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Oxidation of Silicon, Silicon Carbide (SiC) and Silicon Nitride (Si_3N_4)

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The literature pertaining to the oxidation of silicon, silicon carbide, and silicon nitride has been reviewed. The current state of knowledge of the oxidation reactions and mechanisms, particularly the common features applying to the three substances, has been emphasized.

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OXIDATION OF SILICON, SILICON CARBIDE (SiC) AND SILICON NITRIDE (Si_3N_4)

INTRODUCTION

Si, SiC, and Si_3N_4 are important materials. They are widely used for their electrical properties in the construction of semiconductor devices, and SiC and Si_3N_4 have important uses as hard and relatively oxidation-resistant ceramics. The carefully controlled oxidation of Si to SiO_2 is used in the fabrication of semiconductors.

Because of the many similarities in the oxidation chemistry of the three substances, they are treated together in this report so that useful comparisons can be made. The major questions to be addressed are:

1. What are the oxidation reactions and what is the detailed mechanism by which they occur;
2. How do these oxidation processes depend on: (a) the form that the material takes, e.g., processing procedure, crystal structure, (b) temperature, and (c) oxygen pressure. Although other oxidants, e.g., H_2O, either alone or in combination with O_2 also oxidize these materials, this report will deal with O_2 exclusively.

Each of the above questions will be addressed in detail for each of the three materials. However, the report is not intended to be an exhaustive compendium of every available reference, but rather will focus on the major features. particularly on those

Heterogeneous Reaction Kinetics
Thermodynamics

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where general agreement has been reached. Here we begin by listing some general aspects relevant to oxidation.

The common feature of the oxidation of the three substances is that SiO_2 is always a solid product when the O_2 pressure is sufficiently high. At low pressures SiO(g) may form. For the oxidation of Si these are the only possible products. For SiC, CO or CO_2 are also products, for Si_3N_4 possible products are NO, NO_2, and N_2 as gases and an oxynitride solid. Since in virtually all studies the reaction has been found to occur at the reactant surface, the diffusion of oxygen in some form -O_2, O_2^-, and O - to this surface is of major importance. For example, when SiO_2 has already formed, the oxidant must diffuse through it to reach the reactant surface. For SiC and Si_3N_4, and for Si at low pressures, the diffusion of product gases away from the reaction zone may also affect the rate.

The form in which the material is studied is also of great importance. In general, the purest and densest materials should provide the most fundamental information. Silicon single crystals are readily available and most oxidation studies have utilized them. Such crystals also readily lend themselves to studies of impurity effects that can be achieved by controlled doping. SiC single crystals exist, but rarely of the degree of purity achieved for Si. Moreover, these crystals are highly anisotropic with oxidation rates on different faces differing by nearly an order of magnitude. Also, commercially important forms of SiC are made from powders which are rarely very pure, with additives which introduce additional impurities. Explanations provided for the results observed in oxidation studies thus tend to take on an ad hoc character and we are reduced to searching for common features. This situation exists to an even greater extent for Si_3N_4. Single crystals are not available, and even near theoretical density can only be achieved by the addition of materials such as MgO, Al_2O_3, and B_2O_3 which greatly affect the oxidation rate and which are usually not uniformly distributed in the nitride. Therefore reported rate constants and activation energies differ widely and little theoretical significance can be attached to them.

In each of the sections which follow the theoretical understanding of oxidation will be described, followed by a listing of kinetic parameters reported in the literature. Finally, the values obtained for the various materials will be compared to see if useful conclusions can be drawn.

OXIDATION OF SILICON

I. General

All serious studies have utilized single crystals for studying the oxidation of silicon. Frequently, the surface orientation, usually [100] and [111], has been considered a significant variable. Work done before 1965 suffered from the lack of a coherent theoretical framework within which experimental results could be analyzed. In that year Deal and Grove (1) published the first analysis which took previous work into account, and which consisted of a qualitative model and its quantitative consequences. The importance of the Deal and Grove model (D&G) is attested to by the fact that during the last twenty years all papers have referred to it, fleshing it out quantitatively, defining the regions in which it holds, and extending it.

II. The Deal and Grove Theory (1)

A. Qualitative.

D&G found certain qualitative and quantitative features in their own and previous studies which had the following characteristics:

1. Oxidation proceeds by inward movement of oxidant (O_2, H_2O) rather than by outward movement of Si.
2. The transported species goes through the following stages:

    a. It is transported from the bulk of the oxidizing gas to the outer surface where it reacts or is absorbed.

b. It is transported across the oxide film toward the underlying Si.

c. It reacts at the SiO_2-Si interface to form a new layer of SiO_2.

3. The model is steady-state, i.e., it assumes that a SiO_2 layer already exists at the surface. Many subsequent studies have focused on the initial stages of SiO_2 formation. In general, the steady-state model applies for oxide layers at least a few hundred Angstroms thick.

B. Quantitative

1. Model

As a result of the oxidant (generally O_2) gradient from bulk gas to SiO_2-Si interface there will be oxidant fluxes in the three regions as shown in Fig. 1.

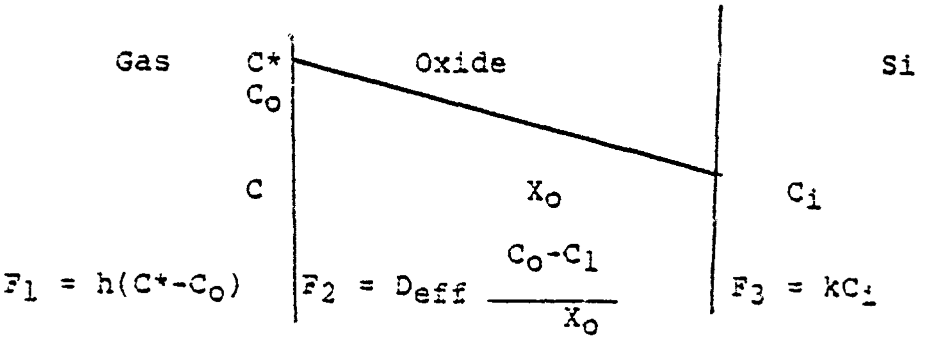

Figure 1

where C^* = equilibrium concentration of oxidant in the oxide.

C_o = concentration of oxidant at the surface.

h = gas transport coefficient.

D_{eff} = effective diffusion constant of oxidant in SiO_2.

X_o = thickness of oxide layer.

C_i = oxidant concentration at the Si-SiO_2 interface.

k = proportionality constant.

2. Assumptions

a. $C^* = Kp$, where K = Henry's law constant. This implies that C^* is the concentration of oxidant free to diffuse through the oxide and is not oxidant bound as SiO_2.

b. The gradient of oxidant in the oxide layer is linear and given by Fick's law:

$$F_2 = -D_{eff}(dc/dx)$$

3. Analysis

Under steady-state conditions

$$dF_2/dX = 0$$

and

$$F_1 = F_2 = F_3 = F$$

For oxide thicknesses > 200Å, $D_{eff} = D$, the actual diffusion constant of oxidant in SiO_2. The rate of growth of the oxide layer is

$$\frac{dX_o}{dt} = \frac{F}{N_1} = \frac{kC^*/N_1}{1 + k/h + kX_o/D_{eff}}$$

where N_1 = number of oxidant molecules incorporated into a unit volume of the oxide layer. This way of measuring reaction rate is necessitated by the fact that the transformation of Si to SiO_2 expands the volume by a factor of 2.5. Since some oxide layer exists before the steady-state analysis applies, let

$$X_o = X_i \text{ at } t_o$$

Considerable mathematical manipulation leads to the rate of oxide formation

$$\frac{X_o}{A/2} = \left[1 + \frac{t + \tau}{A^2/4B}\right]^{1/2} - 1$$

where $A = 2D_{eff}(1/k + 1/h)$

$B = 2D_{eff}\, C^*/N_1$

$\tau = (X_i + AX_i)/B$

τ corresponds to a shift in the time axis which corrects for the presence of the initial oxide layer X_i.

4. Limiting Forms

a. Long times

$t >> A^2/4B$, $t >> \tau$

$$\frac{Xo}{A/2} = \left[\frac{t}{A^2/4B}\right]^{1/2}$$

or $X_o^2 = Bt$

This is the famous parabolic law applicable to thick oxide growth. It is quite similar to results obtained for the oxidation of metals, where the rate is controlled by the diffusion of oxidant through the oxide.

b. Short times

$t << A^2/4B$

$$\frac{X_o}{A/2} \approx \frac{1}{2}\left[\frac{t+\tau}{A^2/4B}\right] \approx B/A\,(t+\tau)$$

This is the linear rate law which applies for short times to which the steady-state model applies. Many subsequent studies have focused on very short times prior to that state.

The combined long-short time model is known as the linear-parabolic model with linear rate constant B/A and parabolic rate constant B.

5. Experimental Results (to 1965)

D&G analyzed previous studies as well as their own new results for both dry and wet O_2, and found them consistent with their model. When the O_2 is wet, the oxidant is H_2O, not O_2. This case will not be treated further here.

From these studies the following conclusions emerged:

a. At 1200°C, parabolic rate constants are linear in $0.1 \leq P_{O_2} < 1$ atom.

b. The temperature dependence of the parabolic rate constant is Arrhenius with an activation energy of 28.5 kcal, the same as for D_{eff}. The constant A is independent of pressure.

c. The temperature dependence of the linear rate constant is also Arrhenius, with an activation energy of 46 kcal, nearly equal to that required to break an Si - Si bond.

d. The diffusing species is some form of O_2, probably the superoxide ion O_2^-.

e. The range of validity of the parabolic and linear portions of the oxidation rate, or "long" and "short" times respectively, depends on oxidation conditions and can be described in terms of a characteristic time.

$$\frac{A^2}{4B} = \frac{D_{eff} V_1}{2C^* (1/k + 1/h)^2}$$

or characteristic distance

$$\frac{A}{2} = \frac{D_{eff}}{1/k + 1/h}$$

For larger times and distances oxidation is parabolic, for smaller times it is linear. As pointed out previously, the entire D&G theory is steady-state and applies only for SiO_2 thickness larger than the space-charge region within the oxide. At 1000°C this occurs at ~ 150A°.

III. Extension of the Variables

The period since D&G has been marked by studying regimes not treated by D&G. These include:

A. Very low pressures.

B. The initial stages, before steady state is reached.
This sometimes means low temperatures so that the growth of thin films can be observed at reasonably slow rates.

