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Surface Scaling in SiC-Whisker–Alumina under Flowing Hydrogen at 1300–1500°C

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Abstract

In this work the high temperature degradation of a 30 vol% SiC whisker reinforced Al_2O_3 *in* H_2 *at 1300–1500°C was investigated. Morphological changes associated with scale evolution indicated that a highly porous scale consisting of mullite and glassy phases is formed during* H_2 *exposure. In particular, it was found that the inner interface of the scale/unreacted matrix was not planar but exhibited some degree of roughness. Furthermore, scale thickening measurements with time followed a nearly parabolic trend. At 1500°C, the Si/Al ratio in the scale surface consistently increased with time up to a maximum. Also, at a given time, a concentration profile in the Si/Al ratios was found to develop between the inner and outer scale interfaces. This suggested that a Si-rich glassy phase was continually forced to flow from the reaction front to the scale surface.*

In der vorliegenden Arbeit wird die Hochtemperaturdegradierung von mit 30% SiC-Whiskern verstärktem Al_2O_3 *in einer* H_2*-Atmosphäre bei 1300–1500°C untersucht. Morphologische Veränderungen in Verbindung mit der Entwicklung der Zunderschicht lassen schließen, daß sich eine hochporöse Schicht, bestehend aus Mullit und einer Glasphase, bei der Anwesenheit von* H_2 *bildet. Es zeigte sich, daß besonders die Grenzfläche zwischen der Zunderschicht und der unveränderten Matrix nicht eben ist, sondern eine gewisse Rauheit aufweist. Ferner zeigte das Schichtwachstum ein nahezu parabolisches Verhalten. Bei 1500°C vergrößerte sich das Si/Al-Verhältnis dementsprechend mit der Zeit bis zu einem Maximum. Weiterhin ergab sich ein Konzentrationsprofil im Si/Al-Verhältnis zwischen der inneren und äußeren Zunderschichtgrenzfläche bei konstanter Zeit. Dies legt nahe, daß eine Si-reiche Glasphase kontinuierlich von der Reaktionsfront zur Schichtoberfläche fließen muß.*

Dans ce travail, la dégradation à haute température d'une alumine renforcée par 30% en volume de trichites en SiC a été étudiée entre 1300 et 1500°C sous H_2*. Les modifications morphologiques associées à l'évolution du dépôt en cours de traitement indiquent qu'un dépôt hautement poreux consistant en de la mullite et de la phase vitreuse résulte de l'exposition sous* H_2*. En particulier, on a observé que l'interface interne entre le dépôt et la matrice intacte (non réagie) n'est pas plan mais présente un certain degré de rugosité. De plus, les mesures de l'augmentation d'épaisseur du dépôt avec le temps suivent une tendance presque parabolique. A 1500°C, le rapport Si/Al se développe entre les interfaces interne et externe du dépôt. Ce fait suggère qu'une phase vitreuse riche en silice est continuellement forcée à migrer du front de réaction vers la surface du dépôt.*

