JOURNAL OF MATERIALS SCIENCE 21 (1986) 2678-2684

Effect of oxidizing and coal-slag environments upon the time-dependent strength behaviour of a sintered SiC

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The time-dependent variations in the high-temperature mechanical properties of a sintered SiC were investigated. The strength of C-ring specimens was determined as a function of temperature and applied stress in oxidizing atmospheres, and the results indicated that both crack-blunting and crack-growth processes were operative when modest stress levels were applied. These results were consistent with the concept of a stress-intensity threshold. In the slag environment, localized reactions between the slag and SiC led to the formation of large surface pits which promoted a time-dependent drop in strength.

1. Introduction

Structural silicon carbide ceramics are leading candidates for use as heat exchangers in a number of energy-related applications such as coal gasification, waste heat recovery in conventional thermal processing, and electricity generation from high-temperature gas turbines [1–5]. In the latter approach a heat exchanger is used to isolate the gas turbine from potentially damaging species in the combustion (coal) environment. The utilization of SiC instead of traditional metallic components offers several advantages including (i) higher temperature capability and thus, increased operating efficiencies, (ii) decreased weight, and (iii) a reduction in the use of strategic raw materials. Unfortunately, a key factor which has prevented the extensive use of SiC in these applications is the lack of information pertaining to the long-term chemical and mechanical stability of this material. Of particular concern is the effect of both oxidizing and corrosive (in the case of coal combustion) environments upon the mechanical reliability.

Recent studies [6–10] have shown that in the case of coal combustion atmospheres the extent of the SiC corrosion is determined by the nature of the coal-ash chemistry. Specifically, it was found that basic coal slags produced significant material loss in a variety of SiC materials. This corrosion involved at least three mechanisms including passivation of the SiC surface due to formation of an SiO_2 layer, dissolution of the SiO_2 by the coal slag, and the formation of Fe–Ni-silicide [11]. This latter mechanism, which dominated the overall corrosion when the slag thickness exceeded 100 micrometres, was responsible for the formation of large spherical pits in the SiC surface.

Limited mechanical-property tests [11, 12] revealed a complex time-dependent behaviour for the sintered SiC ceramic. When massive basic coal-slag deposits were present, the formation of the aforementioned corrosion pits resulted in a significant reduction in strength with time. However, in the absence of the slag (i.e. oxidizing conditions) the strength increased with time, with the rate of increase being greatest when modest stresses were applied. The reasons for this behaviour were not clearly understood.

This paper describes the results of a recent investigation involving a comprehensive examination of the high-temperature mechanical properties of a sintered SiC. Particular emphasis was placed upon measuring the strength as a function of temperature, time and applied stress in both oxidizing and basic coal-slag environments.

2. Experimental procedure

All test samples examined in this investigation were prepared from 305 mm long tubes (25.4 mm outer diameter and 19.0 mm inner diameter) of a sintered alpha-silicon carbide (iso-pressed Hexoloy SA SiC from Carborundum Co., Niagara Falls, New York). A C-ring diametral compression test was employed in the strength characterization. The primary advantage of this technique is that test samples could be readily prepared from the initial tabular section. As shown in Fig. 1, the test specimen is compressively loaded so that fracture is initiated at the outer surface, where the tensile stresses are the greatest. The maximum stress at the midplane of the C-ring, σ_m, is given as

$$\sigma_m = \cos\theta\left(\frac{P}{A}\right)\left(\frac{R(r - r_a)}{r(R - r_a)}\right) \qquad (1)$$