To some extent A and B are connected, since films will also grow more slowly at low pressures. For this reason, the results are discussed together.

An important question in the study of silicon oxidation concerns the initial stages, i.e., before the D&G steady-state model applies. There seems to be general agreement that the lower D&G limit lies near 250-500Å, but it is not clear whether this initial region is itself to be subdivided further, e.g., into a "very thin" region below 25-50Å, and an intermediate region above that. The questions to be addressed are: (a) what rate law applies in the thin region, i.e., what is the thickness-time relation, and what model accounts for it, and (b) how does this rate depend on P_{O_2}. This region is of particular importance to the growth of semiconductors.

The sometimes contradictory literature of the last twenty years (3-8) has recently been summarized and discussed by Massoud, Plummer, and Irene (9).

Experimentally, it is observed that:

(a) Growth rates in the thin regime are greater than in the linear-parabolic region.

(b) This faster growth rate can be thought of either as an "excess growth rate" which decays exponentially to the linear region, or considered as a separate region with its own growth law. In the former case, it is handled as an exponential term added to the D&G equation; in the latter is is usually described as being "inverse logarithmic." In general, the D&G region extends from 250-300Å up; the region below it can be divided into an initial region extending from the native oxide thickness up to 80-100Å where the rate rapidly decreases with increasing thickness, and a further region in which the rate decreases asymptotically to the D&G region. Some authors (4, 10) have tried to work with extremely thin films, even less than 10Å, by cleaning the Si surface with HF. For example, Fehlner (10) found that below 600°C film growth up to 50Å was inverse logarithmic. Such behavior is best accounted for by the Cabrera-Mott (11) theory developed for the oxidation of metals. In this regime space-charge is quite important and requires the motion of cations to the oxide surface. These would have to be Si^{4+} for Si oxidation and thus seems somewhat unlikely. However, similar results were also obtained by Kamigaki and Hoh (6) by studying oxidation below 10^{-2} atm at 950-1100°C. Thus, by adjusting temperature and pressure the initial stages of oxidation can be carefully studied.

(c) The pressure dependence of the various rate constants - inverse logarithmic, linear, parabolic - is also of interest, and the literature is somewhat contradictory. For example, Ghez and van der Meulen (5) have found that K_{lin} depends on pressure, temperature, and crystal orientation, tending to $p^{1/2}$ behavior at lower temperatures, and toward linear behavior at higher temperatures for both <111> and <100> orientations. In the thin regime the oxidation rate has a pressure dependence of ~ $p^{0.8}$, with variations being observed, depending on the method of data analysis, temperature, and film thickness.

To account for the experimental results, various theories have been proposed. These fall into four groups:

(a) Space-charge effects where the enhancement is electrochemical. In this type of theory, widely applied by Cabrera and Mott (11) to metal oxidation, oxidant transport is enhanced by an electric field existing across the oxide layer. This theory yields an inverse logarithmic relation between oxide thickness and time, as has been observed by several authors. One form of this theory was recently proposed by Hu(9) who proposed an intermediate oxygen chemisorption step. The chemisorbed O_2 would directly oxidize Si, dissociate into atomic oxygen which would oxidize Si rapidly, or diffuse as O^-. This mechanism would cease for oxide thicknesses >150Å. This interpretation has been criticized by Massoud et.al.(9) who argue that space-change is not responsible for the observed effect.

(b) Oxide-structure effects that provide enhanced oxidant transport. These consist of micropores or channels perpendicular to the surface through which oxidant could diffuse more readily. Such channels are more likely in amorphous or fused silica, and some channels of various sizes, generally less than 50Å, have been observed. Diffusion through such channels would enhance the linear and parabolic growth as well.

(c) Stress in SiO_2 has been proposed to enhance the rate. Stresses result from the mismatch in the thermal expansion coefficients of Si and SiO_2. However, such stresses should have no effect on the rate when the rate-limiting step occurs on the surface.

(d) A variation of the Henry's law constant for O_2 solubility has been proposed to account for the enhanced rate. Although a higher O_2 solubility in thin films would account for the results, no independent measurements of the solubility in thin films have been performed.

Massoud et. al. (9) propose that the enhanced rates in the thin regime is accounted for by additional reactions occurring on the Si substrate. The nature of the reaction sites is not known, but may result from Si-Si bonds which are more reactive in the surface layer than in bulk, because they are bent or broken. However, no experimental evidence for this has yet been obtained.

Thus, it appears that there is no complete agreement on either the experimental results or the mechanism for oxidation in the thin film regime.

IV. Experimental Results

As shown in the preceding sections, the oxidation rate of silicon depends on several factors: (a) the "stage" of oxidation - parabolic, linear, and inverse logarithmic, (b) temperature, and (c) oxygen pressure. Of these, data for the parabolic and linear stages are least in dispute. Table I shows these rate constants as given by Deal and Grove (1).

Table I. Rate Constants for the Oxidation of Si in Dry O_2 at 1 Atm

Temperature (C)	B(Parabolic-μ^2/h) x 10^3	B/A(Linear-μ/h) x 10^3
700	-	0.26
800	1.1	3.0
900	4.9	20.8
1000	11.7	71.
1100	27	300.
1200	45	1120.

As mentioned previously, activation energies for the linear and parabolic stages are 46.0 and 28.5 kcal, respectively, corresponding to the breaking of an Si - Si bond for the linear, and O_2 diffusion for the parabolic stages. These two stages together cover the range 300-20,000Å. The parabolic rate constant is linear in Po_2, probably at each temperature, although complete data are not available. However, between 1000 and 1200° the slope is independent of temperature when normalized to the 1 atm value, i.e.,

$$\frac{B(p,T)}{B(1\ \text{atm},T)} = p$$

Thus values of B in Table I yield the pressure dependence directly for $0 \leq p \leq 1$ atm. These results have been confirmed experimentally (7). The parameter A in the D&G theory is approximately independent of pressure (7) (theory requires it to be independent) so that the pressure dependence of the linear rate constant B/A is the same as that of B. However, this latter result is contradicted by the results of Kamigaki and Hoh (6) who find A to be proportional to $P_{O_2}^{1/2}$. They therefore argue that in the pressure range $2.5 \times 10^{-2} \leq P_{O_2} \leq 1$ atm the mechanism is a mixture of Mott-Cabrera and Deal and Grove, the latter predominating at the higher pressures.

It thus appears that, except for the parabolic thick film regime, very little can be accepted as definitely settled.

V. Active Oxidation

The preceding discussion has dealt with regimes in which p_{O_2} even when low, was sufficiently high for SiO_2 to be formed. However, when p_{O_2} is sufficiently low, SiO_2 cannot form and SiO(g) is the product. In that case no protective layer can form and the oxidation is quite rapid. This regime is known as "active oxidation".

Gulbransen, Andrew, and Brassart (11) were probably the first to investigate this phenomenon. In addition to the direct oxidation

$$Si(s) + 1/2\ O_2\ (g) = SiO(g)$$

they also studied the reduction of SiO_2 by Si.

$$SiO_2(s) + Si(s) = 2\ SiO(g)$$

The latter reaction occurs when the pressure is lowered after SiO_2 has already formed. In this case, spalling of the protective coating also occurs as the trapped SiO builds up pressure.

The "active" and "passive" regions can be defined thermodynamically. Such a calculation has been carried out by Hinze and Graham (12), based on the JANAF Tables (13) and data of Zmbov (14). Their plot is shown in Fig.2 for 1600K. It can be seen that at this temperature active oxidation will not occur above $P_{O_2} = 10^{-20}$ atm, and in general cannot occur unless P_{O_2} lies below the equilibrium SiO pressure at the SiO_2 - Si interface. A more thermodynamic analysis is provided in the last section of this report.

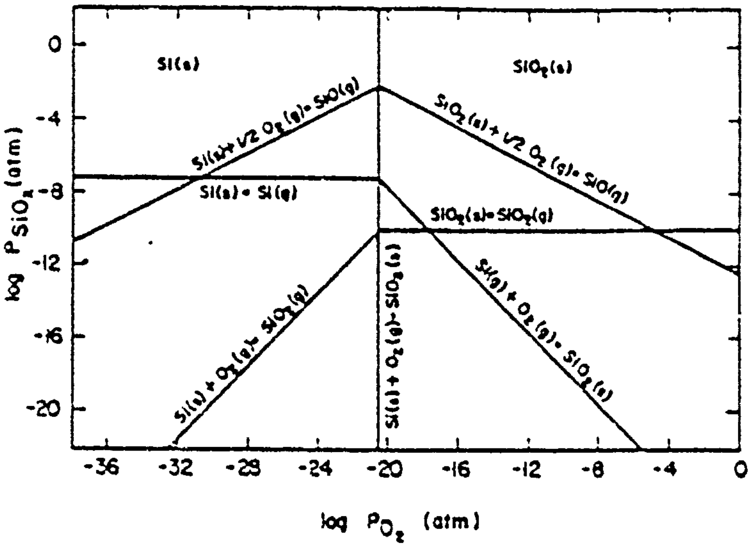

Fig. 2 — Thermodynamics of the Si-O system at 1600°K using data of Smbov et al. (14) and JANAF (13). (Figure 1 on page 1067 from "Journal of The Electrochemical Society," Vol 123, by J. W. Hinze and H. C. Graham, published by The Electrochemical Society, ©1976, used by permission.)

Active oxidation can occur either under molecular flow or viscous flow conditions. The former has been well studied (15, 16, 17). The main result is that the steady-state rate of material loss by SiO evaporation can be calculated from the Hertz-Knudsen equation by equating the rate of O_2 arrival and SiO removal.

$$J_{SiO} = J_{O_2} = 2\alpha P_{O_2}/(2\pi\ M_{O_2}RT)^{1/2}$$

where the J's are the fluxes of SiO and O_2, M_{O_2} is the O_2 molecular weight and α is the sticking probability.

In the viscous flow regime molecules reach and depart from the surface by diffusion and the fluxes are given by

$$J_{SiO} = J_{O_2} = 2D_{O_2}/\delta_{O_2}RT = 2h_{O_2}P_{O_2}/RT$$

where h_{O_2} is the average boundary-layer mass transfer coefficient, δ_{O_2} is the effective thickness of the oxygen boundary layer and D_{O_2} is the O_2 inert gas interdiffusion coefficient. In the theory proposed by Wagner (18), the transition from active to passive oxidation occurs, under laminar flow conditions, when

$$P_{O_2}(\mathrm{max}) = 1/2\ (D_{SiO}/D_{O_2})^{1/2}\ P_{SiO}^{eq}$$

where P_{SiO}^{eq} is the equilibrium pressure for the reaction.

$$1/2Si(s) + 1/2\ SiO_2(s) = SiO(g)$$

The diffusion constant ratio is virtually independent of temperature and gas flow velocity, and can be calculated from gas kinetic equations.

