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SILICON CARBIDE AS AN OXIDATION-RESISTANT HIGH-TEMPERATURE MATERIAL; I: OXIDATION AND HEAT CORROSION BEHAVIOR

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16. Abstract

The oxidation and corrosion behavior of SiC (in the form of a SiC powder and hot-pressed and reaction-bound material were studied. The excellent stability of SiC in an oxidizing atmosphere is due to the development of protective SiO_2 coatings. Any changes in these protective layers (e.g. due to impurities, reaction with corrosive media, high porosity of SiC, etc.) lead in most cases to increased rates of oxidation and thus restrict the field of SiC application.

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SILICON CARBIDE AS AN OXIDATION-RESISTANT HIGH-TEMPERATURE MATERIAL; I: OXIDATION AND HEAT CORROSION BEHAVIOR

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1. Introduction /196*

SiC is being used as a high-temperature material in heat-conductor technology for temperatures up to 1500°C. In addition, it is regarded, along with Si_3N_4, as a future material for such things as high-temperature turbine blades (see, for example, Alliegro and Torti [1], Torti [2], Gorum [3], and McLean [4]).

Silicon carbide today comes in various forms for use; it is seen as a final material for SiC rock with a silicate, nitride, or oxynitride binder or for pure SiC material as hot-pressed, reaction-bound, or recrystallized material. Hot-pressed SiC (HPSiC) contains a few percent of aluminum [5, 6] or perhaps boron as a sintering agent [7]. These substances display theoretical densities and are identified by a high RT stability, which nevertheless decreases sharply at about 1200 to 1400°C [8]. Indeed, high RT stabilities are obtained with the addition of Al rather than boron, but the decrease in stability at higher temperatures is greater than for boron addition, for which the stability still increases somewhat [9]. The stability of reaction-bound SiC (RBSiC), on the other hand, amounts to only a third of that with a hot-pressed material; however, it can survive temperatures up to 1600°C, if the content of residual silicon (from the manufacturing process) is as small as possible [10]. In general, the Si content is 8 to 10%. Developments in recent years have further shown that it is also possible to manufacture dense SiC by means of pressure-less sintering [11-15]. The final product here is a very fine SiC powder (grain size <1 μm), to which boron and carbon are added (about 1.5% by weight). These substances exhibit sufficient RT stability to survive temperatures up to 1700°C (Draft and Dooher [16]).

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*Numbers in the margin indicate pagination in the foreign text.

2. Oxidation Mechanism

The oxidation resistance of SiC is based on the development of SiO_2 glass layers at temperatures >800°C.

It has been known for some years that protective layers of SiO_2 are built up opposite oxide layers, such as in the oxidation of superalloys (such as Al_2O_3 and Cr_2O_3), which present the best protection against oxygen at high temperatures. In contrast to other oxides, no transport takes place through these layers via metal or oxygen ions. The upper use-temperature is limited to 1700°C, due to the low viscosity of the SiO_2 glass.

It is generally known that molecular oxygen can pass through the open pore structure of SiO_2 glass. These findings were established by Norton [18] by means of permeability measurements. He further determined the oxygen diffusion coefficient in SiO_2 glass through exchange reactions with an O_2-gas atmosphere by the tracer method. In this connection, the data obtained can be correlated with the above-mentioned permeability data, because in both cases, similar activation energies were determined (83 to 125 kJ/mole) (see the summary considerations of Schäffer [19]). As early as 1964, Motzfeld [20] showed similar values could also be derived for activation energy from kinetic measurements for the oxidation of silicon and silicon carbide. Thus it is possible to correlate transport processes in SiO_2 (oxygen diffusion, oxygen permeability) with the increase in a protective SiO_2 layer in SiC [19]. For the oxidation of SiC applied, this means the rate-defining step is represented by the permeability of molecular oxygen through the already-formed protective SiO_2 layer. Hence, an exchange takes place with the oxygen incorporated into the SiO_2 lattice. This exchange reaction, however, has no effect on the kinetics of the oxidation reaction. /197

With these statements, the oxidation behavior of silicon carbide has already been described and characterized in its essentials, and it can be confirmed with very pure SiC materials. However, some variation occurs in relation to the apparent discrepancies which must be considered in more detail. In the following, the most important data from the literature are critically discussed and brought face to face with the mechanism set up.