where A is the cross-sectional area $(r_o - r_i)w$, P is the

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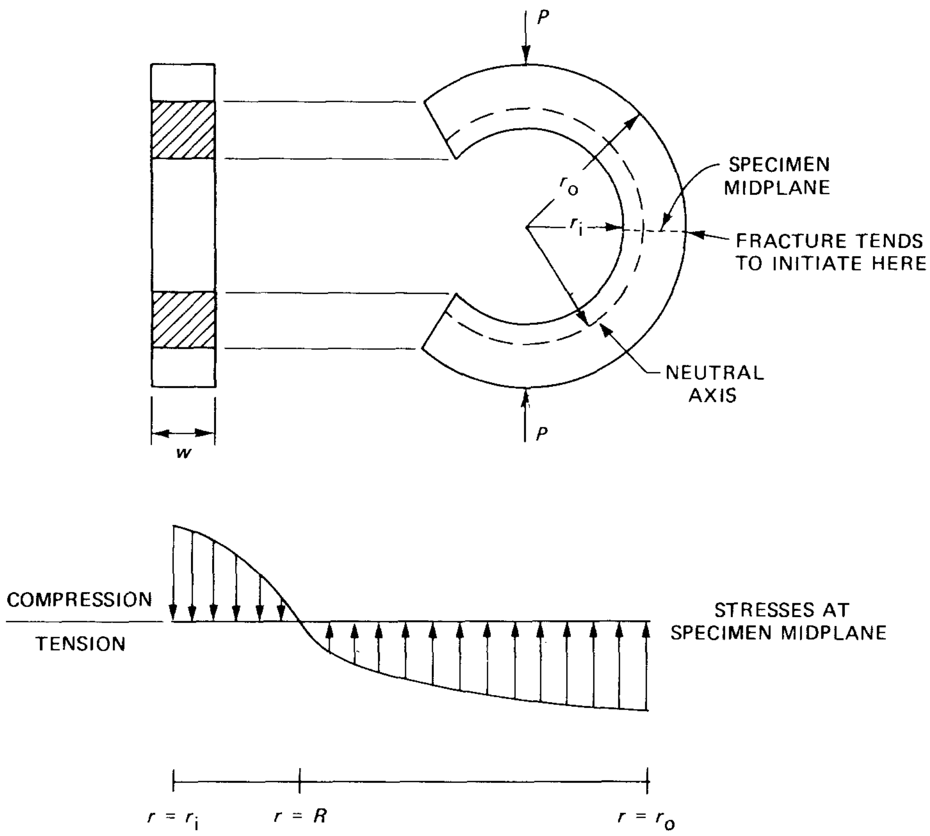

Figure 1 Schematic representation of the C-ring specimen and associated stress distribution.

breaking load (negative for compressive loading), $r_a = (r_o + r_i)/2$, $R = (r_o = r_i)/\ln(r_o/r_i)$, and θ is the angle between the fracture plane and the midplane of the specimen (Fig. 1).

The values of temperature T, time t and applied stress σ_a associated with the strength tests conducted in oxidizing and basic slag environments are given in Tables I and II, respectively. For each combination of temperature and time, the applied stress was maintained at either zero or 70% of the respective short-term strength. The short-term strengths for each temperature were determined after a 1 h hold with $\sigma_a = 0$ in the oxidizing environment at that temperature. The exposure times typically ranged from 1 to 1008 h in the oxidizing atmosphere. However, in the case of the slag tests, severe corrosion problems greatly limited the time of the exposure. The number of samples tested per condition varied between six and ten.

TABLE I Air-exposure conditions prior to determining fracture strengths at given temperatures in air†

Time (h)	Temperature (° C)							
	1150		1200		1250		1300	
	Stress level‡							
	0%	70%	0%	70%	0%	70%	0%	70%
1	*	*	*		*		*	
6								*
15								*
24	*	*	*	*	*	*	*	*
168				*		*		*
336	*	*	*	*	*	*	*	*
1008			*		*		*	*

†Asterisks indicate time of exposure prior to strength measurement.
‡70% level represents 70% of average fracture stress obtained after a 1 h test at the respective temperature.

Two specially designed globular furnaces capable of testing multiple C-ring samples were used to measure high-temperature strength. As shown in Fig. 2 the mechanical loads, generated by pneumatically driven air cylinders (Bellofram diaphragm air cylinder, Burlington, Massachusetts) were transmitted into the hot zone of the furnace through high-temperature silicon carbide rams. For a given exposure duration, the load was adjusted such that the desired σ_a was maintained. Following this period, all samples were fractured at temperature at a loading rate of 345 kPa sec^{-1} which was maintained by means of an air flow valve.

The slag was applied to the outer C-ring surface in the form of a slurry (powdered coal slag and glycerine). Specially designed SiC fixtures (Fig. 2) were used to ensure that the slag remained in contact with the C-ring at elevated temperature. A chemical analysis of this coal slag (Table III) revealed significant concentrations of silicon, iron, aluminium, calcium and magnesium (reported as equivalent oxides). Direct

TABLE II Slag exposure conditions prior to determining fracture strength at given temperatures in a basic slag environment†

Time (h)	Temperature (° C)							
	1150		1200		1250		1300	
	Stress level‡							
	0%	70%	0%	70%	0%	70%	0%	70%
24	*	*	*				*	*
168					*			*
336	*	*					*	

†Asterisks indicates times at which measurements were made.
‡70% level represents 70% of average fracture stress determined for 1 h test at the respective temperature in the oxidizing atmosphere.