A competing model successfully applied to the oxidation-enhanced vaporization of metals (19) has also been tested for the active vaporization of silicon (12). In this theory SiO_2, formed by the reaction $Si(g) + O_2(g) = SiO_2$, is formed as a fog at some distance from the Si surface. The rate of Si removal is controlled by O_2 diffusion through the boundary layer ahead of the fog-formation front according to the equation

$$J_{Si} = J_{O_2} = h_{O_2} P_{O_2}/RT$$

The active-passive transition occurs when the front reaches the surface. For this condition

$$P_{O_2}(\max) = \frac{P_{Si}^{eq}}{h_{O_2}} \left(\frac{RT}{2\pi M_{Si}}\right)^{1/2}$$

where P_{Si}^{eq} is the equilibrium pressure for the process

$$Si(l,s) = Si(g)$$

The rate of Si consumption predicted by the Turkdogan (19) model is half that predicted by the Wagner model (18). An experimental test (12) shows that SiO is indeed the active species at the surface, as predicted by the Wagner theory, but that the oxidation occurs in two stages, rather than the single one predicted by both theories. However, after P(max) of the Wagner theory was exceeded, SiO_2 grew as whiskers rather than laterally. Lateral growth occurred only after a second P(max) was exceeded.

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OXIDATION OF SILICON CARBIDE

I. General

In proceeding from the oxidation of the element silicon to that of the compound silicon carbide, additional complexities are necessarily encountered because both constituent elements are oxidized at high temperatures. Further complexities arise from the fact that SiC exists in several crystalline modifications, and that the crystal structure is anisotropic (see below).

Viewed as a compound in the Si-C system, the substance exhibits a peritectic near 2700°, well above the temperature range of interest in oxidation studies - generally below 1600°- and so thermal decomposition is not a factor. SiC is the only compound in the Si-C system and therefore other stoichiometries need not be considered.

II. Forms of SiC

SiC has been prepared for practical applications by several different methods: Chemical vapor deposition (CVD), plasma-assisted CVD (PACVD), hot-pressing, and RF sputtered films. Some of these forms incorporate additives which increase the density, but usually affect oxidation rates.

From a fundamental point of view, single crystals are expected to provide the most reliable oxidation data, but even these are less meaningful than for Si because (a) the purity achieved for Si is rarely available for SiC, (b) SiC exists in at least two major crystal modifications, α and β. The form usually produced is α, and special procedures must be used to obtain β. In most respects the two forms appear to have similar properties

(1,2). In addition, many different types, differing in packing and interatomic spacings have been described for α (3). Most of these are achieved by stacking simple tetrahedra in different ways. (c) SiC may be non-stoichiometric and values as large as 1.04 have been reported for the Si/C ratio (1). (d) SiC is non-isotropic, the opposite faces of a single crystal being either silicon or carbon, the oxidation rates of the respective faces differing by a factor of 6 or 7 (4) and obeying different rate laws (5). The reason for the anisotropy lies in the tetrahedral structure of SiC, as shown in Fig. 1.

It is clear that, for the above reasons, oxidation rates might differ widely, particularly for polycrystalline materials whose surface will have different fractions of the Si and C faces of the constituent crystallites exposed. Impurities are also expected to exert major effects on the oxidation rates, particularly since they are usually not uniformly distributed, but tend to concentrate in grain boundaries.

III.. Oxidation Reactions

There is general agreement that Si and C are oxidized simultaneously. At sufficiently high O_2 pressures the reaction is

$$SiC(s) + 2O_2(g) \quad = \quad SiO_{2(s)} + CO_2(g) \qquad [1]$$

whereas at lower pressures CO is formed:

$$SiC(s) + 3/2\ O_2(g) \quad = \quad SiO_2(s) + CO(g) \qquad [2]$$

At extremely low pressures SiO(g) may also form, as it does for Si, presumably by

$$SiC(s) + O_2(g) = SiO(g) + CO(g) \qquad [3]$$

The stability regime for these three reactions can be calculated from thermodynamic data, but the results may have only limited applicability to the kinetic situation encountered in rate studies. An example of such a plot is the diagram prepared by Fitzer and Ebi (6), Fig.2, which shows the stability domains for SiO_2 and SiO at various oxygen pressures as a function of temperature. For example, at 1 atm SiO is not formed below 2100K, but at 10^{-5} atm SiO is favored above 1350K. Further thermodynamic information is provided in a later section.

IV. Oxidation Mechanisms

Just as Deal and Grove analyzed data for Si oxidation obtained prior to 1965, so were data for SiC oxidation prior to 1964 analyzed by Motzfeld (7). The temperature range covered is 900-1600°. There seemed to be general agreement among the authors cited by Motzfeld that the reaction [1] is controlled by diffusion of O_2 to the SiC-SiO_2 interface and that because twice as many moles O_2 are required to oxidize one mole of SiC than one mole Si, the oxidation rate of SiC should be half that of Si. Although the data are somewhat scattered, agreement is quite good. Moreover, the temperature dependence is also the same, indicating that the work cited by Motzfeld is in the parabolic thick film regime where the rate-determining step is the diffusion of O_2 in, and not the diffusion of CO_2 out.Since the oxidation rates and mechanisms may depend on the form and impurities of the SiC we discuss these in separate sections.

A. Single Crystals

There are very few studies of single crystals and most of them have concentrated on the form of the oxide scale. For example, Heuer, et.al (7) oxidized various grades of α-SiC in ambient air at 850°-1500°C. They found that SiO_2 first forms as amorphous layers which subsequently devitrify to cristobalite spherulites. In a more detailed study, Ogbuji (8) obtained essentially the same results.

A careful examination of oxidation on the various faces of n- and p- type SiC was carried out by Münch and Pfaffeneder (9) at 1070°C in H_2O-saturated O_2. They confirmed the well-known fact (5) that oxidation on the carbon $(000\bar{1})$face is about ten times that on the opposite silicon face. Rates for the (1120) and (1100) planes containing equal concentrations of carbon and silicon, were intermediate. In general, doping increased the oxidation rate.

Harris (5) measured oxidation rates on the Si and C faces of single crystals (otherwise not further described) in flowing O_2 and interpreted his data in terms of the Deal and Grove constants.

Strangely, Harris refers to the "thin" and "thick" film sides after oxidation without identifying them as the faces which were originally Si and C. On the "thick-film" side, growth was parabolic for films $\geq$ 2500Å with an activation energy of 47 kcal, determined from the temperature dependence. On the "thin" side rates are linear at all temperatures and times with an activation energy of 85 kcal. This implies that on the thick side oxygen diffusion is rate determining, whereas on the thin side a surface chemical reaction is. These results are strange, since they imply that the oxidation chemistry of the two faces remains fundamentally different although the entire crystal consists of alternate C and Si layers. However, Harris' results have been confirmed by an oxidation study of the SiC faces (1) which explicitly gives 47 kcal and 85 kcal for the carbon and silicon faces of α - SiC. However, no detailed mechanism has yet been proposed to account for these differences.

B. Sintered SiC

SiC can be sintered above 1900°C, the density achieved depending on the temperature and additives (11) used as densification aids. Without such aids only ~70% of theoretical density is achieved. The most effective additives are boron and carbon, e.g., by heating a commercial "pure" α-SiC powder with 7.3w% B and 0.6% C at 2150°C, 96% of theoretical density was obtained. SiC has also been sintered with much smaller (~1%) concentrations of boron, and aluminum has also been used as sintering aid.

These sintering aids markedly increase the oxidation rate over that of pure SiC (12, 13, 14). The additives, e.g. boron, concentrate in the grain boundaries in which their diffusivity is very high. Thus the measured diffusity of B in polycrystalline SiC is several orders of magnitude that in the single crystal material. As oxidation proceeds,boron diffuses into the SiO_2 layer driven by a concentration gradient. In this film its diffusivity is also much higher than in pure SiO_2. It appears likely that the O_2 diffusivity in this quasi B_2O_3-SiO_2 layer is also higher than in SiO_2 and consequently the oxidation rate of sintered SiC will be enhanced by the additive.

With respect to activation energies the situation is quite complex and a range of values has been reported (13). This is not surprising since the microstructure varies with the method of preparation. Since the oxidation kinetics are generally parabolic, the rate-determining process is presumed to be the diffusion of O_2 through SiO_2. The low end of the reported activation energy range is near that for SiO_2 formed during Si oxidation. It should be remembered that the activation energy measures the temperature coefficient of the rate and means that the rate for SiC oxidation changes more rapidly with temperature than for Si oxidation. Changes in SiO_2 structure with temperature have been proposed, but so far there is no convincing explanation for the phenomenon.

C. Hot-pressed SiC

The results for hot pressed (HP) SiC are quite similar to those for the sintered material. In order to achieve theoretical density additions of aluminum and (frequently) boron are required. These additives increase the oxidation rate considerably (up to several times) over that of the pure material. The literature up to 1979 has been reviewed by Schlichting (15,16), cf. Fig. 3, and is also confirmed by later work (13).

Oxidation is parabolic, implying that O_2 diffusion inward is the rate determining step. The oxidation produce is SiO_2, which forms in a glassy layer which gradually crystallizes, at least partly, to cristobalite. The impurities (additives) diffuse from the SiC into the SiO_2 layer. If the boron concentration and the temperature are sufficiently high, B_2O_3 may vaporize. In some cases mullite has been detected in the oxidation layer. Over the temperature range usually studied, 1000-1600°C, Arrhenius plots are not linear, but exhibit several well-defined changes in slope (Fig3). It is tempting to associate these with changes in mechanism, but those proposed - mainly in terms of changes in the permeability of the SiO_2 layer for O_2 - have an ad hoc character.

D. Powder

Oxidation studies of SiC powders offer attractions: Pure SiC can easily be obtained in powder form, each of the grains is 100% dense, and the method is easily adapted to thermogravimetry since the large surface area of a powder leads to an easily measurable weight change during oxidation. On the other hand, one must be aware of potential pitfalls. If the grains of the powder are small and closely packed, the diffusion of O_2 to the surface of the grains might become rate-determining, and no significant information is obtained. For SiC an additional problem is the sintering of the SiO_2-covered grains above 1400°C which both restricts O_2 access and leads to a reduction of surface area (17). This problem can be avoided to some extent by forcing the reactant gas through a powder bed (18). A further problem arises from the grain geometry itself. If each grain is assumed to be spherical the surface area will decrease as the reaction front advances into the grain, and be reflected as an apparent decrease of rate, although the rate/unit area is constant. This is a well-recognized problem in topochemical studies with powders.