3. Active and Passive Oxidation

The formation of a protective SiO_2 layer in the oxidation of SiC occurs on the basis of the reaction equation:

$$2\ SiC_{(s)} + 3\ O_{2(g)} \rightarrow 2\ SiO_{2(s)} + 2\ CO_{(g)}.$$

The stability of the protective SiO_2 layer is determined through vaporization or decomposition of $SiO_{2(s)}$ during the formation of various gaseous species.

According to the calculations of Singhal [21], it results that vaporization of a protective SiO_2 layer from a silicon-bearing substance cannot be determined in an oxidizing environment. This can, however, become critical in a reducing atmosphere, i.e. at low oxygen partial pressure during SiO formation. According to Fitzer and Ebi [38, 39], SiO formation is already beginning at 1050°C at a stated partial pressure of 10^{-5} bars.

In addition, the protective SiO_2 layer reacts with the base material in SiO and CO. The equilibrium partial pressure of SiO can be calculated in advance. Fig. 1 shows this as a function of temperature. High SiO vapor pressure leads to explosion of the protective SiO layer at high temperatures and increases oxidation. It is more important, however, that free surfaces are thus created, for which an active oxidation analogous to the equation:

$$SiC_{(s)} + O_{2(g)} \rightarrow SiO_{(g)} + CO_{(g)}$$

can occur. The straight line indicated in Fig. 1 shows the oxidation relationships in two regions.

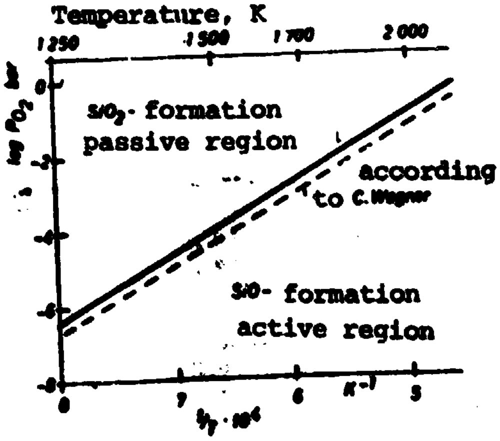

Fig. 1. SiO equilibrium partial pressure for the SiC/SiO_2 boundary as a function of temperature.

Above this line, we have a passive relationship with the formation of a protective SiO_2 layer: below is an active relationship with SiO formation, i.e. destruction of the material. The region of passivity was put forth in 1958 by Wagner [22]. The straight line calculated according to his formula for the boundary of the areas of active and passive oxidation is included in Fig. 1.

The validity of Wagner's theory has been proven by various authors. Several corrections have been made to it. According to Gulbransen and Jansson [23] and Hinze and Graham [24], these boundary lines between active and passive oxidation should be lowered, because the CO partial pressure must be taken into account. In addition, a possible SiO transport along pore channels is to be considered. Bennett and Chaffey [25] confirm these data for reaction-bound SiC, as well as Antill and Warburton [26, 27] for SiC powder. The latter authors of course found corrosion rates in the active area which were on the order of 5 times smaller than those theoretically predicted. Rosner and Allendorf [28] found a lowering of the boundary line on the order of 7 times for very high flow rates (10^4 cm/sec).

In spite of these modifications, the Wagner prediction appears to be a sufficient criterion for the active-passive transition in the oxidation of SiC.

For the SiC + SiO_2 reaction at higher temperatures during SiO formation, see Pultz and Hertl [29] and Borisov and Yudin [30].

See Dillon [31] concerning the primary stage of oxidation for oxygen adsorption and the formation of a protective SiO_2 layer resulting from this.

4. Oxidation of Pure SiC (Powder, Single Crystals)

Oxidation in the passive area (oxidation in air of air-oxygen at temperatures above 800°C) is characterized by a parabolic time law. In spite of a few points of view to the contrary, this fact is proven.