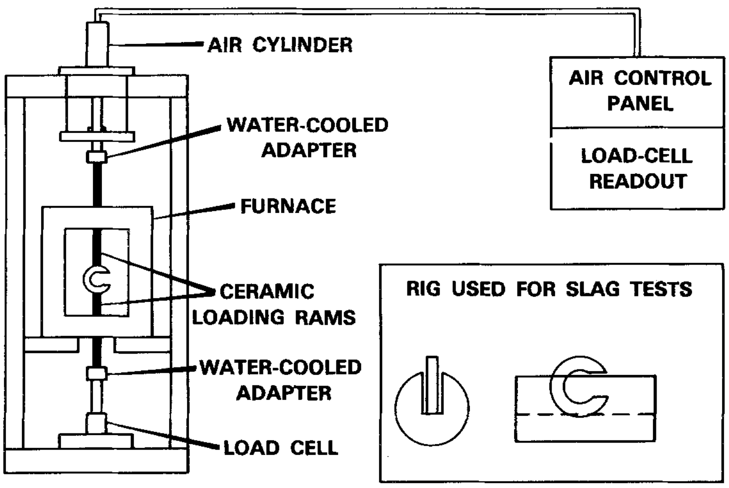

Figure 2 Overview of high-temperature mechanical property facility for testing C-ring specimens. (The insert shows the ceramic specimen holder used in the slag tests.)

observations of the slag at elevated temperatures in an oxidizing environment indicated that it was quite fluid above 1225° C. Such behaviour would be expected in view of the relatively high base-to-acid ratio of 0.63 [13, 14].

Several additional techniques were used to supplement the mechanical strength testing. For example, the C-ring fracture surfaces were routinely examined with a scanning electron microscope (SEM) to (i) identify the failure origin and (ii) study corrosion processes arising from the presence of the coal slag. Finally, changes in the predominant crystalline phases resulting from the high-temperature exposure were determined from X-ray diffraction analyses.

3. Results and discussion

3.1. Time-dependence of strength in oxidizing environments

The strength data obtained from tests conducted in air at temperatures of 1150, 1200, 1250, and 1300° C are shown in Figs 3a to d, respectively. The numbers in parentheses represent the level of the applied stress. The specific magnitude of σ_a associated with the 70% level is also indicated by the solid lines. During testing under stress, several C-ring samples failed prior to reaching the desired exposure time. These failures are designated by the open squares.

When σ_a was zero, the fracture strength S_f exhibited little or no change with time (for $t > 1$ h) at all temperatures with the possible exception of $T = 1150$° C. The average S_f generally fell within the range 325 to 400 MPa. It should be noted, however, that at room temperature (rt), the as-received strength was only 214 MPa. The fact that the short-term strength of alpha-SiC increases appreciably for the 22° C compared with $\geqslant 1150$° C tests suggests that some type of residual stress-relief mechanism was operative during the initial high-temperature exposure period ($t < 1$ h). This conclusion was substantiated by measuring the room-temperature S value for samples annealed at 1300° C for various times. The resulting strength at 22° C increased to 358 MPa after 1 h and then remained independent of time. Although the formation of a silica scale undoubtedly modified the surface flaws during this annealing process, the overall effect of this oxidation upon strength was negligible since failure always occurred from volume defects (refer to discussion below).

The application of the 70% stress σ_a to the C-ring samples led to a time-dependent increase in S_f at all temperatures considered. These strength values were substantially larger than those associated with the "$\sigma_a = 0$" group. There was also a tendency for the rate of strength rise to increase slightly with temperature. Finally, subsequent rt measurements of S_f, involving specimens that had been stressed at temperature but not broken, indicated that these high strength values were also retained at 25° C.

Examination of the C-ring fracture surfaces with an SEM showed that failure sites were almost always associated with large, internal spherical processing voids (Fig. 4). There was evidence that some of these voids were generated due to differential shrinkage between the SiC matrix and spherically-shaped agglomerates which formed during the initial processing. These defects were typically situated within a region extending 300 μm below the outer tensile surface. In a few instances, narrow cylindrical channels linked the spherical void directly to the outer surface.

A second feature detected in the SEM study was the extensive oxide scale along the outer face of the C-ring (Fig. 4). Such oxidation is often cited as a potential mechanism for strength enhancement at elevated temperatures when fracture is controlled by surface flaws [15]. However, since no substantial silica scale was

TABLE III Chemical analysis* of the basic coal slag

Equivalent oxide	Amount in coal slag (wt %)	Equivalent oxide	Amount in coal slag (wt %)
SiO_2	45.77	Na_2O	1.10
Fe_2O_3	10.72	K_2O	0.52
Al_2O_3	14.17	TiO_2	0.26
CaO	18.75	SrO, BaO	0.16
MgO	7.08	V_2O_5	0.03
NiO	0.01	LOI†	0.17
SO_3	0.055	Base/acid‡	0.63
P_2O_5	0.51		

*Wet chemical analysis provided by Spectrochemical Laboratories, Pittsburgh, Pennsylvania.
†Loss on ignition.
‡Defined as $(Fe_2O_3 + CaO + MgO + Na_2O + K_2O)/(SiO_2 + Al_2O_3 + TiO_2)$.