Its solution is known as the "contracting sphere" model, and it has been applied to SiC oxidation (19). If O_2 is assumed to reach the grain particles by diffusion the fraction R of the oxidation completed is:

$$[1 - (1-R)^{1/3}]^2 = \frac{2\lambda^2}{r_o^2} k_o kt$$

where λ is the cube root of the volume of the diffusing species, r_o is original grain radius, and k_o is a factor introduced to allow for surface roughness, and the number of surface sites available for reaction. Since all the factors multiplying t are constant, a plot of the left side against t should be linear at constant temperature, as is observed, the slopes increasing with increasing temperature.

The studies cited above agree with the results obtained for other forms of SiC: The reaction is controlled by the diffusion of O_2 through SiO_2, which grows at the Si-SiC interface.

V. Summary

1. The oxidation rate is parabolic, which indicates that diffusion of O_2 through SiO_2 is rate-determining, i.e., reaction occurs at the SiC-SiO_2 interface.
2. The reaction of product gases (CO,CO_2) out is not rate-determining.
3. At very low Po_2 oxidation is active - the products are SiO and CO - and no protective scale forms.
4. The initial (pre-parabolic) stages have not yet been studied, as they have for Si.

5. The effect of impurities, usually Al and B added as densification aids increase the oxidation rate, probably because they diffuse into the SiO_2 and make it more permiable to O_2.

6. A wide range of activation energies has been reported, and the values seem to be temperature dependent. In general, these energies are higher than for Si oxidation. If diffusion of O_2 through SiO_2 is rate-determining in both cases this requires explanation. One such explanation is based on the occurrence of the glass-cristoballite transition, the diffusivity of O_2 being different in the two materials. However, although the oxidation rate of pure SiC is ~ half that of Si, as might be expected on the basis of stoichiometry, the addition of impurities greatly increases both the rate and the activation energy. No convincing explanation has yet been offered.

7. SiC is anisotropic - opposite faces are Si and C. Their oxidation rates, studied with single crystals, differ by a factor of 6-10. No detailed model has yet been offered which explains this in terms of the oxidation of successive layers of Si and C which is the same for both faces, i.e., why is the initial layer so important in determining the rate?

8. Polycrystalline SiC is likely to contain a mixture of Si and C faces on the original crystallites. On statistical grounds alone the Si/C area ratio should

be unity, but processing techniques may produce deviations. Thus a comparison of rate for different starting materials is not expected to provide any fundamental insight into oxidation mechanisms.

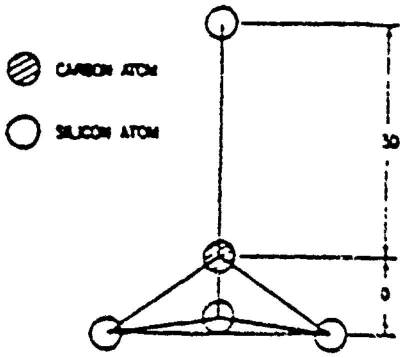

Fig. 1 — Basic tetrahedral bond of SiC (from ref. 5). (Figure 1 on page 7 from "Journal of the American Ceramic Society," Vol. 58 by R. C. Harris, published by The American Ceramic Society, ©1975, used by permission.

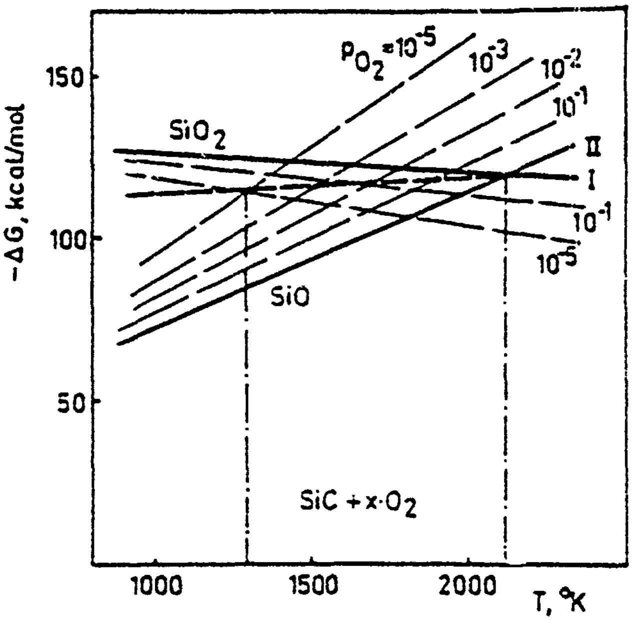

Fig. 2 — Free energy of reaction for the oxidation of SiC by oxygen, related to 1 mol SiC (6). (Figure 1 on page 320 from "Silicon Carbide," by E. Fitzer and R. Ebi, published by University of South Carolina Press. ©1973, used by permission.)

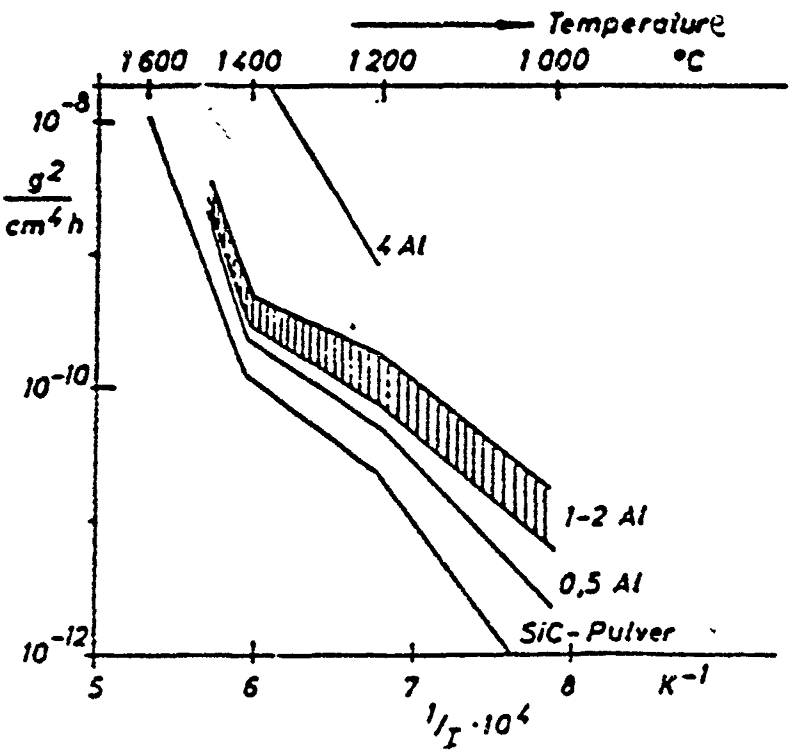

Fig. 3 — Temperature dependence of the oxidation rate of hot-pressed SiC for various added Al concentrations (after 15). (Figure 4 on page 256, Vol. 56, No. 9, by J. Schlichting from "Berichte Deutsche Keramische Gesellschaft," ©1979, used by permission.)

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OXIDATION OF SILICON NITRIDE (Si_3N_4, SN)

I. Forms of Si_3N_4

Silicon nitride, frequently abbreviated SN in the literature, has not yet been prepared as single crystals. Consequently, oxidation studies deal with SN prepared in particular ways, the products containing densification additives and/or pores. In that respect the situation is similar to that for SiC, except that single crystals are not available.

Listed here are the common methods for preparing SN and their commonly used abbreviations:

1. Reaction-bonded Si_3N_4 (RBSN)

   This material is produced by in-situ reaction of Si/metal particulate compacts with N_2. Si_3N_4 crystallizes into the pores of the initial compact, resulting in substantial densification. However, the material may still be porous. It also contains the originally added metal.

   A method for obtaining at least films of near-theoretical density is sputtering. For example, SN films up to 25um thickness have been prepared by reacting Si pressed on top of RBSN billets with N_2, O_2, and N_2O.

2. Chemical Vapor Deposition (CVD)

   This method is frequently used to deposit SN films of near-theoretical density on Si. The substrate is heated to 800-1800°C in an atmosphere of SiH_4 + NH_3 and SN deposits.

3. Hot-pressed SN (HPSN)

Si_3N_4 powder is pressed with a sintering aid, usually MgO, for a few hours at 1600-1800°C. The grains are bonded by a glassy phase containing the major part of the sintering aid. Y_2O_3, ZrO_2, ZrN, ZrC, CeO_2, and Ce_2O_3 have also been used as sintering aids. Oxidation of these materials may affect the SN and the glassy phase differently.

4. Pressureless Sintering

Similar additives and temperatures are used as in hot-pressing. N_2 atmospheres have been used to inhibit decomposition. 90-95% of theoretical density has been achieved.

II. Oxidation Reactions

Oxidation reactions for Si_3N_4 are very similar to those for SiC. At higher oxygen pressures SiO_2 is formed as a protective coating. Instead of CO_2 or CO, N_2 or oxides of nitrogen are evolved as products (1):

$$Si_3N_4(s) + 3O_2(g) = 3\,SiO_2(s) + 2N_2(g)$$

$$Si_3N_4(s) + 5O_2(g) = 3\,SiO_2(s) + 4NO(g)$$

which may be followed by

$$2NO(g) = N_2(g) + O_2(g)$$

Under some conditions an oxynitride may form:

$$Si_3N_4(s) + O_2(g) = Si_2ON_2(s) + SiO(g) + N_2(g)$$

III. Thermal Decomposition

Above 1500°C Si_3N_4 decomposes to the elements (2).

$$Si_3N_4(s) = 3\ Si(l) + 2N_2(g)$$

The stability diagram for Si_3N_4 (3) is shown in figure 1. It is obvious that sintering under high N_2 pressure will inhibit this decomposition. A more detailed discussiion is given in a later section.

If other materials, e.g., oxides, have been added as densification aids, decomposition will yield other materials besides SiO and N_2.

Since this report is primarily concerned with oxidation, it will focus on studies below 1500°C, where decomposition can be neglected.