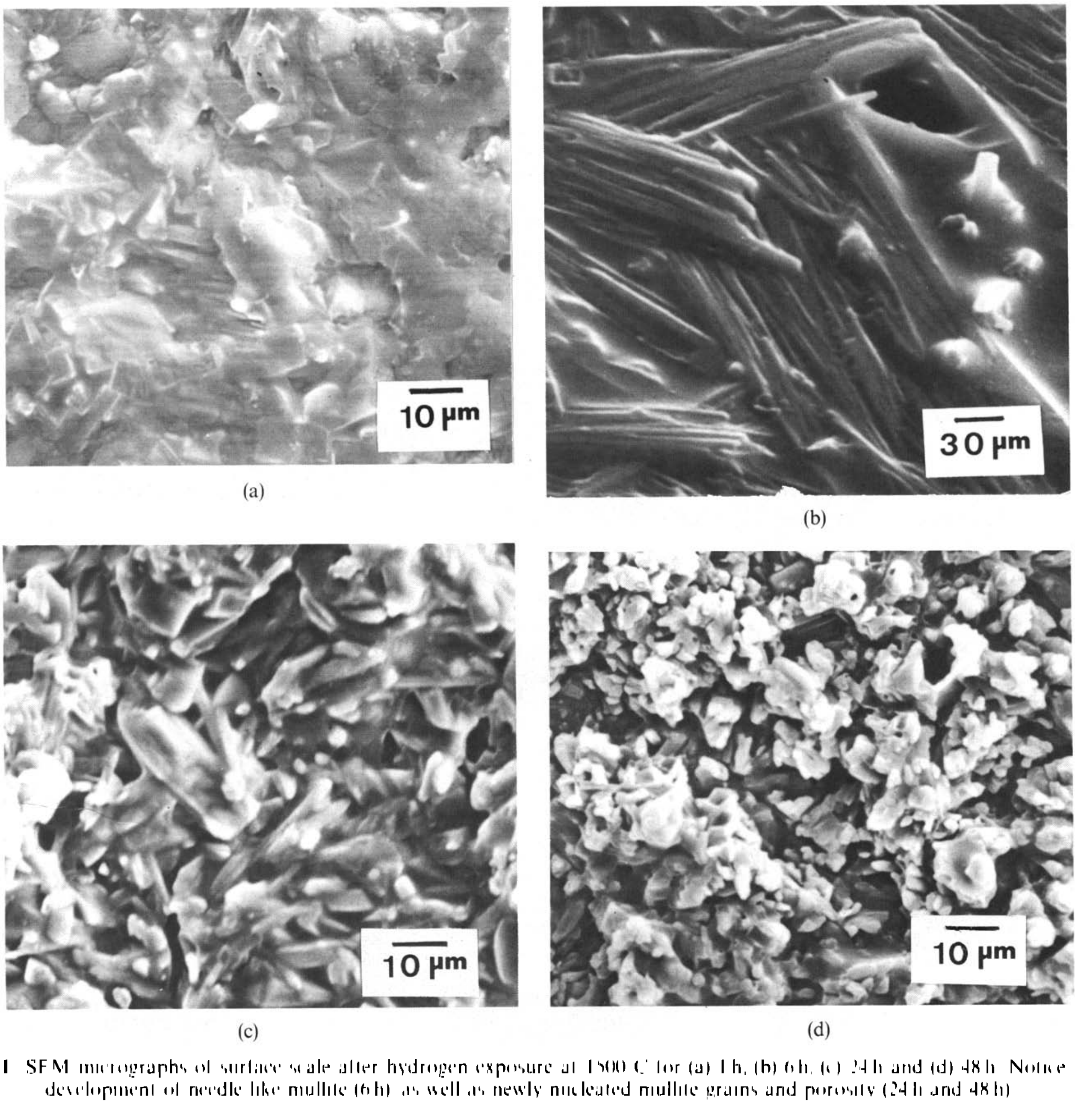
1 Introduction

In recent years considerable interest has been placed in the development of structural ceramics for high-temperature applications. In particular, conventional ceramics reinforced by SiC whisker additions exhibit substantial upgrading of their mechanical properties. Among these composites, SiC-reinforced alumina displays significant improvements in toughness,[1,2] creep strength,[3,4] wear and thermal fatigue.[5] Nevertheless, these composites are not stable in oxidizing[6–10] or reducing[11] atmospheres. Furthermore, the scale product is not thermodynamically in equilibrium with the surrounding alumina matrix. Thus, additional reactions are found to occur[9] which include the development of glassy phases and mullite in the scale product.

The kinetic aspects associated with the oxidation of SiC-reinforced alumina have been investigated by various authors.[6–10] Nevertheless, little is known on the material stability in high-temperature hydrogen. Kim & Moorhead[11] recently found that at a given temperature, a critical water vapor pressure has to be exceeded for active oxidation. Moreover, relatively low vapor pressures ($P(H_2O) < 10^{-5}$ MPa) resulted in severe weight and strength losses. Under these conditions SiC etching by flowing hydrogen was considered as the relevant degradation mechanism. At relatively high water vapor pressures ($P(H_2O) > 5 \times 10^{-4}$ MPa at 1400°C), Kim & Moorhead[11] found significant weight increases which were associated with the development of a surface scale. Also, the weight gain exhibited a parabolic trend. X Ray diffraction and microstructural evaluations of the scale formed indicated the presence of aluminosilicate glass and mullite. Nevertheless, the mechanistic aspects of the degradation process are not clear and further work is needed in this area. In the present study, H_2 degradation of a 30 vol.% SiC whisker reinforced Al_2O_3 at 1300–1500°C was investigated. In particular, possible degradation reactions are suggested to explain the experimental outcome of the scale evolution.