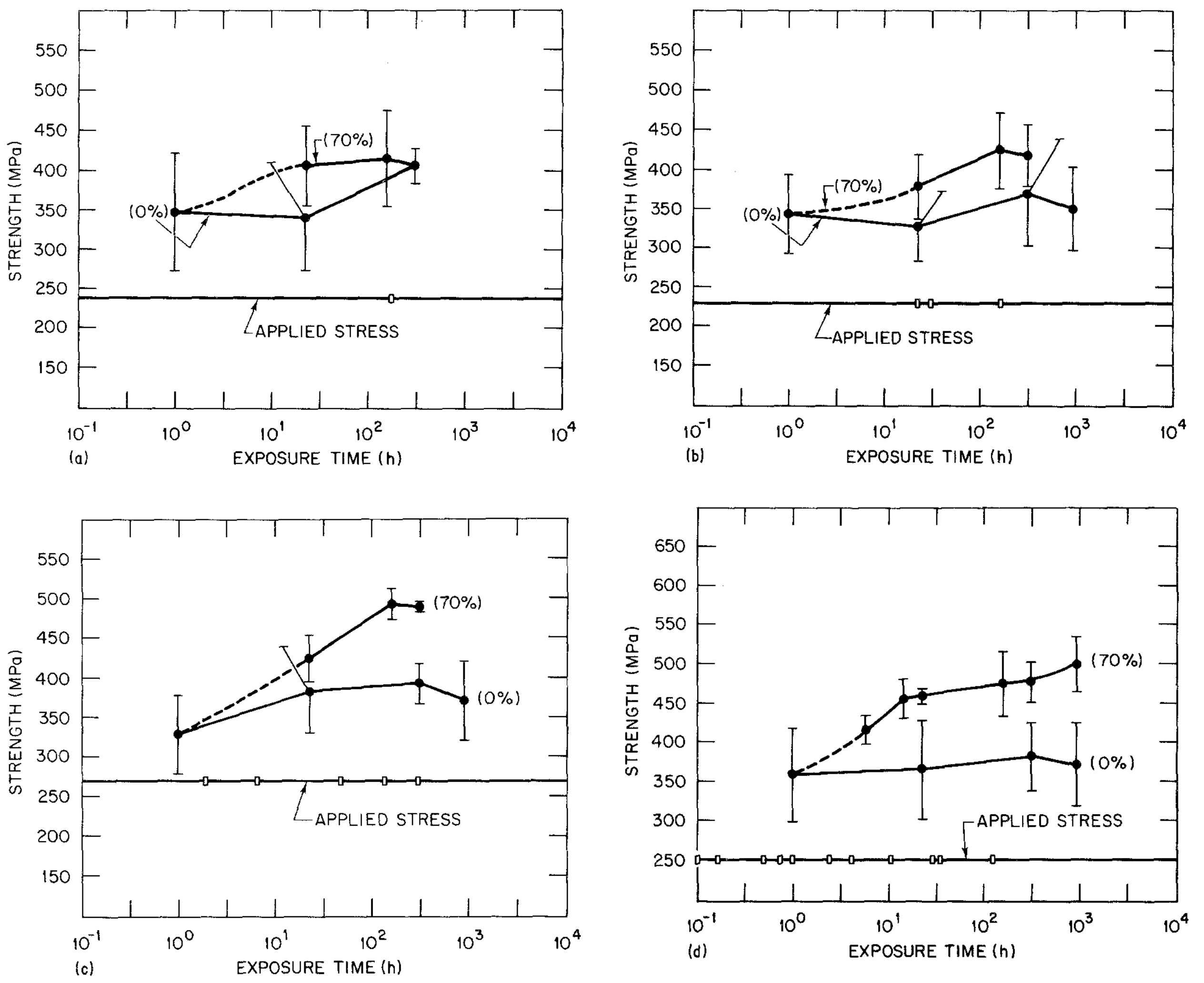

Figure 3 Time dependence of SiC strength measured in air at temperatures of (a) 1150, (b) 1200, (c) 1250, and (d) 1300° C. The error bars represent standard deviations.

detected along the surfaces of the isolated internal defects in the present investigation, this mechanism was apparently inoperative and not a significant factor in the obtained strengths. This conclusion is consistent with the observed insensitivity of S_f to exposure time for the unstressed samples.

The strength–time behaviour obtained under oxidizing conditions can be adequately described in terms of a simple crack-growth model which assumes the existence of a threshold stress intensity factor K_{th} [16, 17]. When the applied stress intensity K_{Ia} is greater than K_{th} the crack may grow subcritically, thereby lowering S_f increases with time. These effects are schematically illustrated in Fig. 5. The magnitude of the initial K_{Ia} generated from the application of the stress σ_a is given as

$$K_{Ia} = K_{IC}\sigma_a/S_i \qquad (2)$$

where K_{IC} is the fracture toughness and S_i represents the initial distribution of strengths for the as-received samples (see Fig. 5). The quantity S_{th} corresponds to the particular S_i value at which $K_{Ia} = K_{th}$. If the strength exceeds S_{th}, the applied stress intensity will be in the blunting regime. However, if $S_i < S_{th}$ the resulting slow crack growth will promote a time-dependent reduction in S_f. Failure will occur when $S_f = \sigma_a$.