IV. Oxidation of Si_3N_4

Since SN is generally not available in the pure state, except perhaps for powders, we discuss first oxidation studies of relatively pure materials, before commenting briefly on studies in which additives are major constituents.

A. Powder

There is very little work on the oxidation kinetics of SN powder. Horton (4) found that after an initial period (not further studied) the oxidation was parabolic from 1065 to 1340°C. Only a small fraction of the total mass was oxidized, thus obviating the need for the contracting sphere model. The activation energy was 68 kcal in dry air and 61 kcal in dry O_2, which is about twice the activation energy for O_2 diffusion through silica glass. However, the higher values may result from the formation of α tridymite. The structure of this material is sufficiently open for N_2 diffusion out not to be rate-determining.

B. CVD Films

These films are of considerable interest both as semiconductors, in which case they are deposited on a silicon substrate, and for high temperature applications, such as in gas turbines, where the substrate is a structural alloy. The importance of this form of SN lies in the high purity which can be achieved. For control of electrical properties this is a necessity; for high temperature uses the high purity also leads to higher oxidation resistance, which tends to be lowered by additives.

SN films can be prepared by several methods. In addition to the method already mentioned in I.2, they can also be prepared by reactively sputtering Si with $N_2(g)$ (5). If $O_2(g)$ is added, oxynitride films are formed. In this case a continuous series of compounds with changing oxygen and nitrogen compounds are formed, rather than a mixture of SiO_2 and Si_3N_4. (6).

In contrast to other studies, an examination of SN by ESCA of films oxidized at 1070°C found a surface layer of oxynitride, rather than SiO_2 (7).

The oxidation of both crystalline and amorphous SN films deposited on graphite were also studied thermogravimetrically at 1550° - 1650°C (8). For crystalline SN, oxidation is always parabolic (after an initial period, which was not further studied), the coating consisting of α-cristobolite. Amorphous SN oxidized parabolically at first, and then switched to linear growth. For both kinds of SN the surface was dense and pore-free during parabolic oxidation, but was porous during linear growth. No oxynitride was detected for either material. The activation energies for the parabolic growth were 93 and 110 kcal for the crystalline and amorphous forms, respectively, much greater than for the diffusion of O_2 through glassy SiO_2.

Recently a quantitative theory for SN oxidation on Si has been proposed (9). It is similar to the Deal and Grove model except for the "extra" layer of SN.

$$\text{Gas} \mid Si_3N_4 \mid SiO_2 \mid Si$$

The theory assumes that SiO_2 is much more permeable to O_2 than Si_3N_4 is and predicts that the oxidation rate of Si_3N_4 is constant and that of Si is zero if the SN film is much thicker than the diffusion length of the oxidant species in SN; in that case SiO_2 will grow only at the outer SN surface. For thin SN film some oxidant may diffuse through the SN, and perhaps the SiO_2, and increase the thickness of the inner SiO_2 layer.

C. Hot-pressed Si_3N_4

This material always contains additives whose composition and concentration vary widely. Oxides of Mg, Co, Fe, and Al are common, but rare earth oxides such as

CeO_2 and Y_2O_3 have also been used. Concentrations vary from impurity levels present in commercial powders, generally < 1% to purposely added concentrations >10%. Even at the lowest levels all impurities lower the oxidation resistance.

For example, the oxidation of SN with a total impurity level of ~1%, began at 700°C (10). An amorphous SiO_2 layer formed at 750°C, which tended to crystallize to cristobalite as the temperature was raised toward 1000°. Above 1000° the impurities began to react in the surface layer, forming a variety of structures: enstatite ($MgSiO_3$), akermanite ($Ca_2MgSi_2O_7$), forsterite (Mg_2SiO_4), and diopside ($Ca_2Mg(SiO_3)_2$). The relative concentrations of these materials changes with time and temperature. Their concentrations in the surface layer, mostly SiO_2, is much higher than in the bulk. The most likely reason is that the bulk impurities (additives) are not uniformly distributed but are concentrated in a glassy intergranular phase from which they diffuse readily into the oxidized layer.

The oxidation kinetics of hot-pressed billets of near theoretical density and similar impurity level (1%/MgO) has also been studied (11). Between 1200 and 1400°C, oxidation is parabolic with an activation energy of 90 kcal, similar to that reported for pure thin films. Otherwise the results resemble those of Kiehle et. al. (10).

In contrast to the rather sparse literature on Si_3N_4 hot-pressed with low concentrations of impurities, far more work has been reported for materials containing high concentrations. From a phase rule point of view, such materials can be viewed as compounds of Si_3N_4 with additives in ternary or higher systems. Babini and Vincenzini (12) have reviewed much of this literature, as well as carrying out experiments in the Si_3N_4 - Y_2O_3 - MgO system.

In spite of the variety of compositions employed in various studies, the results can be described by relatively few generalizations.

1. Parabolic weight gains are observed for all systems, irrespective of additives and temperature.
2. Additives diffuse from the bulk to the surface layer.
3. Oxidation rates vary with the nature of the additives and their concentrations, but there is no simple correlation.
4. Arrhenius activation energies vary with the nature and kind of additive, but there is no simple correlation.

F. From a practical point of view, additives aid densification and increase mechanical strength, while lowering the oxidation resistance. Consequently the composition chosen always involves a trade-off. It is therefore not surprising that many compositions have been studied in order to design SN ceramics for particular applications. One result of this work has been to develop some generalizations which are useful in maximizing both mechanical strength and oxidation resistance. For example, the system $Si_3N_4 - Y_2O_3 - SiO_2$ compositions in the compatibility field $Si_3N_4 - Si_2N_2O - Y_2Si_2O_7$ fill the requirements, but the occurrence of the four quaternary compounds $Y_{10}Si_7O_{23}N_4$, $YSiO_2N$, $Y_2Si_2O_7N_2$, and $Si_3Y_2O_3N_4$ is to be avoided (13,14,15).

D. Reaction-bonded Si_3N_4 (RBSN)

As described in I.1 this material suffers from open porosity, although it is of interest because of its high-temperature properties and fabricability. So far, oxidation studies have been limited, but some results are available (16, 17, 18). These are summarized here.

Oxidation at relatively low temperatures, 700-1200°, is parabolic and occurs both internally - in the pores-, and externally. The oxidation rate is thus dependent on the porosity. The formation of a coherent and dense surface layer of SN deposited on the surface of porous RBSN can slow the oxidation rate. Even more effective is a surface layer of Si_2ON_2, which may be deposited by sputtering (18).

Near 1500°C, gas evolution is observed which probably comes from thermal dissociation

$$Si_3N_4 = 3Si + 2N_2$$

and/or reaction between oxidation and dissociation products:

$$SiO_2 + Si = 2SiO$$

Thus 1400°C probably represents the upper temperature limit for this material.

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DECOMPOSITION AND OXIDATION OF SILICON OXYNITRIDE (Si_2N_2O)

The formation of this compound under certain conditions during the oxidation of SN has been described in the previous section. Here the rather sparse literature pertaining to the stability of Si_2N_2O is reviewed. One reason for doing so is that the oxynitride has recently been recognized as a useful ceramic in its own right (1).

The compound can be prepared by reacting SiO_2 with N_2 under an appropriate pressure of O_2 at 1400 - 1500°C (2) or by reacting a 3:1 mixture of Si-SiO_2 with N_2 at 1450°C (3). Thermodynamic aspects of the stability will be discussed in the next section. Here we summarize work on the decomposition reactions. Based on analysis of evolved gases and X-ray diffraction of the condensed phases, the overall decomposition is (3).

$$3Si_2N_2O(s) \;=\; 3\,SiO(g) + N_2(g) + Si_3N_4(s)$$

Both in vacuum and argon, this reaction begins at 1250-1300°C and becomes quite rapid at 1400°. Both α and β Si_3N_4 are formed. At the higher temperatures Si_3N_4 is also unstable. From the time dependence of the reaction products, the authors deduced the following reaction sequence:

$$\begin{aligned} 2Si_2N_2O(s) &= SiO_2(s) + Si_3N_4 \\ Si_3N_4(s) &= 3Si(s) + 2N_2(g) \\ SiO_2(s) + Si(s) &= 2SiO(g) \end{aligned}$$

In order to obtain dense ceramic bodies from Si_2ON_2 powders, additives such as BeO and MgO are required. Nearly pore-less specimens were obtained with 5% BeO(3).

The oxidation proceeds in a manner similar to that of Si_3N_4, being virtually unnoticeable at 1400°C, and becoming rapid above 1500°.

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OXIDATION THERMODYNAMICS OF SILICON, SILICON CARBIDE, AND SILICON NITRIDE

I. General

The oxidation of the above materials has been discussed in the preceding sections, with emphasis on the nature of the reactions and their kinetics. It is, however, also very useful to examine the thermodynamics of oxidation and, to a lesser extent, thermal dissociation. For example, all of these materials exhibit a transition from passive to active oxidation which depends on the O_2 pressure for the reaction

$$SiO_2(s,l) = SiO(g) + 1/2O_2(g)$$

The stability ranges of various materials and oxidation products frequently depends on gas pressures in an analogous way. Thus the stability ranges provide valuable insight into what reactions are to be expected, since reactions which are thermodynamically unfavorable cannot occur to a significant extent.

Thermodynamic information can be given in various forms. In simple systems, where only a single reaction is operative, a tabulation of the equilibrium constant as a function of temperature may suffice; alternatively, log K may be plotted as a function of temperature. When a system becomes more complex, generally when several equilibria operate simultaneously, a listing of several equilibrium constants is of limited utility. It has therefore become more popular in recent years to construct "stability diagrams" which indicate the range of conditions, generally gas pressure and temperature, over which various materials are stable. Several authors have published such diagrams for the materials of interest here, and these are reproduced and discussed below.

Table I lists ΔG°f for the major species occurring in the Si-O-C-N system as reactants and products from 1200 to 1800K. The data are taken from JANAF (1). A similar table was published by Gulbransen and Jansson (2) for the Si-O-C system in the form of Log K_p. These values were used by these authors to construct stability diagrams which are also given in this report. It should be noted that the small shifts in the diagrams which would occur by considering values for the various modifications in which some solids exist, are not significant.

