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Corrosion of Non-Oxide Ceramics

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Abstract: Corrosion of non-oxide ceramics is reviewed here concentrating on Si_3N_4- and SiC-based materials. The basic attack types (active I and II, passive, local) and the factors influencing them are described. It is shown that material engineering (choice, microstructural development, post-treatment, protection) is capable of improving corrosion resistance significantly. © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Corrosion is the physical and chemical alteration of a material resulting from its interaction with the application environment. In order to react with the environment the material must be in non-equilibrium with it. This is true for practically all non-oxide ceramics in almost every application environment. Their applicability—not unlike metals—thus rests on the kinetics of the processes. There are several parameters used to classify corrosion: the attack mode, the medium and the locus. The appropriate names associated with these parameters are shown in Fig. 1. There are many reasons for the often observed degradation of properties caused by corrosion: From simple geometric relations (the cross-section carrying the load may, for example, decrease in size) the list runs to pitting, phase change induced stress, grain separation and other features. The difficulty of dealing with corrosion behaviour is caused by the variability of actual chemical environments and that it is not a material property but a system property. The definition of physical conditions on top of chemistry and microstructure of the material and the surroundings is crucial for the evaluation of corrosion behaviour. The main regions of attack of Si_3N_4 and SiC are crudely outlined in Fig. 2. As a rule of thumb, the 'passive' region in Fig. 2 is the most promising region for long-time applications and all types of 'active' corrosion have to be avoided. The details of the processes are described below, here we only want to emphasize the possibilities for material engineering: The expansion of the modus 'active II' may be controlled by tailoring the material at hand. Recently the corrosion behaviour has gained increasing attention[1–5] as ceramics have to prove high reliability at high temperatures. The main possible influences of corrosion on strength and lifetimes are illustrated in Fig. 3: Crack healing and wedging may have beneficial effects on lifetime, stress corrosion may induce faster slow crack growth or creep, limiting lifetimes.

Corrosion is thus capable of influencing strength both in short and long times. While these shifts are relatively easily measured, the biggest problem is the nucleation and subsequent growth of new flaws like pits as they will need an incubation period to take effect and this is poorly understood, hard to predict and thus one of the major challenges in corrosion science.

It appears that things like the formation of cracks beneath corrosion scales is a measurable feature,[7] just as the connection between bubbles in scales and pits, but the mechanisms await clarification.

2 ATTACK MODES

2.1 Active (I) and passive mode: conditions and transition

The two major corrosion modes (active I, passive) are visualised most easily for the case of attack by hot gases. Here the prime characterisation of atmospheres of interest is in terms of their oxygen content. Partial pressures of oxygen range from several bars in pressurised lean combustion environments

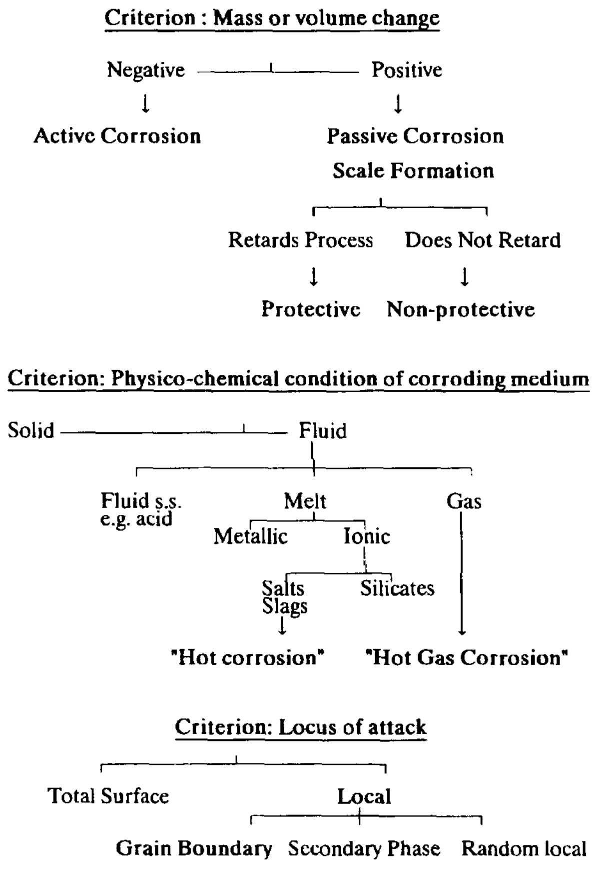

Fig. 1. Three major classification schemes of corrosion.