SiO_2 formation occurs at the SiO_2/silicide interlayer [32, 33]. Table 1 gives the oxidation rates indicated in the literature [26, 27, 34-53]. Fig. 2 shows the temperature dependence of comparable oxidation rates. It is known that these data lie very close together in range of values, which is recognized from the uniform activation energy of 83 to 125 kJ/mol (solid line). It is further known that below 1200°C, the oxidation rates fall sharply (heavy dashed line), [48], as it also is for RBSiC (Bennet and Chaffey [54], Schlichting [55]). Fitzer and Ebi [38, 39] explain the change in activation energy at 1200°C by crystallization of the protective SiO layer upon the formation of cristobalite in the range of 1200 to 1400°C. The number of the crystalline phases was hence determined by X-ray for up to 80% by volume. Above 1400°C, Fitzer and Ebi [38, 39] as well as Adamsky [34] found a further increase in activation energy, i.e. a strong increase in the oxidation rates. This phenomenon is explained by the change in the viscosity of the SiO_2 glass layer (facility of oxygen transport).

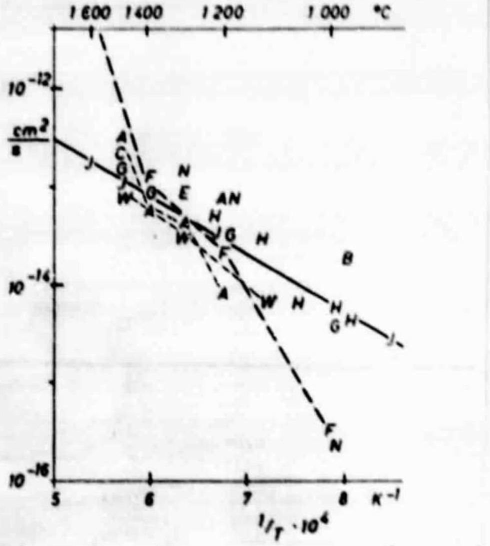

Fig. 2. Temperature dependence of oxidation rates for pure silicon carbide powder and single crystals. A = Adamsky, AN - Antill, B = Bartlett, C = Cappelen, E = Ervin, F = Fitzer, G = Gugel, H = Harris, J = Jorgensen, N = Nakatogawa, W = Wiebke.

Various statements regarding the oxidation behavior of the different SiC modifications are under consideration. Their basis would be better sought in the various addition of foreign elements. According /19 to Suzuki [31], β-SiC acts more slowly than α-SiC, while according to Konopicky, Patzak and Dohr [57], black Al-dosed α-SiC and green SiC are oxidized least and β-SiC (N_2-stabilized) most strongly. β-SiC should exhibit an active surface [60]. Black and grey SiC are oxidized more rapidly than green SiC (Nakatogawa [48]), but more slowly for a longer oxidation time (Wiebke [52]).

See Kapitel: Hot-Pressed SiC, on the effect of contamination.

The oxidation behavior of SiC single crystals varies according to crystallographic orientation (Harris [43]). There is a diffusion-controlled increase through surface reaction at the silicon face of the crystal being studied.

The oxidation of SiC proceeds with the formation of a protective SiC_2 layer which may be of a glassy or partially-crystallized nature. Whereas Adamsky [34] found no cristobalite at 1200 to 1400°C, Gugel et al. [40, 41] indicate cristobalite formation above 1000°C (development of rosette-like surface structures), Michel [58] above 1150°C, Fitzer and Ebi [38, 39] above 1200°C and Dillon [31] above 1300°C. The differences are probably attributable to the different crystallographic construction and different portions of various materials (see Sharma [60] on this).

5. Oxidation Behavior of Pure SiC Substances (Porous SiC, CVD Layers)

The oxidation behavior of porous SiC substances is very different. Fig. 3 shows typical curves for a reaction-bound material with 10% pores by volume [55]. These oxidation isotherms are recognized at low temperatures such as 1000°C by very high oxidation rates, while at high temperatures, the increase in weight in the first hour is very sudden and then it proceeds very slowly. Hence oxidation (preferably at high temperatures) in the primary stage for the protective SiC_2 layer increases at open pores with the formation of a closed uniform protective layer, whereby the reaction surface of this porous material decreases in the course of the reac- /200 tion [38, 39]. Oxidation behavior is thus not a substance-specific property of the material, but of the pore structure, i.e. the effective surface at any given time is controlled by the availability. SiO_2 layers forming in the oxidation