The data in Fig. 3 clearly suggest that the initial distribution of strengths S_i covered both the crack-blunting and slow crack-growth regimes. The mechanism responsible for the flaw blunting apparently required the presence of modest stress levels, since no time-dependent strength increase was observed for $\sigma_a = 0$. Evidence of the slow crack-growth phenomenon was provided by the significant number of failures (open squares in Fig. 3) occurring during the testing at the 70% stress level. The fact that the number of failures increased with temperature is consistent with studies [16, 18] showing a reduction in both K_{th} and the resistance to slow crack growth with increasing T in the range 1200 to 1400° C. Unfortunately a thorough application of the model in Fig. 5 to the present results is complicated by several factors. First the distribution of S_i was not constant but varied during the initial stages ($t < 1$ h) of exposure, due to the residual stress relief mechanism. Secondly, for those flaws near the surface, penetration of oxygen may have promoted a time-dependent reduction in K_{th} [18, 19].

Although the exact mechanisms of the blunting and subcritical crack growth were not determined, there is considerable evidence to suggest that both processes are critically dependent upon the presence of a viscous grain boundary phase [16, 20].While this phase is not present in the as-received alpha-SiC, it can form with time due to the internal oxidation of the grain-boundary region. Since in the present study the strength was

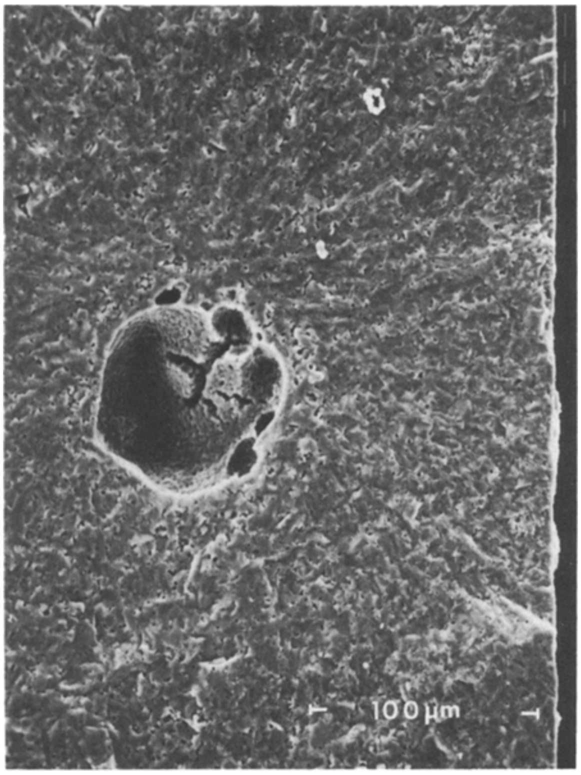

Figure 4 SEM micrograph showing spherical void responsible for failure in stressed sample exposed to air at 1300° C for 1008 h. This defect was typical of those observed for all other test conditions, involving an air environment.

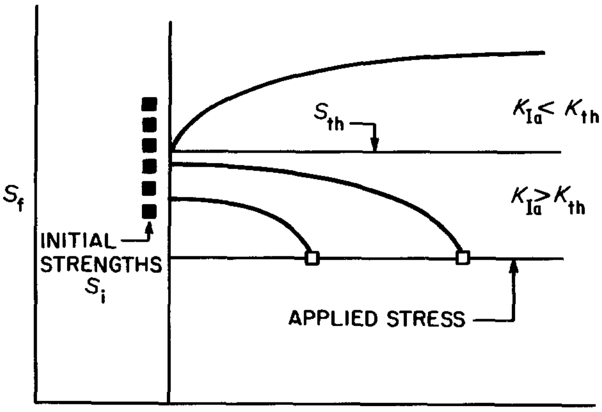

Figure 5 Schematic representation of the strength–time behaviour for stressed samples, illustrating the combined effects of slow crack-growth and crack-blunting processes.

controlled by volume defects, oxygen penetration into the bulk would be required for crack blunting and growth to occur.* However, recent work [19] has shown that the maximum depth of oxygen penetration at 1300° C is approximately 15 μm. Although this value increases slightly when a modest stress is applied, it is still much smaller than the depth at which most flaws were observed.