to extremely low values ($< 10^{-15}$ bar) in coal gasification. Further important classifications are by the activity of CO_x, H_2O, SO_x. Other gas species may be of interest in special environments. Stability calculations yield partial pressures of oxygen as low as $P(O_2) \approx 10^{-15}$–10^{-30} bar for the stable coexistence of SiO_2 with metallic Si or Si-based ceramics in the temperature range 800–1200°C. Thus reactions to yield a layer of SiO_2, which is capable of protecting the material from further attack other than the relatively slow process of diffusion through this layer ('passive oxidation'), should take place over a very wide range of conditions (even high-purity-gases usually contain some ppm or ppb oxygen). Examples for the reaction equations, indicating a weight gain for the material, on which these calculations are based, are:

$$Si + O_2 \rightleftharpoons SiO_2 \tag{1}$$

$$SiC + 1.5\ O_2 \rightleftharpoons SiO_2 + CO \tag{2}$$

$$2\ Si_3N_4 + 1.5\ O_2 \rightleftharpoons 3\ Si_2N_2O + N_2 \tag{3}$$

$$3\ Si_2N_2O + 4.5\ O_2 \rightleftharpoons 6\ SiO_2 + 3\ N_2 \tag{4}$$

The fact that no SiO_2-layer is found on these materials at oxygen pressures much higher than the values predicted by the stability calculations and the fact that this is accompanied by material loss to the atmosphere ('active oxidation') is commonly explained by the so-called 'Wagner-theory':

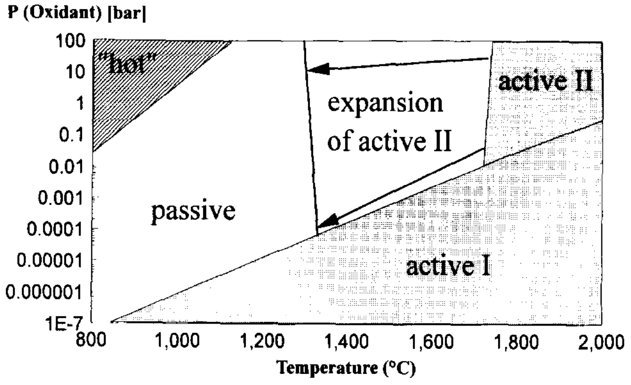

Fig. 2. Schematic regions of main corrosion attack modes of Si_3N_4 and SiC.

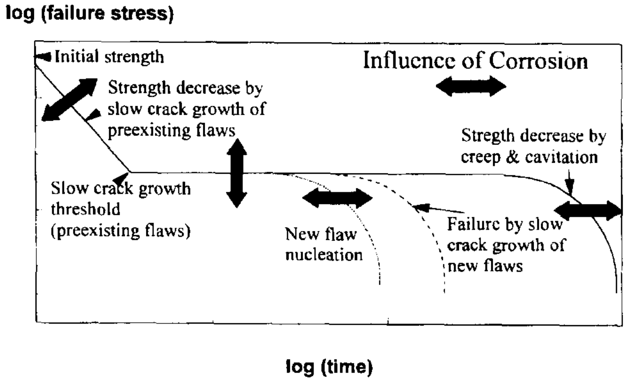

Fig. 3. Schematic illustration of the effect of corrosion on the lifetime of a ceramic component after Tressler[6] and van der Biest & Weber.[7]

Wagner[8] argued that (for silicon) the establishment of a concentration gradient in a boundary layer in the atmosphere adjacent to the sample surface is responsible for this effect. For example, if reaction (1) is fast, depleting the boundary layer in oxygen at the interface between the atmosphere and a Si-containing substrate, then very low local partial pressures may be established, favouring the emanation of the gaseous species SiO instead of SiO_2-formation.

Clearly the removal of material in active corrosion is faster if the partial pressure of the product gas species is higher. This is a function of the material and of the atmospheric composition, temperature and pressure.