2 Experimental

The investigated material was supplied in the form of slabs by Advanced Composite Materials, and it consisted of alumina reinforced with 30 vol.% SiC whiskers. Energy dispersive X ray analyses indicated the presence of Fe, Na, Ca, and K traces in this material. Specimens of 6 mm × 6 mm × 4 mm were cut and then exposed to ultra high purity flowing H_2 at 1300–1500°C for various periods of time. The gas was filtered through $CaSO_4$ and alumina before flowing inside a resistance heated horizontal alumina tube furnace. The H_2 flow pressure used was slightly above 0.1 MPa. Weight changes as a function of time and temperature were



(a) (b) (c) (d)

Fig. 1. SEM micrographs of surface scale after hydrogen exposure at 1500°C for (a) 1 h, (b) 6 h, (c) 24 h and (d) 48 h. Notice the development of needle like mullite (6 h) as well as newly nucleated mullite grains and porosity (24 h and 48 h).

measured in a highly sensitive microbalance. This was followed by scale thickness measurements using optical means. Since the scale-matrix interface exhibited some roughness, thickness measurements were made from the external surface to an average inner interface. Scanning electron microscopy (SEM) was used to investigate the morphological changes occurring in the scale regions, whereas X-ray diffraction was used for evaluations of phases and scale composition. Finally, cross sections of oxidized specimens were etched by exposing them to molten KOH for approximately 10 s before they were examined.

3 Results

3.1 Scale evolution

The morphological aspects of scale evolution in H_2 at 1500°C were followed by SEM and optical means. Accordingly, it was found that after exposure at this temperature for 1 h, a scale had already developed (Fig. 1(a)). Exposure to hydrogen for 6 h gave rise to needle like mullite (Fig. 1(b)) and some degree of porosity. Further H_2 exposure for 24 h (Fig. 1(c)) led to a porous scale with newly nucleated mullite grains. In particular, long exposure times (48 h) gave rise to very fine mullite grains and relatively high porosity at the gas scale interface (Fig. 1(d)). X Ray diffraction measurements (Fig. 2) confirmed the presence of mullite after 1 h at 1500°C concurrently with Al_2O_3 and SiC. A Si rich phase was also detected, but the peaks were too weak to be clearly resolved. No evidence of SiC in the scale was found after exposure times in excess of 1 h at 1500°C. An examination of the cross section indicated that the inner scale matrix interface was not planar but exhibited a wavy profile (Fig. 3). In particular, SEM observations (Fig. 4) of the scale matrix interface revealed a scale made up by fine grains and pores with a glassy phase. Furthermore, slight scale etching removed some of the aluminosilicate phase and exposed continuous strings of pores (Fig. 5(a)). Heavy etching completely removed the glassy phase, as shown in Fig. 5(b) leaving a highly porous scale uncovered.