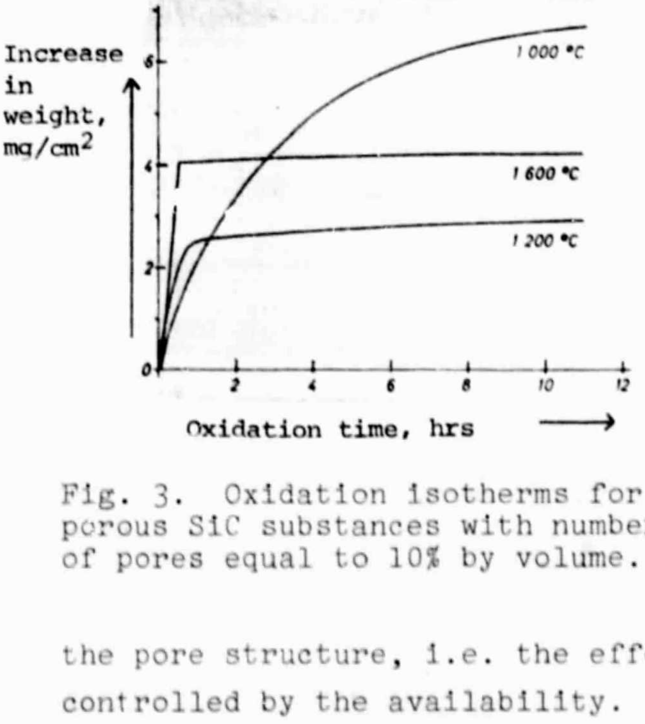

Fig. 3. Oxidation isotherms for porous SiC substances with number of pores equal to 10% by volume.

TABLE 1.

Author	Method	Test Material	Atmos-phere	Temp. °C	Exper. Dur., hr	Oxidation Rate $[g^2/cm^4\ h]$	Oxidation Rate $[cm^2/s]$	E [kJ/mol]
amsky 1959 [34]	CO_2 Adsorption	Crystals 200 μm	O_2	1200 1300 1400 1500	3,3		$9.3 \cdot 10^{-15}$ $4.0 \cdot 10^{-14}$ $7.0 \cdot 10^{-14}$ $3.2 \cdot 10^{-13}$	276 125 327
Antill Warburton 1969 [26, 27]	Thermo-gravimetry	SiC- layered UO_2	O_2	1200	?		$7.7 \cdot 10^{-14}$	
Bartlett 1971 [35]	Interference	β-SiC Crystals	O_2	985	46,5		$2.9 \cdot 10^{-14}$	
Cappelen Johansen Motzfeld 1963 [36]	Thermo-gravimetry	Powder 1000 μm	O_2	1500	20		$1.6 \cdot 10^{-13}$	
Ervin 1958 [37]	Gravimetry	Powder 150 μm	Air	1300	40		$9.7 \cdot 10^{-14}$	209
Fitzer Ebi 1973 [38, 39]	Thermo-gravimetry	Powder 40 – 63 μm	O_2	1000 1200 1400 1600	10	$3.8 \cdot 10^{-13}$ $2.5 \cdot 10^{-11}$ $1.3 \cdot 10^{-10}$ $1.6 \cdot 10^{-8}$	$3.4 \cdot 10^{-16}$ $2.1 \cdot 10^{-14}$ $1.2 \cdot 10^{-13}$ $1.0 \cdot 10^{-11}$	335 167 410
			Air	1000 1200 1400 1600	10	$8.0 \cdot 10^{-11}$ $4.4 \cdot 10^{-12}$ $5.6 \cdot 10^{-11}$ $4.7 \cdot 10^{-9}$	$7.8 \cdot 10^{-17}$ $4.2 \cdot 10^{-15}$ $5.4 \cdot 10^{-14}$ $4.1 \cdot 10^{-12}$	314 251 460
Gugel Hennicke Schuster 1969 [40, 41] = Schuster	Thermo-gravimetry	Powder 43 – 67 μm	Air	1000 1200 1400 1500	120 120 90 10		$5.0 \cdot 10^{-15}$ $4.5 \cdot 10^{-14}$ $8.0 \cdot 10^{-14}$ $1.4 \cdot 10^{-13}$	82
Gulbransen Andrew Brassart 1966 [42]	Thermo-gravimetry	Crystals α-6H	O_2 0,5 torr	1300	4 min	$1.2 \cdot 10^{-2}$ $g/cm^2\ h$		
Harris 1973/75 [43]	Interference	Crystals α-6H	O_2	970 1015 1060 1170 1245	166		$4.0 \cdot 10^{-15}$ $5.2 \cdot 10^{-15}$ $7.0 \cdot 10^{-15}$ $3.8 \cdot 10^{-14}$ $6.0 \cdot 10^{-14}$	196
Jorgensen Wadsworth Cutler 1959 [44]	Thermo-gravimetry	Powder 37 – 44 μm	O_2	903 1215 1502 1600	120 120 60 30		$2.7 \cdot 10^{-15}$ $3.2 \cdot 10^{-14}$ $1.2 \cdot 10^{-13}$ $1.9 \cdot 10^{-13}$	85
Khrycheva Bresker 1969 [45]	Gravimetry	Powder 60+120 μm	Air	1300 1400 1500 1600	50	$3.2 \cdot 10^{-8}$ $4.4 \cdot 10^{-8}$ $1.6 \cdot 10^{-7}$ $3.8 \cdot 10^{-7}$		80
Lambertson 1956 [46] fr.: Clark	Thermo-gravimetry	Powder	?	800 1000 1200 1400 1600	?	$1.8 \cdot 10^{-10}$ $2.2 \cdot 10^{-11}$ $3.2 \cdot 10^{-10}$ $4.4 \cdot 10^{-7}$ $3.5 \cdot 10^{-6}$		377 628
Lea 1949 [47]	Gravimetry	Powder 20 – 41 μm	Air	900 1000 1100 1200	140 90 70 40		$1.1 \cdot 10^{-14}$ $8.8 \cdot 10^{-14}$ $1.7 \cdot 10^{-13}$ $4.9 \cdot 10^{-13}$	209

