times or greater thickness of the layer than in the case of silica.

Below the hillocks, and ultimately everywhere on the interface to the substrate,  $\text{SiO}_2$  is formed by diffusion of oxygen and reaction with  $\text{Si}_3\text{N}_4$ . Cristobalite crystallizes and the corrosion rate is controlled through external parameters like it is for silica. The difference is that a main portion of the damaging corrosion has occurred before external control can take place: there is no feasible external condition to stop reaction (5) when a low  $p(\text{O}_2)$  is involved. Thus in the case of silica formers there is a long and very active period of internal control.

It is therefore not necessary to involve secondary phases like free carbon in  $\text{SiC}^5$  to have reducing agents to make hot corrosion as effective as it is. This will certainly promote it as well, but the silica formers can do it by themselves. Further evidence for this is for example the finding of Kern *et al.*,<sup>35</sup> who reported that the corrosive attack on  $\text{Al}_2\text{O}_3/\text{SiC}$  composite materials by molten  $\text{Na}_2\text{SO}_4$  increases in regions with SiC particles.

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