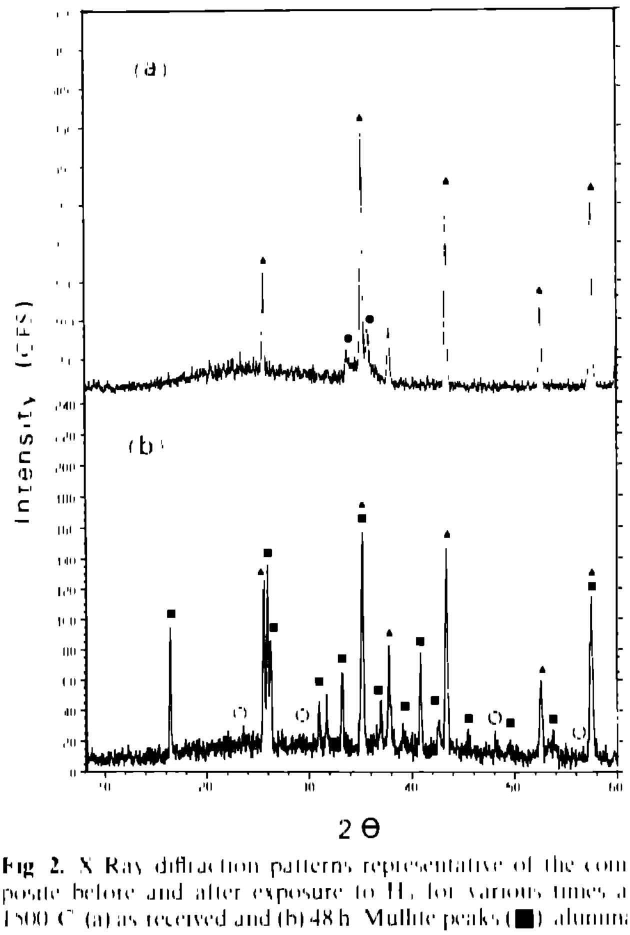
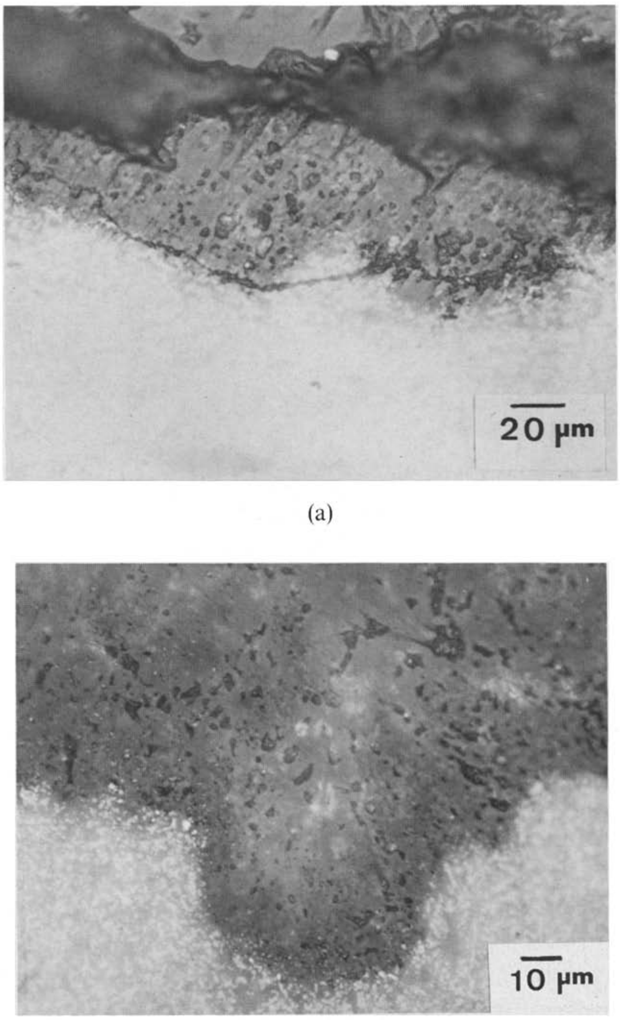


Fig. 2. X Ray diffraction patterns representative of the composite before and after exposure to H_2 for various times at 1500°C: (a) as received and (b) 48 h. Mullite peaks (■), alumina (▲), silicon carbide (●), and Si rich phase (○).



(a)

(b)

Fig. 3. Optical micrographs of scale cross sections showing mullite grains surrounded by interconnected pores filled with an amorphous glassy phase. Notice the wavy appearance of the inner interfaces.

Si Al ratios in the scale surface at 1500°C were determined from energy dispersive X ray analyses in the SEM as a function of time. It was found that

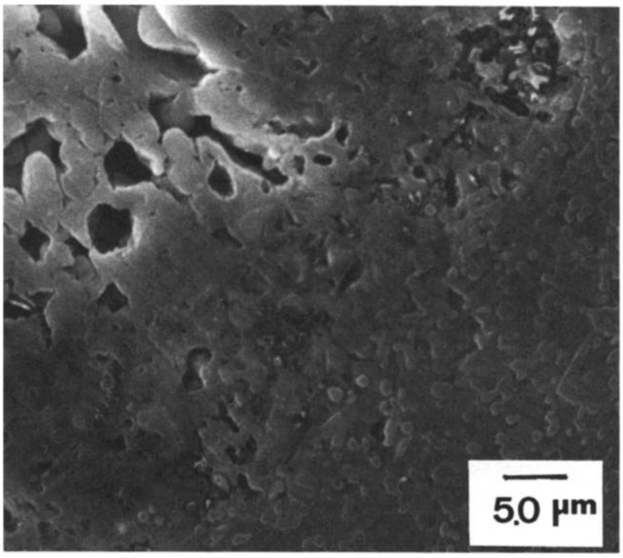


Fig. 4. SEM micrograph of the scale matrix interface after 48 h at 1500°C showing the development of fine scale grains as well as uncovered porosity