Table I. Thermochemical Data of Compounds and Species in the Si-O-C-N System (1)

	ΔG°f (Kcal/mol) at temp(°K)			
	1200	1400	1600	1800
Si(g)	65.257	58.335	51.459	45.445
Si_2g)	87.392	78.806	70.306	63.523
Si_3(g)	93.331	84.131	75.084	68.631
SiO(g)	-48.672	-52.491	-56.244	-59.118
SiO_2(s)[a]	-166.296	-158.134	-150.585	-141.148
SiO_2(g)	-73.755	-73.753	-73.722	-72.844
SiCα(s)	-14.818	-14.450	-14.085	-12.899
SiC(g)	116.945	107.832	98.799	90.661
Si_2C(g)	72.448	63.683	55.049	48.172
C(g)	126.035	118.469	110.919	103.388
CO(g)	-52.049	-56.189	-60.284	-64.337
CO_2(g)	-94.681	-94.716	-94.739	-94.750
Si_3N_4s)	-83.005	-67.354	-51.850	-34.043
NO(g)	17.981	17.373	16.765	16.156
NO_2(g)	25.921	28.951	31.975	34.992
N_2O_4g)	86.726	100.369	113.888	127.299

[a] Cristobalite, high

II. The Si-O System

Figures 1-4 show the partial pressures of various species in this system from 1200 to 1800. The vertical lines give the oxygen pressures for the dissociation reaction.

$$SiO_2(s) = Si(s) + O_2(g)$$

The horizontal lines show the equilibrium pressures of Si(g), $Si_2(g)$, and $Si_3(g)$ over Si(s), at the left, and of $SiO_2(g)$ over $SiO_2(s)$ at the right. The lines of variable slope show equilibrium pressures of SiO(g) and the Si(g) species over Si(s) on the left and over $SiO_2(s)$ on the right. The CO/CO_2 and H_2/H_2O ratios shown on the bottom give the O_2 pressure at the top. Note that when SiO_2 becomes the stable phase, the importance of SiO(g) diminishes.

III. The Si-C System

Figure 5 is a log p_{SiC_x} vs log p_C diagram for 1600K. p_{SiC_x} refers to all the different gaseous species including Si and its polymers. The vertical line separates the existence regions of Si(s) and SiC(s). The dashed vertical line gives the vapor pressure of C(s). Pressures of carbon greater than this vapor pressure have no physical meaning.

IV. The Si-O-C System

The Si-O and Si-C systems are part of the Si-O-C system. Thus, the information in Figures 1-5 applies to parts of the Si-O-C system. The additional data needed to characterize the Si-O-C system relate to the coexistence of $SiO_2(s)$ with SiC(s) and C(s). Diagrams are shown in Figs. 6-9. The heavy horizontal, vertical, and slanted lines define boundaries between the condensed phases. The thin, slanted lines show the values of log p_{CO} from the equilibrium

$$C(s) + 1/2O_2(g) = CO(g)$$

The log p_{CO}/p_{CO_2} at the bottom of the diagram relate CO and CO_2 pressures according to the equilibrium.

$$CO(g) + 1/2O_2 = CO_2(g)$$

The figures show that $SiO_2(s)$ is the stable condensed oxide on SiC(s) in oxidizing atmospheres. The stability range for SiC(s) is very small.

V. The Si-N System

Jansson and Gulbransen (3) have published the stability diagram for this system at 1800K, shown in Figure 10. Si(g) is the major gaseous species over Si(l) and also over $Si_3N_4(s)$ for log $p_{N_2} \leq 0.8$. The nitride is unstable for N_2 pressures below 0.01 atm.

VI. The Si-O-N System

The thermochemistry of this system is not as settled as that of the others, primarily because data for Si_2ON_2 are not well established. In addition, there are still arguments whether α - Si_3N_4 is actually a material containing some oxygen, and only β - Si_3N_4 is oxygen-free (3). In Fig. 11 we show a stability diagram for the Si-N-O system at 1600K, as given by Singhal (4), which is based on the thermodynamic data of Blegen (5). In this diagram any distinction between different crystal structures of Si_3N_4 has been neglected, and the stability range of Si_2ON_2 is quite large. A somewhat different choice of data would shrink this region considerably (3). More definitive thermodynamic data for the oxynitride are certainly needed.

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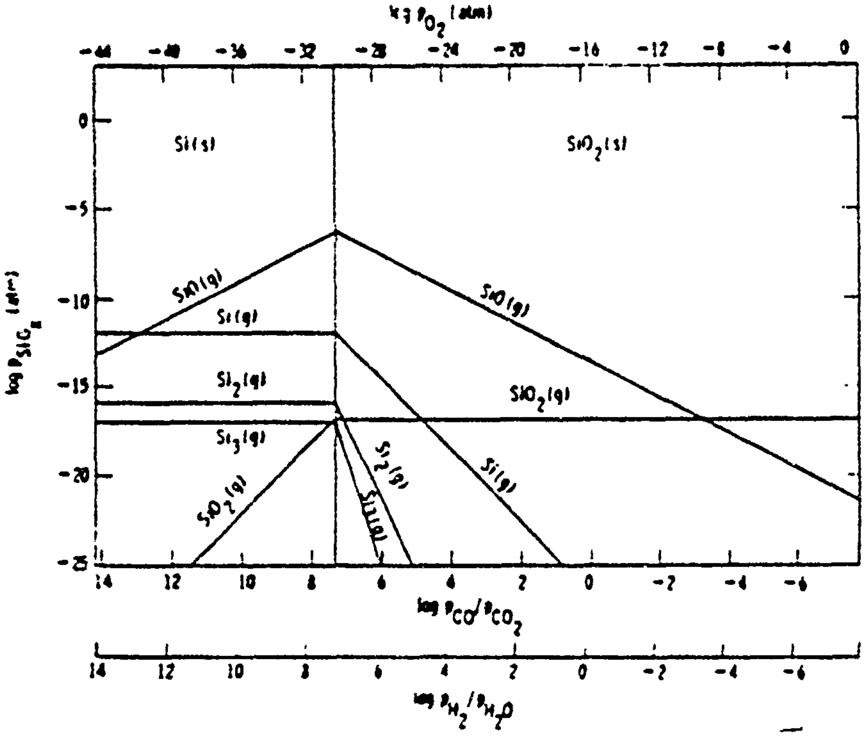

Fig. 1 — Stability diagram for silicon-oxygen system at 1200°K. (Figure 1 from Oxidation of Metals, Vol. 4 entitled "The High Temperature Oxidation, Reduction and Volatilization Reactions of Silicon and Silicon Carbide," page 181 by E. A. Gulbransen and Sven A. Jansson, ©1972, used by permission.)

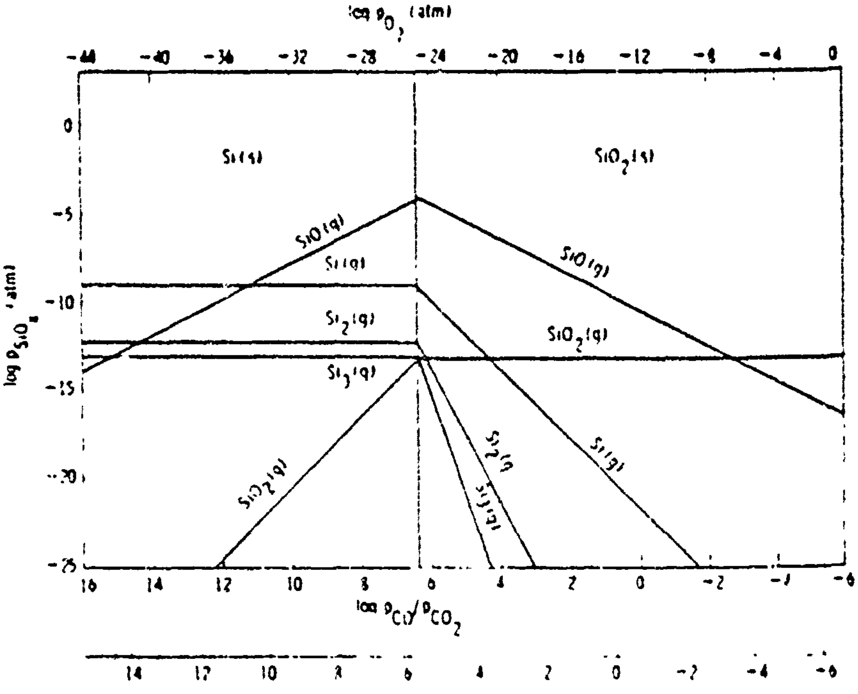

Fig. 2 — Stability diagram for silicon-oxygen system at 1400°K. (Figure 2 from Oxidation of Metals, Vol. 4 entitled "The High Temperature Oxidation, Reduction and Volatilization Reactions of Silicon and Silicon Carbide," page 181 by E. A. Gulbransen and Sven A. Jansson, ©1972, used by permission.)

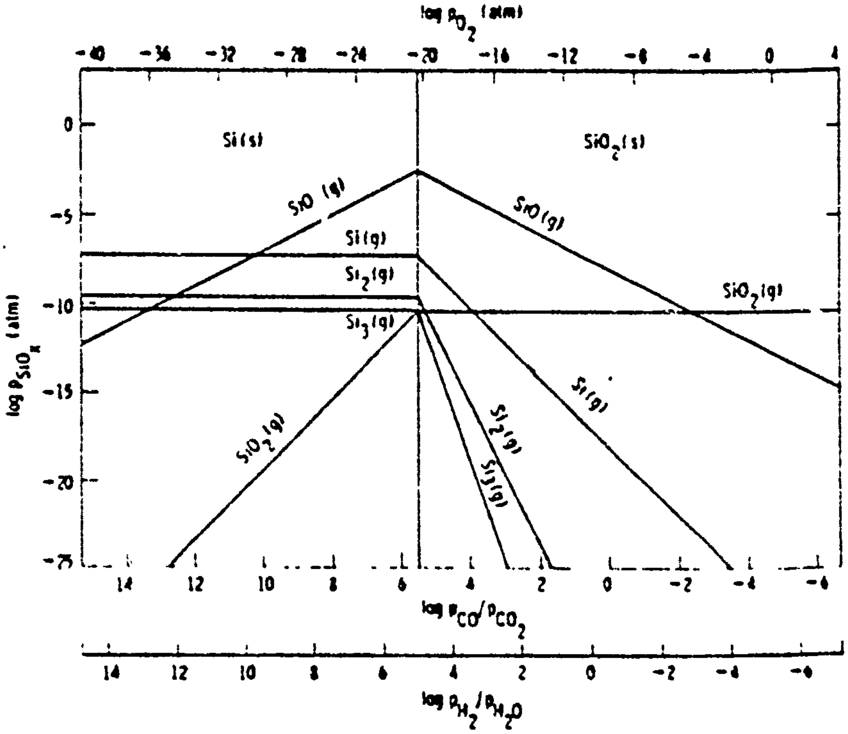

Fig. 3 — Stability diagram for silicon-oxygen system at 1600°K. (Figure 3 from Oxidation of Metals, Vol. 4 entitled "The High Temperature Oxidation, Reduction and Volatilization Reactions of Silicon and Silicon Carbide," page 181 by Earl A. Gulbransen and Sven A. Jansson, ©1972, used by permission.)