The removal depends also on the physical environment: interdiffusion of gas species can be critical in a furnace environment with constant volume. In most technical environments the gas supplied is replenished during the application, which induces a linear relationship between weight loss and time. The corrosion rate in the active mode is strongly influenced by the gas flow mode (laminar or turbulent), which determines the existence of boundary layers,

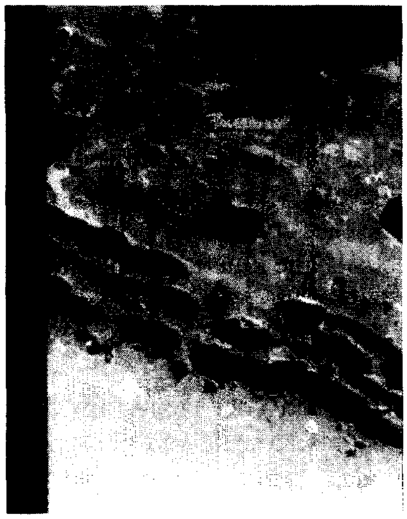

Fig. 4. Cross-section of a sintered Si_3N_4 after 110 h at 1400°C in air: bubbles are trapped at the interface between material (bottom) and scale (top).

and by the ratio of gas speed [volume/time] to exposed surface, which is related to the capacity of the gas to incorporate emitted gas species. Models for corrosion rate prediction under these circumstances are given in Tressler and McNallan[2] and Nickel.[5] From the practical point-of-view the linearity of the kinetics will mean a non-applicability of the material in the active region for most circumstances. The boundary should therefore be known.

A 'true' active–passive boundary can be calculated in terms of the equilibrium partial pressure of the critical reaction between the substrate and the scale material, which is related to the partial pressure of oxygen in the bulk gas by the interdiffusion behaviour of the reacting and product gas species. Most workers on ceramics have applied the Wagner theory. The difficulties here are the complexities of the systems: many equations could be selected as defining the critical partial pressures because intermediate phases like Si_2N_2O or SiO (condensed) may play a role; intermediate steps in the oxidation reactions have accordingly to be considered as possible critical reactions. Further, system properties like the activity of carbon in SiC have to be considered in the evaluation of critical reactions.[9]

Despite such problems with the theories it is clear from experimental evidence[10,11] that the active (I)/passive boundaries for Si_3N_4 and SiC are very similar and coincide roughly with the according line in Fig. 2. From Fig. 2 it is clear that at $T < 1600°C$ many application atmospheres will be in the passive regime for these ceramics.

For AlN both theory and experiment indicate a passive, for C an active oxidation mode in all cases of interest. B-based materials are susceptible to active oxidation at high temperatures. B_4C and BN both form B_2O_3, which has a very low m.p. (≈450°C) and a low boiling point (≈1500°C). Therefore the vaporisation of B_2O_3 becomes appreciable at high temperatures, which results in mass losses in air at $T > 900$–1200°C, depending on the substrate, e.g. pyrolytic BN: 900°C, graphite-like BN: 1200°C,[4] and on the physical environment. Thus zero weight change corrosion is envisaged in special physical environments: the material may be transformed into oxides and thereby gain weight only to lose a balanced amount of it via evaporation.

Active–passive boundaries for species other then oxygen are rarely known. As a rule of thumb, gas species forming highly volatile species (e.g. F, Cl_2 or H_2S forming SiF_4, $SiCl_4$ or SiS from Si-based ceramics) will foster active oxidation, most oxygen bearing species (H_2O, CO_2, SO_2) will oxidise passively. For special atmospheres an appropriate boundary may be calculated thermodynamically.[12]

2.2 Active (II) mode

The active corrosion mode II occurs when the corrosion reaction results in the production of a gas, which cannot be removed fast enough through the formed layer by diffusion or small bubble migration. Then large bubbles form and concentrate in layers, making the condensed part of the scale susceptible to spallation under stress. The temperature of enhanced bubble formation in the scale will coincide for many applications with the upper temperature limit for long-time use. An extreme case has been suggested for SiC at ≈1700–1800°C in air, where the pressure in the bubbles exceeds the atmospheric pressure.[9] Pure Si_3N_4 may have similarily high temperatures limits, but in sintered Si_3N_4 such bubble formation can start at much lower temperatures (down to ≈1300°C) depending on the chemistry and post-treatment of the ceramic. Figure 4 shows a Si_3N_4 with high (Y, Al)-sintering additive contents after 110 h at 1400°C in air.