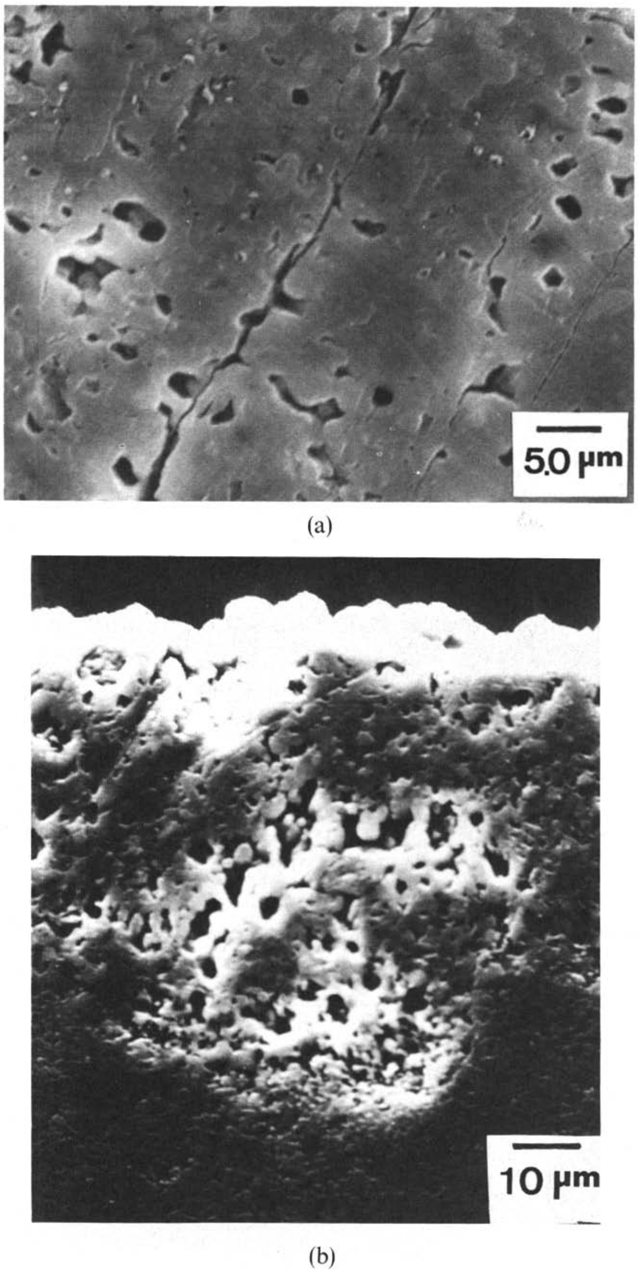
these ratios successively increased until an almost constant ratio was reached (Fig. 6). Moreover, at a given time (25 h), the Si/Al profile exhibited a continuous reduction from the scale surface to the scale matrix interface (Fig. 7). Plots of scale thickness versus time indicated that the oxidation process exhibited a nearly parabolic trend (Fig. 8a). Finally, no mass gain was found in specimens exposed to temperatures of 1300°C for 1 h (Fig. 8b).

4 Discussion

According to Kim & Moorhead,[11] active oxidation, and hence the development of a scale, is strongly influenced by the actual water pressures. Although the H_2 gas employed in this work was of ultra high purity, apparently residual water in the gas was not effectively eliminated. Fischman *et al.*[12] using the SOLGAMIX PV computer code[13] predicted that 25 ppm by volume water in H_2 is sufficient for active oxidation of SiC to SiO(g) and CO(g). Accordingly, the findings of mass gain and a surface scale of this work indicated that water vapor pressure conditions for active oxidation were present. In this case, Kim & Moorhead[11] suggested the following reaction.

$$SiC_{m}(s) + 3H_2O(g) \rightleftharpoons SiO_2(s) + CO(g) + 3H_2(g) \quad (1)$$