A second possibility is that boron and not oxygen was involved in the blunting and crack growth processes. Studies [21] have shown that boron redistribution can readily occur in the temperature range 1200 to 1300° C. Furthermore, since boron was already present in the as-received alpha-SiC, the necessity for long diffusion distances would be eliminated. However, the rate of boron redistribution would have to exhibit a rather strong stress dependency to adequately account for the time-independence of S_f for the unstressed samples. Microprobe studies are currently underway to explore this potential mechanism.

3.2. Time dependence of strength in the basic coal-slag environment

Figs 6a and b illustrate the strength–time behaviour obtained for the samples exposed to basic slags at temperatures of 1150 and 1300° C, respectively. At 1300° C, the strengths fell well below those measured in air at the zero applied stress level. For exposure periods exceeding 1 h, S_f was essentially independent of both t and σ_a. Similar reductions in strength (determined at 0% stress) were also found at 1200 and 1250° C (Table IV). In both cases, S_f was lowered below the average strength measured in air (0% stress) by a factor of 0.9. However, for $T = 1150°$ C (Fig. 6a), the extent of the strength degradation at the 0% σ_a level was minimal. In addition, when the 70% stress was applied S_f increased with time in a fashion similar to that observed in the air environment.

Examination of the tensile surfaces of the fractured C-ring samples revealed the presence of spherical metallic inclusions randomly distributed along the SiC–slag interface (Fig. 7a). X-ray studies showed that these inclusions were composed primarily of an Fe–Ni silicide phase which apparently formed from a reaction between the iron and nickel in the slag and the SiC [12]. This reaction was ultimately responsible for the generation of surface pits, which were observed on the tensile surface after removal of the slag by HF acid etching (Fig. 7b).

The tendency of the slag–SiC reaction to occur at isolated regions along the SiC surface (as opposed to the generation of a uniform zone) suggests that the silicide formation was favoured only at certain locations. Since recent thermodynamic calculations [22] have shown that the stability of the silicide phase requires highly reducing conditions, these sites may have contained relatively high concentrations of carbon (probably as a grain-boundary phase). Although the average size of the resulting corrosion pit increased slightly with temperature, it was fairly insensitive to the effects of time (for $t > 24$ h). Such behaviour suggests that the overall rate of reaction was diffusion-controlled. In particular, the initial formation of the Fe–Ni silicide would lead to a depletion of the iron and nickel in the adjacent slag matrix. Generation of additional silicide phase would then require diffusion of these constituents through the depletion zone. The existence of such a zone was confirmed in an earlier study [10].

As shown in Fig. 8, the large surface pits resulting from the flaw-generation process generally controlled the strength for temperatures above 1200° C. The lack

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*In those limited cases involving defects connected directly to the outer surface, oxygen penetration would not be required.