The corrosion mode 'active II' is thus occurring under conditions which belong to the 'passive' region from the point-of-view of a boundary layer theory. It is an application limit which is highly susceptible to material chemistry and microstructure. This is indicated in Fig. 2 and material engineering can help to extend the useful temperature range.

2.3 Passive mode: kinetics

The kinetics of scale growth in the 'passive' region of Fig. 2 involves three main processes: (1) the gas must be supplied from the bulk gas; (2) the gas has to pass the scale; and (3) the gas has to react with

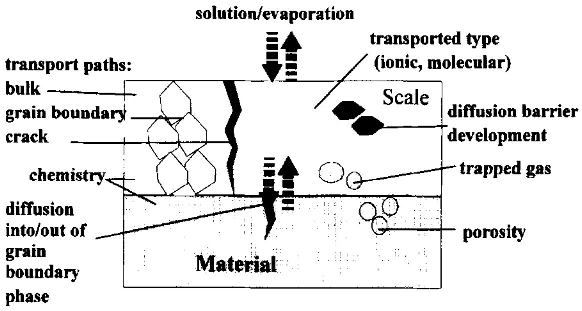

Fig. 5. Illustration of some common parameters influencing the kinetics of passive corrosion.

the material. Any of these steps may be rate limiting and thereby determine the growth law. The classic model for such a process was developed by Deal and Grove[13] for silicon. Under steady state conditions the fluxes of steps 1–3 must be equal. Depending on the values of gas transport coefficient, chemical reaction coefficient and diffusion coefficient(s) for the gas(es) in the scale, a linear behaviour of scale growth with time (layer growth Δx or weight gain (Δwt/area) = linear rate constant k·time) for short periods and a parabolic behaviour (($\Delta x)^2$ or (Δwt/area$)^2$ = parabolic rate constant k_p·time t) for longer times are predicted.

For many conditions, parabolic behaviour has been confirmed or assumed in oxidation processes at high temperature. The diffusion process through the scale (or inside the ceramic) is then much slower than gas transport in the atmosphere or surface chemical reaction speed. In ceramic corrosion often a product gas evolves (cp. eqns (2)–(4)). The diffusion of this gas outwards through the scale may become rate determining.

Thus the diffusion properties of the scale or the material determine the scale growth kinetics and hence the corrosion process. They are influenced by a number of factors, the most common ones being illustrated in Fig. 5. The most obvious ones are related to the homogeneity of the growing scale. The defect structure of the scale plays a major role. In a crystalline scale, grain boundaries may simply be viewed as an area of high defect concentration. Therefore, D(bulk) < D (grain boundary) and thus a polycrystalline scale will transport the gas faster than would be predicted from single-crystal measurements.

Partial crystallisation of an amorphous scale often has the opposite effect. This is because the newly formed crystalline phase has usually a much lower D compared to its mother liquid and thus acts as a diffusion barrier, limiting the effective surface for the diffusion of the gas through the remaining glass. If such a crystallisation is continuous over time it will slow down oxidation over time. These cases can often be modelled via a logarithmic growth law ($\Delta x = k_1 + k_2 \cdot \log(\text{time})$).

If the scale cracks, e.g. because of volume expansion mismatch between material and scale, crystallisation within the scale, polymorphism or limited adhesion, gas is re-supplied by transport through the gas phase and the scale becomes non-protective. The kinetics then jump back to fast linear growth laws (break-away-effect). Some gases, notably H_2O at levels of several percent, foster this effect.

Clearly diffusion coefficients are dependent on the chemistry of the scale and the type of diffusing species (ionic, molecular, complex). Advanced ceramics, in particular Si_3N_4, are usually sintered with additives. The diffusion of these species into the scale brings about a change in the chemistry of the scale with associated changes in viscosity and in the crystallisation of secondary phases. Thus the corrosion behaviour is strongly dependent on the type of additive and its amount. The presence of a grain boundary phase, in which oxygen is transported ionically and is thus capable of reacting within the bulk material, leads to inner oxidation. The transport of the balancing cations (e.g. Mg^{++} in Si_3N_4 materials) can become rate determining.[14] A consequence of these complex processes acting simultanously is that the simple parabolic behaviour will never be true in detail. Currently, new modelling strategies are developed[15,16] to take this into account, because simple models will fail to predict the long-time behaviour accurately.