(Table continued on following page.)

TABLE 1. (Cont'd)

Author	Method	Test Material	Atmosphere	Temp. °C	Exper. Dur., hr	Oxidation Rate (g^2/cm^4h)	Oxidation Rate (cm^2/s)	E (kJ/mol)
Nakatogawa **1954 [48]**	Thermo-gravimetry	Powder	O_2 + Air	1000	4		$2.2 \cdot 10^{-15}$	322
				1300			$1.3 \cdot 10^{-13}$	
Pultz **1967 a [49]**	Gravimetry	Powder 10 μm	O_2 205 torr	1355	3			632
				1400				
				1475				
Pultz 1967 b [50]	Gravimetry	β phases 250 Å ⌀	Air	800	20		$8.0 \cdot 10^{-18}$	167
				900			$4.2 \cdot 10^{-17}$	
				1000			$1.6 \cdot 10^{-16}$	
Suzuki 1957 [51]	Gravimetry	Crystals α-6H 13,4+21,6 μm	O_2	810	50		$1.9 \cdot 10^{-13}$	
				1100			$2.0 \cdot 10^{-11}$	
				1200			$6.4 \cdot 10^{-11}$	
				1400			$1.2 \cdot 10^{-10}$	
Wiebke 1960 [52]	CO_2 Adsorption	Powder 63 μm	O_2	1100	20		$7.0 \cdot 10^{-14}$	92
				1300	20		$3.9 \cdot 10^{-14}$	
				1500	10		$9.8 \cdot 10^{-14}$	
Yavorskii 1968 [53]	Thermo-gravimetry	Crystals +RBSiC	Air	1500	5	$5.0 \cdot 10^{-10}$		960
				1600		$2.0 \cdot 10^{-9}$		

are extremely crack-sensitive; however, they close up again with new heat treatment (Lange [61]).