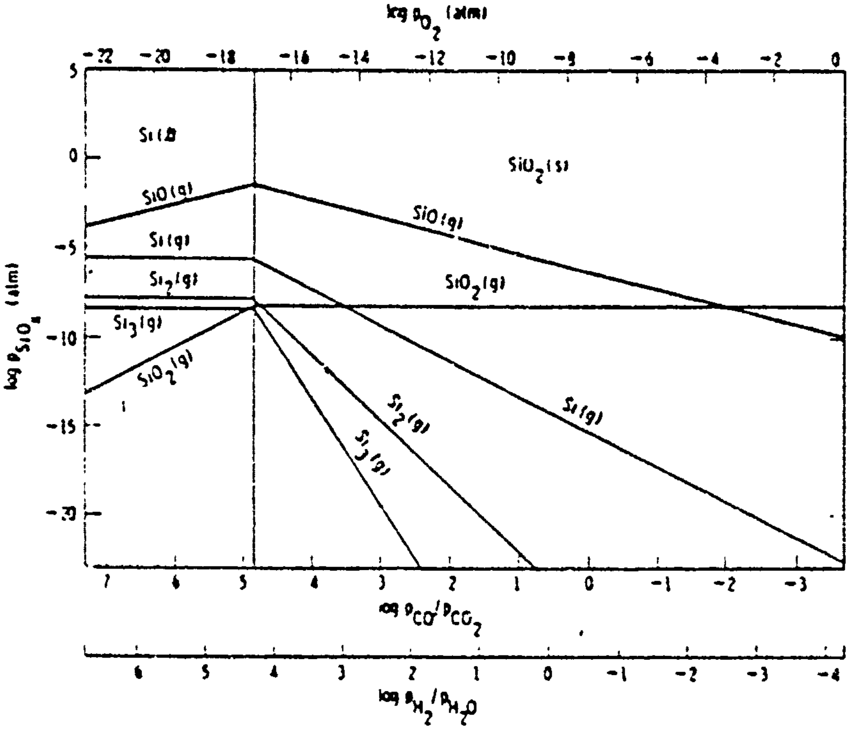

Fig. 4 — Stability diagram for silicon-oxygen system at 1800°K. (Figure 4 from Oxidation of Metals, Vol. 4 entitled "The High Temperature Oxidation, Reduction and Volatilization Reactions of Silicon and Silicon Carbide," page 181 by Earl A. Gulbransen and Sven A. Jansson, ©1972, used by permission.)

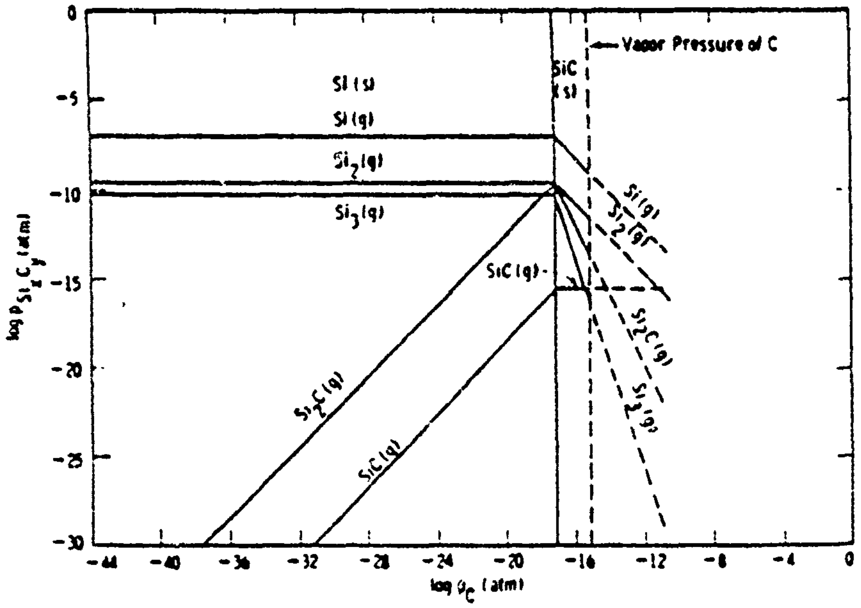

Fig. 5 — Stability diagram for silicon-carbon system at 1600°K (Figure 5 from Oxidation of Metals, Vol. 4 entitled "The High Temperature Oxidation, Reduction and Volatilization Reactions of Silicon and Silicon Carbide," page 181 by Earl A. Gulbransen and Sven A. Jansson, ©1972, used by permission.)

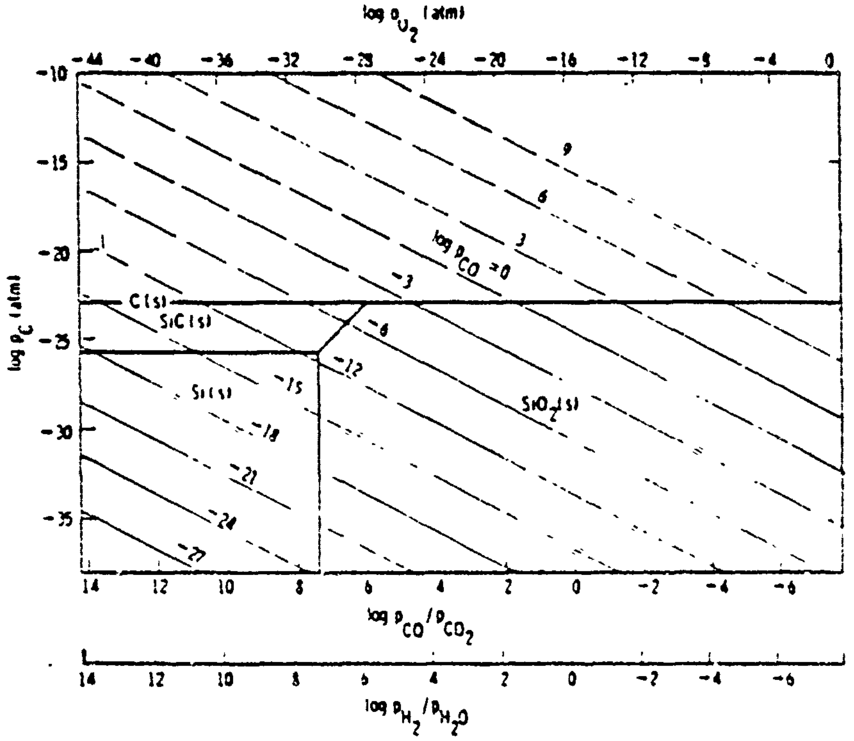

Fig. 6 — Stability diagram for silicon-carbon-oxygen system at 1200°K (Figure 6 from Oxidation of Metals, Vol. 4 entitled "The High Temperature Oxidation, Reduction and Volatilization Reactions of Silicon and Silicon Carbide," page 181 by Earl A. Gulbransen and Sven A. Jansson, ©1972, used by permission.)

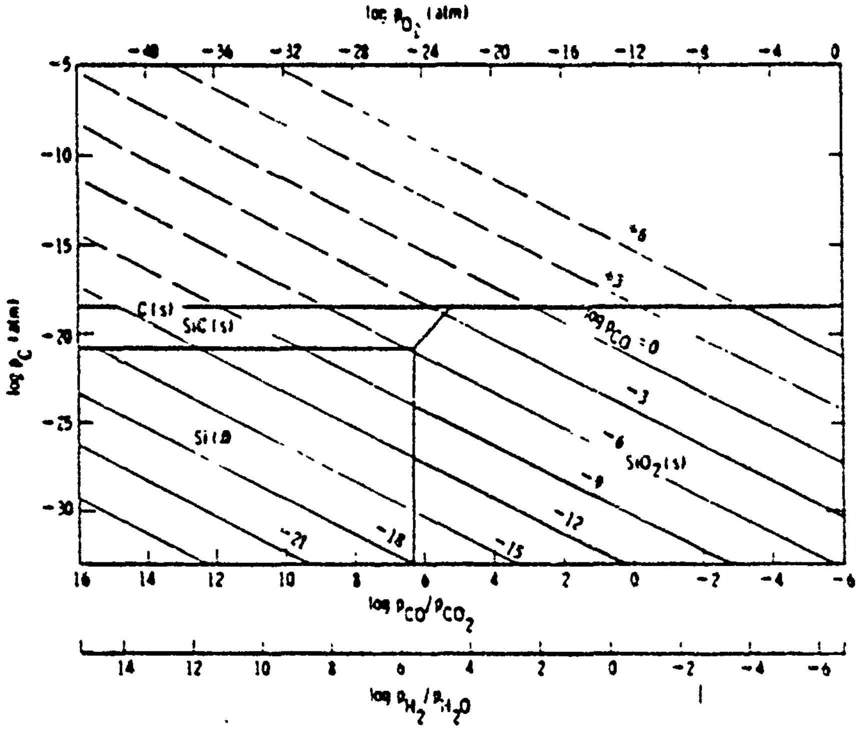

Fig. 7 — Stability diagram for silicon-carbon-oxygen system at 1400°K (Figure 7 from Oxidation of Metals, Vol. 4 entitled "The High Temperature Oxidation, Reduction and Volatilization Reactions of Silicon and Silicon Carbide," page 181 by Earl A. Gulbransen and Sven A. Jansson, ©1972, used by permission.)