2.4 Corrosion

Further, from the points outlined above, it is plain that different phases will have different corrosion properties. Almost all ceramic materials are polycrystalline and the grain boundary may be viewed as an area of high defect and/or impurity concentration, which is thus more susceptible to corrosive attack than the bulk material. If this difference is large enough we may encounter the first form of local attack: grain boundary corrosion. This feature is observed to be more pronounced in the presence of grain boundary phases from sintering additives and material impurities, because this makes a material a multi-phase compound. Likewise, deliberately structured composites are susceptible to local corrosion (preferential secondary phase corrosion). A classic example is the leaching of free Si in SiSiC by acids or bases. Reactions in the solid state, with a gas or a fluid phase, can give rise to similar etching features. Figure 6 shows the etching of a grain boundary phase in a Mg-doped Si_3N_4 by a surface layer of NiO at a temperature of only 900°C.

Fig. 6. Etching of grain-boundary phase by NiO (900°C, O_2, 100 h).

Sample destruction caused by volume expansion misfits is found where grain boundary phases in non-oxides are oxidised to yield phases with significantly larger specific volume. Some phases, like N-apatite in Si_3N_4, are known to give rise to such catastrophic oxidation at relatively low temperatures (< 1000°C).[17] Impurities encountered by the scale during system application will act in much the same manner as additives.

In SiO_2-forming ceramics a rule of thumb for the potential danger of an impurity or additive can be gained from the familarity with the viscosity reducing additions used in the glass industry. Increasing amounts of alkalis will foster oxidation. Also, typical glass constituents like V_2O_5, B_2O_3, PbO or P_2O_5 may cause dramatic changes in the viscosity at high temperatures. A more precise method of predicting corrosion behaviour is obtained by thermodynamic reasoning and looking at well-known phase diagrams.[18]

2.5 Hot corrosion

Hot corrosion is caused by the interaction of scales and molten salts. The interaction is well known for Na_2SO_4–SiO_2 systems; it has been studied because in many environments combustion in the presence of Na from NaCl in the vapour phase and SO_x from S-bearing fuel leads to the formation of the sulphate as a deposit. Critical temperature limits are the melting and dew point of the salt; for Na_2SO_4 this is between ≈875 and 1100°C (in detail it is dependent on P(SO_3) and P(NaCl)).

Within this range the salt may act as a basic melt in reducing and as an acidic melt in strongly oxidising environments. A basic melt based on Na_2SO_4 will decompose and the Na_2O formed reacts with SiO_2 to yield Na_2SiO_3, enhancing oxidation rates. Acidic deposits should act less strongly but tend to devitrify the scale causing cracking. The most dangerous local corrosion occurs when the substrate interacts with the scale to make the melt at the interface with the substrate basic (e.g. by the presence of free C), while the atmosphere–scale interface stays acidic: this induces a fluxing mechanism,[19] often with concurrent pitting (Fig. 7). Other salts may act in a similar way, because their decomposition releases harmful elements or oxides. Thus, alkali-, V-, Pb-, B-carbonates, sulphates or phosphates should be considered dangerous.

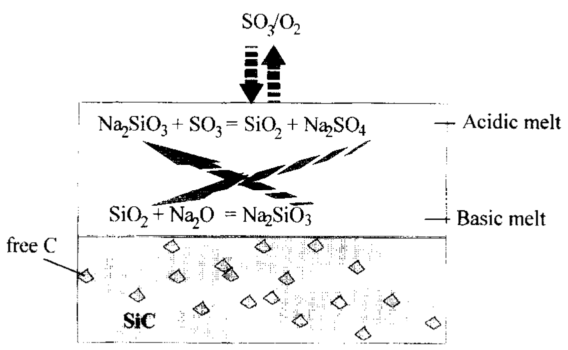

Fig. 7. Proposed fluxing mechanism for SiC corrosion by Na_2SO_4 in the presence of free carbon.[19]

3 MATERIAL ENGINEERING FOR CORROSION RESISTANCE

3.1 Material choice

Corrosion problems are not a fate one has to live with under all circumstances. An initial improvement can be made by checking the current literature about the corrosion behaviour for different types of ceramics in a given environment. Here some handbooks give a good first impression.[20,21] More detailed knowledge is gained by studying literature about the state-of-the-art corrosion of advanced ceramics,[1–5] e.g. that Si_3N_4 materials are often more resistant to slags and molten salts compared with SiC, while the latter is usually more resistant to high temperature gaseous oxidation.