Nevertheless, other reaction products are likely to form such as SiO(g) or CH_4(g). Moreover, kinetically, it is expected that the scale will be rate controlled by competitive transport mechanisms through the scale thickness. Under these conditions, reduction reactions effectively compete with oxidation reactions in the resultant scale product



(a)

(b)

Fig. 5. SEM micrographs after H_2 exposure at 1500°C for 48 h (a) Slightly etched scale cross sections showing partial removal of glassy phase along strings of pores and (b) after complete removal of the glassy phase showing a large degree of interconnected porosity

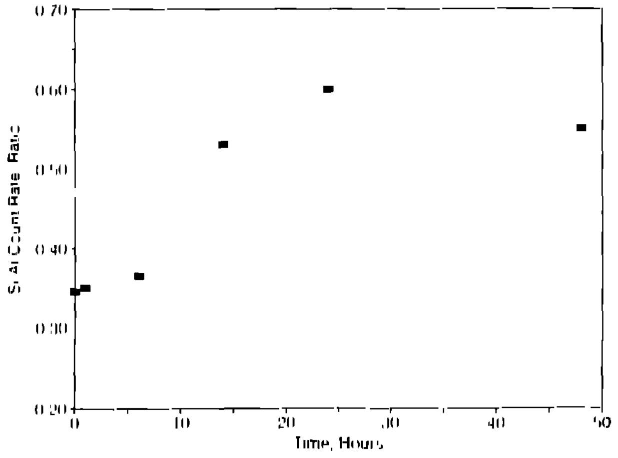


Fig. 6. X Ray count rate ratios for Si/Al in the gas/scale interface after H_2 exposure for various times at 1500°C

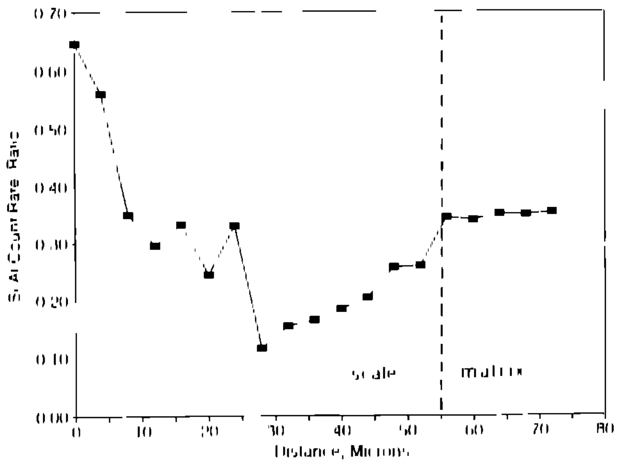


Fig. 7. X Ray count rate ratios for Si Al in the scale cross section after H_2 exposure for 24 h at 1500 C

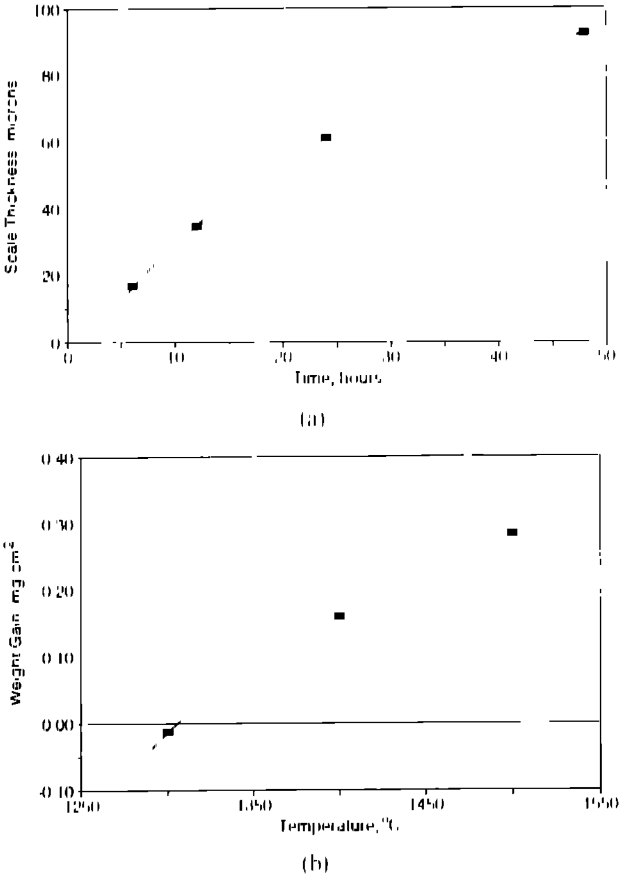


Fig. 8. (a) Scale thickness versus time at 1500 C under flowing H_2 and (b) effect of temperature on the mass gain exhibited after exposure to hydrogen for 1 h