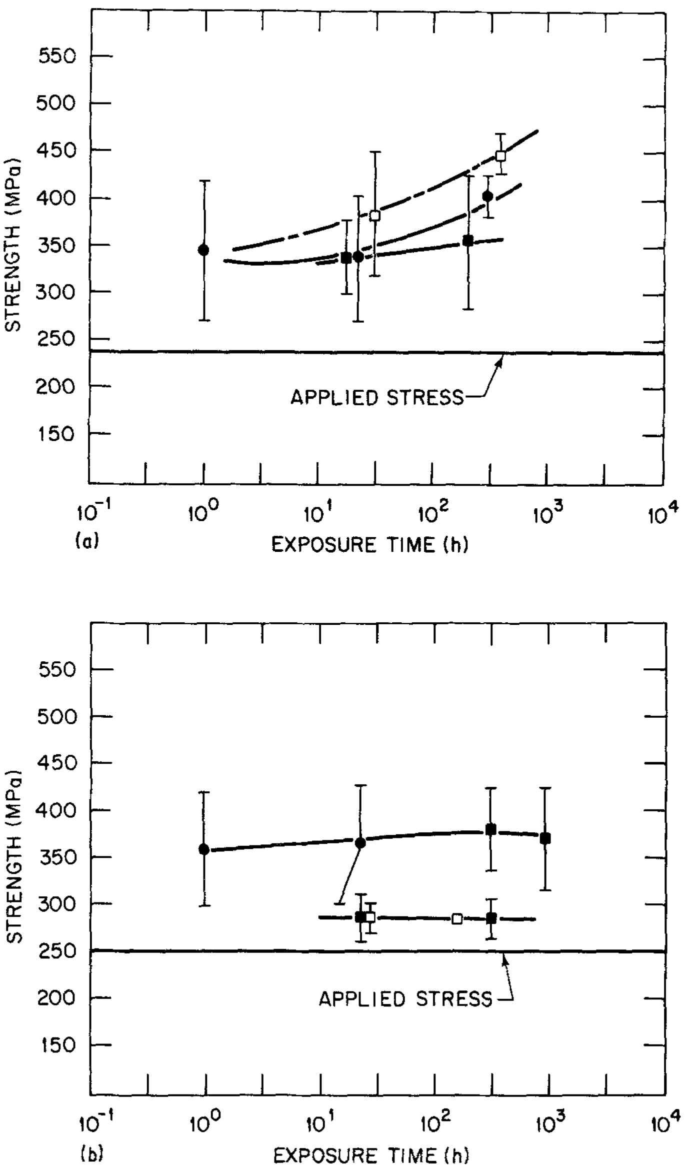

Figure 6 Time dependence of SiC strength for samples exposed to basic coal slag at temperatures of (a) 1150 and (b) 1300° C. The error bars represent standard deviations. (●) Air, 0% stress; (■) slag, 0% stress; (□) slag, 70% stress.

of any significant applied stress dependency (Fig. 6b) suggests that the rate of flaw generation at 1300° C exceeded the rate associated with the blunting mechanism. However, at 1200° C and below a mixed-mode fracture was observed with failure occurring from both the internal defects (Fig. 4) and the surface pits. In this case both the rate of silicide formation and the size of the corresponding surface pit were limited by the increased slag viscosity. These conclusions are consistent with the increase in S_f with time observed for the stressed samples at 1150° C (Fig. 6a).

4. Conclusions

The strength of C-ring specimens was determined as a

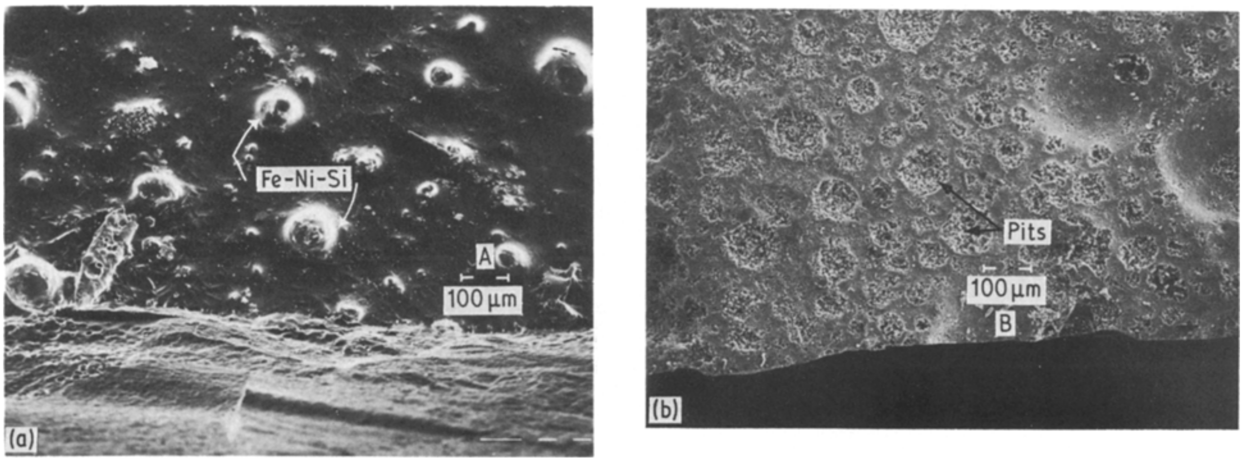

Figure 7 Tensile surface of C-ring samples fractured after 24 h exposure at 1300° C (0% stress level) illustrating (a) Fe–Ni silicide phase formation and (b) corresponding surface corrosion pits observed after removal of slag by HF etch.

TABLE IV Summary of S_f values obtained for samples exposed to slag at 1200 and 1250° C

T (° C)	σ_a level (%)	t (h)	S_f (MPa)*	S_f/S_{fa}†
1200	0	24	297 ± 64.8	0.85
1250	0	168	325 ± 12.1	0.88

*± standard deviation.

†S_{fa} represents the strength averaged for all exposure times in air at 0% applied stress.

function of time, temperature and applied stress in oxidizing and basic coal-slag environments. Data obtained in oxidizing atmospheres indicated that both crack-blunting and crack-growth processes were operative when modest stress levels were applied. These results were consistent with the concept of a stress-intensity threshold. However, when the applied stress was zero the strength was independent of time, which suggests that the blunting process required the presence of some mechanical driving force.

In the coal-slag environment, a localized reaction between the slag and SiC to form an Fe–Ni silicide led to the generation of large surface pits. Although the ultimate size of these pits was limited by diffusion considerations, they were generally larger than the intrinsic volume defects at temperatures exceeding 1200° C. As a result, the corresponding strength fell well below the value obtained in oxidizing atmospheres but was fairly independent of time. At temperatures of 1200° C and below, the increased slag viscosity limited the size of the surface pits such that a mixed-mode fracture behaviour was observed.