The oxidation rates indicated in the literature for RBSiC with various porosities, as well as for the final SiC from the gas phase, are shown in Table 2 [26, 27, 54, 55, 62-70]. The values for RBSiC are very non-uniform and cannot be compared. For solid, poreless RBSiC materials, the similar or insignificantly increased oxidation rates are presented in comparison with pure SiC powder (Gnesin [71], Schlichting [55]). For the effect of porosity on the oxidation behavior of RBSiC, see Kaynarsky [72], Gropyanov [65], Rubisch and Schmitt [73], and Kuznetsova [68], primarily interesting for the manufacture of heat conductors.

The grain structure of these materials also has an effect (Taylor [74]). Refining the grain size produces improvement in oxidation behavior, but it increases temperature sensitivity [72].

For recrystallized SiC, the data show that in the process of recrystallization at high temperatures in manufacturing, the oxidation behavior can be substantially improved (Alliegro [75]).

TABLE 2. OXIDATION RATES FOR SiC SUBSTANCES

Author	Method	Test Material	Atmosphere	Temp. °C	Exper. Dur., hr	Oxidation Rate $[g^2/cm^4\,h]$	Oxidation Rate $[cm^2/s]$
Antill **Warburton** **1969 [26, 27]**	Thermo-gravimetry	RBSiC	O_2	1200	?		$9.1 \cdot 10^{-14}$
Bennett **Chaffey** **1971 [54]**	O_2 consumption	RBSiC	O_2	950	400	$1.3 \cdot 10^{-11}$	$6.3 \cdot 10^{-15}$
Elchin **1971 [62]**	Gravimetry	RBSiC	Air	2097 2447	9.6 min 3 min	2.61 g/cm h 5.64 g/cm h	
Garshin **Nikitina** **1971 [63]**	Gravimetry	RBSiC 12 – 33 % Si	Air	1200	30	$2.7 \cdot 10^{-7}$ $4.7 \cdot 10^{-8}$	
Giddings **1975 [64]**	Thermo-gravimetry	sintered CVD-SiC	Air Air	1600 1600	100 9	$4.9 \cdot 10^{-8}$ $2.7 \cdot 10^{-8}$	
Gropyanov **1970 [65]**	Gravimetry	RBSiC 10 % Pores	Air	1310 1420 1510	10	$4.8 \cdot 10^{-8}$ $1.6 \cdot 10^{-7}$ $1.2 \cdot 10^{-6}$	
		31,8 % Pores		1310 1420 1520		$2.0 \cdot 10^{-5}$ $8.0 \cdot 10^{-5}$ $2.0 \cdot 10^{-2}$	
Kern **Hamill** **Jacobson** **1968 [66]**	?	CVD-SiC	Air	800 900 1000	300 350 600		$2.3 \cdot 10^{-16}$ $4.0 \cdot 10^{-16}$ $7.0 \cdot 10^{-15}$
Kosslowsky **Singhal** **1975 [67]**	Gravimetry	CVD-SiC	O_2	1370	24	$4.0 \cdot 10^{-10}$	
Kuznetsova **1972 [68]**	Electron microscope	RBSiC	Air	1300 1500	5		$1.1 \cdot 10^{-12}$ $5.8 \cdot 10^{-12}$
McHenry **Tressler** **1977 [69]**	Gravimetry	RBSiC	Air $3 \cdot 10^{-6}$ atm	1000	15	$4.0 \cdot 10^{-8}$	
Restall **Gostelow** **1973 [70]**	Thermo-gravimetry	RBSiC	Air	1300	100	$<1.0 \cdot 10^{-10}$	
Schlichting **1978 [55]**	Thermo-gravimetry	RBSiC 10 % Si 1 % Pores	Air	1000 1200 1400 1500	100	$3.5 - 56 \cdot 10^{-13}$ $2.5 - 6.0 \cdot 10^{-11}$ $1.6 - 1.8 \cdot 10^{-10}$ $1.6 \cdot 10^{-9}$	

The most wide-ranging oxidation values for pure SiC powder could be realized by Fitzer and Ebi [38, 39] for SiC substances which suffered broken SiC surface layers through gas-phase discharge and thus could be regarded as pure, compact, pore-free SiC substances (Ebi [39], Schlichting [76]). The excellent oxidation behavior of CVD-SiC can be applied in the construction of protective coatings for graphite and refractory metals [77, 78].

(To be continued)