3.2 Microstructural engineering

Within a class of material, e.g. Si_3N_4, material engineering has usually been performed to gain higher density, strength or toughness. It has often been overlooked that some improvement techniques can lead to dramatically lower corrosion resistance. An example is shown in Fig. 8. In a study[22] one type of Si_3N_4 (Y–Al-doped) was pressureless sintered ('SSN'). A portion of the

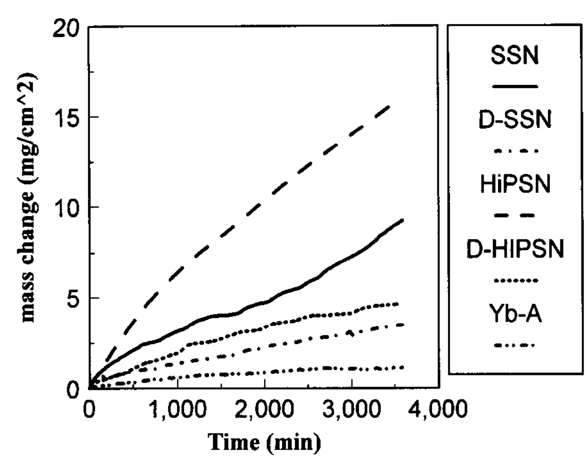

Fig. 8. Comparison[22] of pressureless sintered, HiPped, devitrified Y–Al–Si_3N_4 and Yb–Si_3N_4 oxidised at 1370°C in O_2.

material was afterwards HIPped ('HIPSN'). The SSN contained after sintering some unconverted α-Si_3N_4 and a partially crystalline grain boundary phase. After HIPping at 2000°C all α-Si_3N_4 was converted into β-Si_3N_4, but the grain boundary phase was completely amorphous.

Oxidation tests at high temperatures showed that the HIPped material had a much lower oxidation resistance (Fig. 8). To combat this effect both SSN and HIPSN were post-treated at 1350°C in N_2 to crystallise the grain boundary phase. The desired Y-silicate phases were observed after the process and this improved the oxidation resistance greatly. However, as shown in Fig. 8, the post-treated SSN ('DSSN') was still superior to the treated HIPSN ('D-HIPSN'), indicating that the HIPping made the grain boundary phase not only amorphous but also increased the amount (possibly by dissolving more Si_3N_4 or N_2 into the grain boundary phase).

Figure 8 also shows that the change of the sintering additive (from Y–Al to Yb) had an even larger effect on the oxidation resistance at high temperatures. This is because of a lower diffusivity of Yb-ions in the grain boundary phase. In general, sintering additives with high eutectic melting points in the system sintering additives + SiO_2 will be of superior oxidation resistance.

3.3 Protection by coating

In some cases the corrosion behaviour can not be improved within the material. Hot corrosion by basic salts will damage all SiO_2-formers relatively quickly. Here it may be advisable to use coatings. Mullite is a good candidate to coat SiC, as both have very similar thermal expansion coefficient and the lowered activity of SiO_2 in mullite makes this material substantially more resistant to hot corrosion.[23]

3.4 Environmental engineering

If it comes to corrosion problems in a number of cases it is possible to improve the material behaviour not via the material itself but its application environment. If a material is in the active (I)-regime it could be easily brought into the passive region by the introduction of some air. For temperatures $< 1600°C$ a minute amount would suffice as the boundary is below 10^{-3} bar O_2-pressure. The improvement by O_2-addition has also been observed in environments with dangerous gases like Cl_2.[24] Likewise the problems of hot corrosion may be limited by raising the temperature above the dew point.

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