Among the potential reactions are:

$$\mathrm{SiC_w(s) + 2H_2(g) \rightleftharpoons Si(s) + CH_4(g)} \qquad (2)$$

$$\mathrm{SiC_w(s) + H_2O(g) + H_2(g) \rightleftharpoons SiO(g) + CH_4(g)} \qquad (3)$$

$$\mathrm{SiC_w(s) + 2H_2O(g) \rightleftharpoons SiO(g) + CO(g) + 2H_2(g)} \qquad (4)$$

Furthermore, other reactions such as the formation of aluminosilicates are expected to occur

$$x\mathrm{SiO_2} + y\mathrm{Al_2O_3} \rightleftharpoons \mathrm{Al_{2y}Si_xO_{2x+3y}} \qquad (5)$$

along with the formation of mullite:

$$\mathrm{2SiO_2 + 3Al_2O_3 \rightleftharpoons 3Al_2O_3 \cdot 2SiO_2} \qquad (6)$$

Under the existing water vapor pressures, active oxidation of SiC to SiO_2 at the scale surface is expected to occur (eqn (1)) This is followed by subsequent reaction with the surrounding alumina to form mullite in agreement with the SEM and X ray diffraction observations Further exposure should lead to coarsening of mullite grains on the scale surface, as well as to inward permeation of water vapor and oxidation at the scale matrix interface

In contrast the scale surface exhibits a Si build up with time whereas at a given time a Si Al concentration profile is developed across the scale thickness The apparent Si enrichment of the gas scale interface explains the observations of continuous nucleation of mullite grains. Furthermore the Si Al profiles across the scale thickness suggest that the reaction product consists of a solid and liquid mixture, as suggested by other workers This product is forced to flow towards the gas oxide interface through interconnected porosity in order to accommodate volume changes linked to oxidation

Although the rate of scale thickening tends to be parabolic, in agreement with Kim & Moorhead,[11] the mechanistic aspects are not clear Assuming that $P(H_2O)$ permeation is rate limiting the rate controlling mechanisms for scale growth would be the slowest of (a) transport of $H_2O(g)$ from the flowing gas to the scale surface or (b) transport of oxidant through the scale thickness When permeation through the scale thickness is rate limiting, a flat matrix scale interface should form, in contrast with the observations of a rugged interface The conditions for the development of wavy scale matrix interfaces were investigated by Wagner in metallic systems.[14] According to his findings a planar alloy oxide interface is not stable if only one component in the alloy is oxidized, and diffusion in the alloy is slow when compared with diffusion in the oxide Nevertheless, in the present case, these arguments are unable to account for the experimental outcome

Because of the complexity of the problem the mechanistic aspects are only described qualitatively According to the literature[9-10] when SiC alumina is exposed to thermal oxidation a flat dark reaction layer develops which is in contact with the unreacted matrix This layer is essentially free from porosity and contains graphitic carbon, as well as partially dissolved carbides Also, the external scale layer consists of mullite and a glassy phase with some degree of porosity Since active oxidation is present during hydrogen exposure, somewhat analogous phenomena are expected to account for the exhibited scaling Hence, the major differences would be related to the slow permeation of water vapor through the scale

Experimentally, none of the aforementioned factors were verified in hydrogen exposed SiC–alumina. Hence, an alternative view is to consider the effect of hydrogen on the scale development. Since hydrogen permeation through the scale product is relatively fast, it is expected that at the inner interface, SiC reduction conditions might be dominant. According to Kim[15] and Readey,[16] at low $P(H_2O)$ and temperatures above 1400°C, transport of H_2O to the sample is expected to be rate controlling. Hence, the expected water pressures in the scale matrix interface are far smaller than those existing at the external scale surface. Therefore, reactions (2)–(6) might be active at the inner interface in accordance with the SOLGAMIX PV[13] predictions carried out in SiC exposed to H_2–H_2O mixtures.[17,18] Consequently, this will lead to the development of a liquid solid aluminosilicate phase which is then squeezed out as it gets fully oxidized by slowly permeating $H_2O(g)$.