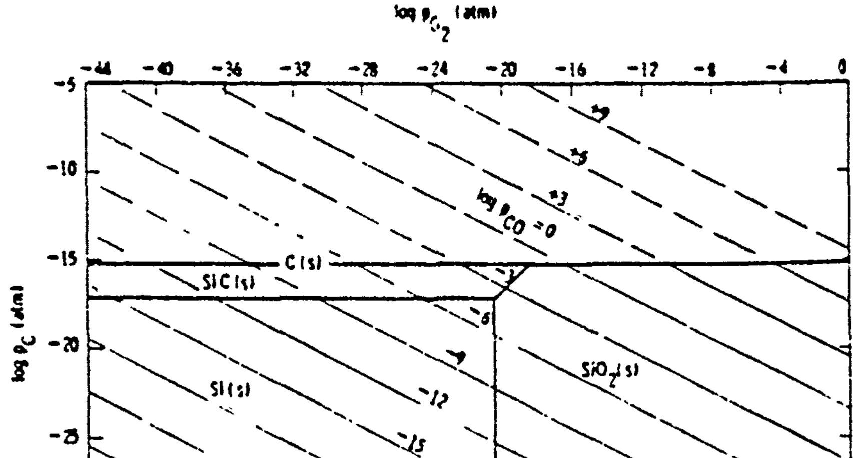

Fig. 8 — Stability diagram for silicon-carbon-oxygen system at 1600°K (Figure 8 from Oxidation of Metals, Vol. 4 entitled "The High Temperature Oxidation, Reduction and Volatilization Reactions of Silicon and Silicon Carbide," page 181 by Earl A. Gulbransen and Sven A. Jansson, ©1972, used by permission.)

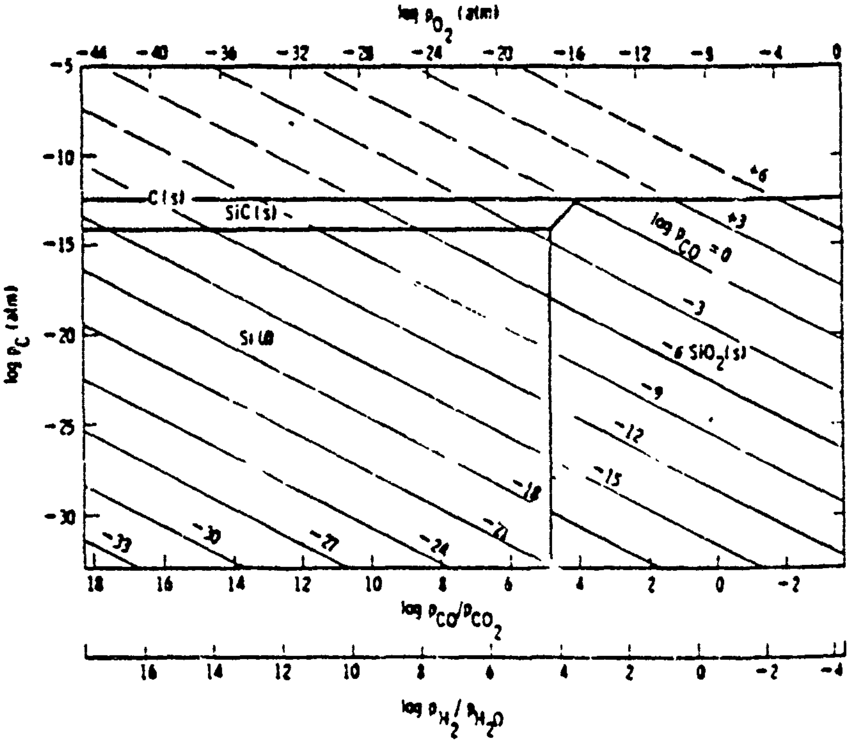

Fig. 9 — Stability diagram for silicon-carbon-oxygen system at 1800°K (Figure 9 from Oxidation of Metals, Vol. 4 entitled "The High Temperature Oxidation, Reduction and Volatilization Reactions of Silicon and Silicon Carbide," page 181 by Earl A. Gulbransen and Sven A. Jansson, ©1972, used by permission.)

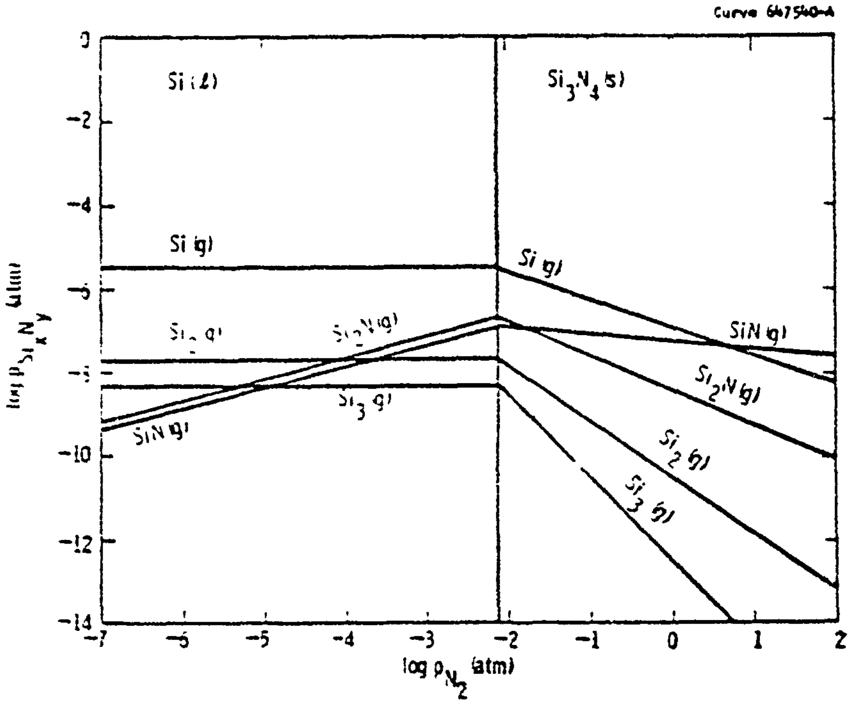

Fig. 10 — Thermochemical data for Si-N system at 1800°K. (Figure 2 from paper by S. A. Jansson and E. A. Gulbransen, pages 2-23, entitled "High Temperature Gas-Metal Reactions in Mixed Environments,' from TMS-AIME, Z. Foroulis, ed., ©1973, used by permission.)

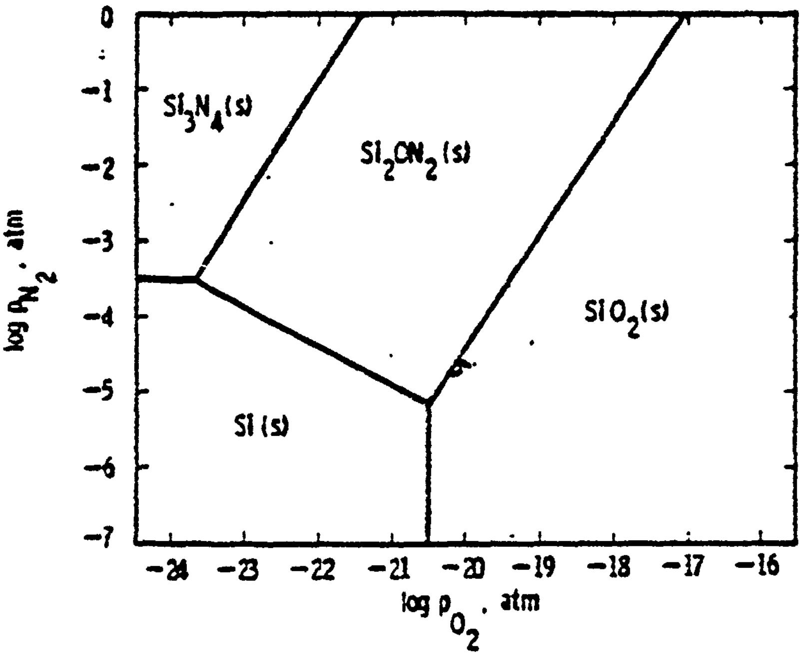

Fig. 11 — Thermochemical diagram for the Si-O-N system at 1600°K. (Figure on page 277, from "Special Ceramics," Vol. 5, by S. Wild et al., edited by P. Popper, ©1972, used by permission.)

SUMMARY

As the foregoing review shows, the oxidation of silicon, silicon carbide, and silicon nitride have much in common:

1. For all three substances there exists a critical oxygen pressure below which oxidation is "active", leading to the formation of $SiO(g)$. Above the critical pressure oxidation is "passive", resulting in a protective layer of SiO_2, which may be glassy, crystalline, or mixed. The critical pressure is that for the equilibrium.

   $$SiO(g) + 1/2O_2(g) \quad = \quad SiO_2(s)$$

2. In the passive regime oxidation occurs at the SiO_2 - substrate (Si,SiC,SN) interface, the rate being determined largely by O_2 transport through the protective layer.

Differences in the oxidation reactions rise primarily from the non-Si element in SiC and Si_3N_4, which also participates in the oxidation reaction. The gases formed - CO or CO_2 and oxides of nitrogen, respectively - may affect the stability of the protective SiO_2 layer, if their transport through this layer is hindered. In that case, the SiO_2 may exhibit bubbles, or spall.

However, our understanding of the oxidation processes is at very different stages for the three substances, both kinetically and thermodynamically.

Thermodynamic data for Si, SiC, and their oxidation products are well established in the temperature range of interest (1000 - 1500°C), and therefore stability diagrams can be drawn with confidence. For Si_3N_4 the situation is not as clear, because data for Si_2ON_2 are still somewhat fragmentary, and because α - Si_3N_4 contains oxygen under some conditions.

With respect to oxidation kinetics the situation is even more disparate. For silicon, rate laws and activation energies are well established over a large part of the kinetic regime. The uncertainties that remain mainly involve the very early stages of oxidation. However, these are of great interest in the preparation of semiconductor devices. A major reason for this understanding lies in the availability of high-purity single crystals. Thus, the effect of even very low impurity levels introduced by doping can be readily assessed.

The situation for SiC and Si_3N_4 is not nearly as fortunate. Si_3N_4 single crystals have not yet been prepared, and work on SiC single crystals, which do exist has been sparse and is made more difficult by the anmisotropy of the materials. Moreover, Si_3N_4 of theoretical density has not yet been formed without additives. These additives generally increase the oxidation rate, probably because they concentrate in grain boundaries which are more permiable to O_2 than the bulk material, and from which they diffuse into the SiO_2 layer to form a variety of compounds. Thus there exists no base line of pure material from which the effect of additives can be assessed. Both SiC and Si_3N_4 prepared by various techniques with a variety of additives, exhibit a range of activation energies, a clear indication that no fundamental rate information on the materials themselves is being obtained.

In order to obtain fundamental information on the oxidation mechanisms of SiC and Si_3N_4, high purity crystals offer the best possibility. For SiC this is within reach, but not much has been done yet. The synthesis of single crystal Si_3N_4 is likely to be a difficult problem. Careful studies on very pure powders could be utilized in the meantime.