Acknowledgements

This research was sponsored by the US Department of Energy (DOE/FE AA 15 10 10 0, AR & TD Fossil Energy Materials Program, Work Breakdown Structure Elements ORNL-5.12) under contract DE-AC05-840R21400 with Martin Marietta Energy Systems, Inc.

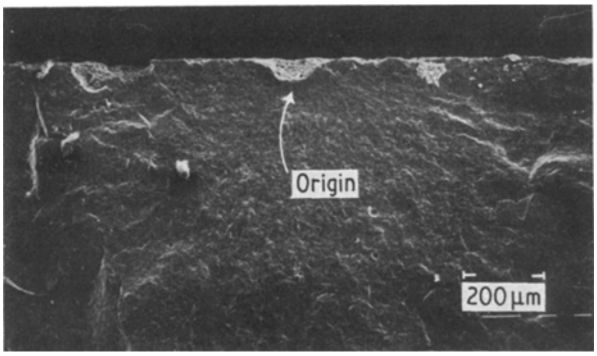

Figure 8 Typical fracture origin associated with C-ring samples exposed to basic coal slag at temperatures above 1200° C.

References

1. V. J. TENNERY, *Mat. Res. Soc. Symp. Proc.* **24** (1984) 433–43.
2. D. C. LARSEN and J. W. ADAMS, IITRI Semiannual Interim Technical Report No. 11, AFWAL Contract No. F33615-79-C-5100 (IIT Research Institute, Chicago, 1981) pp. 1–46.
3. B. A. NAGARAJ and J. R. A. LOWDER, in Proceedings of High Temperature Materials Chemistry Symposium, San Francisco, May 1983.
4. D. J. McFARLIN, C. T. SGAMBOTI and R. D. LESSARD, "Ceramic Heat Exchanger Applications Study", UTRC82-34 (United Technologies Research Center, Connecticut, 1982) pp. 1–13.
5. V. K. NANGIA, "Materials for Coal Conversion and Use", Vol. II, Parts 1 and 2, DOE Report FE-2368-59 (Engineering Societies Commission on Energy, Washington, 1979).
6. V. J. TENNERY, G. C. WEI and M. K. FERBER, in Proceedings of the Educational Symposium on Refractories in Slagging Environments, 83rd Annual Meeting of ACS, Washington, May 1981 (American Ceramic Society, Ohio, 1981) p. 1171.
7. M. K. FERBER and V. J. TENNERY, "Evaluation of Tabular Ceramic Heat Exchanger Materials in Basic Coal Ash from Coal-Oil-Mixture Combustion", ORNL/TM-7958 (Oak Ridge National Laboratory, 1981).
8. *Idem,* "Evaluation of Tabular Ceramic Heat Exchanger Materials in Basic Coal Ash from Coal-Oil-Mixture Combustion", ORNL/TM-8385 (1982).
9. *Idem, Amer. Ceram. Soc. Bull.* **62** (2) (1983) 236.
10. *Idem, ibid.* **63** (7) (1984) 898.
11. M. K. FERBER, J. OGLE, V. J. TENNERY and T. HENSON, *J. Amer. Ceram. Soc.* **68** (4) (1985) 191.
12. P. F. BECHER, *J. Mater. Sci.* **19** (1984) 2805.
13. "Steam, Its Generation and Use", 38th Edn (Babcock and Wilcox, New York, 1975) p. 15-1.
14. W. L. SAGE and J. L. McELORY, *Trans. ASME* **46** (4) (1968) 146.
15. P. F. BECHER, *Commun. Amer. Ceram. Soc.* **66**(8) (1983) C120.
16. E. J. MINFORD, D. M. KUPP and R. E. TRESSLER, *J. Amer. Ceram. Soc.* **66**(11) (1983) 769.
17. S. M. WIEDERHORN, in "Fractures Mechanics of Ceramics 5", edited by R. C. Bradt, A. G. Evans, D. P. H. Hasselman and F. F. Lange (Plenum Press, New York, 1983) p. 197.
18. M. KAWAI, H. FUJITA, Y. KANKI, H. ABE and J. NAKAYAMA, unpublished data.
19. E. MINFORD, J. A. COSTELLO, I. S. T. TSONG and R. E. TRESSLER, in "Fracture Mechanics of Ceramics 6", edited by R. C. Bradt, A. G. Evans, D. P. H. Hasselman and F. F. Lange (Plenum Press, 1983) p. 511.
20. K. D. McHENERY and R. E. TRESSLER, *Amer. Ceram. Soc. Bull.* **59** (4) (1980) 459.
21. J. A. COSTELLO, R. E. TRESSLER and I. S. T. TSONG, *ibid.* **60** (1981) 332.
22. M. K. FERBER, unpublished data (1983).

Received 29 July
and accepted 19 September 1985