A simple calculation of the volume expansion associated with the formation of SiO_2 gives values of ≈50% for whisker contents of 30 vol%.[19] This in turn imposes relatively large compressive stresses in the scale regions. Under these conditions, the unreacted matrix side exhibits tensile stresses which could lead to the development of cracks. Nevertheless, when the reaction product consists of liquid and solid phases, the stress build up can be easily alleviated by squeezing out the liquid phase through the porous scale. This in agreement with observations of a continuous glassy layer on the scale surfaces.[7,8] Moreover, reaction of the liquid phase with dissolved alumina leads to new mullite grains in agreement with Nurishi & Pask[20] and Rana *et al.*[21] of preferential nucleation and growth of mullite grains at metastable liquid aluminosilicate phases. The extent of mullite formation within the aluminosilicate liquid is strongly influenced by the impurity content and firing temperatures. In particular, it is found[22] that Na_2O inhibits the mullite reaction, whereas high temperatures and low silica to alumina plus silica ratios promote the formation of mullite.

Under equilibrium conditions, mullite and alumina are the expected phases in the scale region. Nevertheless, the limited amounts of oxidant available for the development of mullite suggest that the scale formed does not reach equilibrium. Hence, the rate of scale thickening is mainly controlled by the rate at which the Si rich phase is fully oxidized. This in turn depends upon the rate at which water vapor is transported from the main gas stream to the scale surface. Consequently, under these conditions a planar reaction front is not stable and it explains the undular nature of the interfaces, and the presence of pockets or strings of a glassy phase across the scale thickness. Additional evidence for the role of hydrogen is indirectly provided by the missing dark reaction layer. The absence of an inner reaction layer suggests the lack of substantial graphitic carbon or partially dissolved SiC$_p$ in the scale (see Fig. 4).

The development of relatively large amounts of porosity can also be explained by the reduction of whiskers. Since hydrogen permeation is relatively fast through the scale, the reduction reaction will be rate limited by outward permeation of the gas products (CH_4, CO, SiO, and H_2). This explains the lack of a dark reaction layer in the scale developed. The existence of the inner dark layer is attributed to the relatively low permeability of oxidant through the scale thickness. Consequently, if the oxidation reaction were rate limited by inward permeation of water vapor, a relatively thick dark layer region should develop. Furthermore, outward permeation of CO alone would be predominantly molecular, and it would not be able to account for the exhibited porosity.[6–8] The large amounts of porosity and the lack of a dark reaction layer indicate that relatively large amounts of gas products are continually formed. Finally, the oxidation reactions are accompanied by the development of relatively large volume increases. Hence, upon oxidation, compressive stresses are expected to build up in the scale regions.[19] Accommodation of the internal stresses forces the Si rich phase towards the external surface, and accounts for the Si Al profiles developed across the scale thickness.

5 Conclusions

The morphological evolution of the surface scale during H_2 exposure was investigated. It was found that at 1500°C the scale was made up of mullite, an amorphous glassy phase, and porosity with new mullite grains continually evolving in the scale surface. Also, the scale evolution with time exhibited a nearly parabolic behavior. The scale cross section indicated that the reaction front was not planar but exhibited some degree of rugosity. In particular, the mullite grains were surrounded by interconnected strings of porosity filled with glassy phase.

Energy dispersive X ray analyses indicated that a Si Al profile ratio developed across the scale at a given time. This in turn was associated to the distribution of glassy phase in the scale cross section, and it was attributed to outward channeling of this phase through interconnected porosity. It was suggested that full oxidation of the Si rich glassy phase, coupled with reaction with surrounding alumina, gave rise to new mullite grains in the gas/scale interface. The relatively large degree of porosity exhibited was attributed to the outcoming gases produced by the various reactions occurring at the scale-matrix interface. This, in addition to the development of compressive stresses during oxidation, provided the conditions to compel the amorphous phase towards the external surface.

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