

Liquid phase sintered silicon carbide (LPS-SiC) ceramics having remarkably high oxidation resistance in wet air

Kay André Weidenmann^a, Georg Rixecker^{*}, Fritz Aldinger

Max-Planck-Institut für Metals Research and Institute of Nonmetallic Inorganic Materials, University of Stuttgart, Heisenbergstrasse 3, 70569 Stuttgart, Germany

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Abstract

Numerous studies on the oxidation characteristics of common silicon carbide ceramics have revealed very good oxidation resistance in dry atmospheres, provided that the oxygen partial pressure is sufficiently high. On the contrary, as other SiO₂-passivated ceramics, SiC shows poor oxidation resistance in moist atmospheres. In this contribution, the oxidation behaviour at 1400 °C of fully dense SiC samples with Lu₂O₃-AlN and Lu₂O₃-Ho₂O₃ sintering additives is investigated. Similar to results recently reported for a novel Si₃N₄ material, it is demonstrated that Lu₂O₃ yields greatly improved oxidation behaviour as compared to other liquid phase sintered SiC materials. In particular, the Lu₂O₃-Ho₂O₃ additive leads to passive oxidation under a 0.01 MPa partial pressure of water.

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1. Introduction

Many processes used to manufacture products from raw materials require high temperatures. Accordingly, materials used in such processes, e.g., as reaction chamber linings, have to withstand severe environmental conditions. The same is true for high temperature materials in aircraft engines and other gas turbines, where only specially optimised coating/substrate combinations may suffice. State of the art in many niche applications is the usage of non-oxide ceramics, especially silicon carbide, showing good mechanical properties even in harsh environments. For example, SiC materials are employed as wear-resistant components of pumps in the aerospace sector and in heat shields. In recent years, numerous studies have demonstrated very good oxidation resistance of SiC ceramics in dry atmospheres,^{1–4} provided that the oxygen partial pressure is sufficiently high.⁵ On

the contrary, as other SiO₂-passivated ceramics, SiC shows inferior oxidation resistance in moist atmospheres.^{6–9} Considering water vapour to be a major component of combustion environments,^{10–13} this presents a serious limitation for many applications. In the present contribution, it is shown that sintering additives containing lutetium oxide (Lu₂O₃ in combination with either Ho₂O₃ or AlN) can improve the oxidation behaviour of LPS-SiC substantially, even under wet conditions.

Generally, two types of oxidation may be distinguished. Firstly, passive oxidation according to Eq. (1) which in long-term usage leads to the evolution of a protective oxide layer mainly consisting of silica^{2,14}:



In the presence of passive oxidation, various mechanisms can be discriminated. Among the relevant models are the following. Firstly, parabolic oxidation, where the oxidation process is controlled by diffusion of the oxidising species (e.g., molecular oxygen) through the oxide layer; the corresponding diffusion rate is constant.¹⁵ An alternative model is

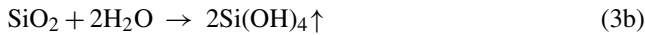
^{*} Corresponding author.

E-mail address: rixecker@aldix.mpi-stuttgart.mpg.de (G. Rixecker).

^a Present address: Institute of Materials Science and Engineering I, University of Karlsruhe, Kaiserstrasse 12, 76131 Karlsruhe, Germany.

referred to as non-parabolic oxidation: this process is equally diffusion-controlled, but is characterised by a time-dependent diffusion rate.¹⁶

Secondly, active oxidation which causes corrosion of the substrate material, for either no formation of a protective layer at all (Eq. (2)) or the simultaneous formation and volatilisation of the oxide film takes place (Eqs. (3a) and (3b)).



The latter process is referred to as parilinear oxidation.^{8,17} For the parilinear oxidation of silicon carbide the predominant mechanism is hydrolysis of silica, which results in the formation of gaseous $\text{Si}(\text{OH})_4$ at high temperatures, leading to a perpetual recession of the oxide layer.^{11,18,19}

With a water partial pressure of 0.01 MPa at 1400 °C, the wet oxidation conditions used in the present work are less severe than the high gas velocity/high pressure environments encountered in gas turbine engines.^{13,18,20–23} On the other hand, they are well controlled, very reproducible and permit comparison with a wide range of relevant literature data.^{7,8,24}

2. Experimental

The starting materials used in the present study were α -SiC, β -SiC, AlN and Y_2O_3 powders with a high sintering activity obtained from H.C. Starck, Goslar, Germany, and reagent-grade Lu_2O_3 and Ho_2O_3 powders purchased from ABCR, Karlsruhe, Germany. One powder batch, denoted as Ho–Lu, was prepared from 90 vol% SiC (with an α -to- β ratio of 1:9) and 10 vol% of equimolar amounts of Lu_2O_3 and Ho_2O_3 as sintering additives. Two more batches, denoted as Al–Lu and Al–Y, contained AlN and either Lu_2O_3 or Y_2O_3 in equimolar amounts. The material Al–Y was included in this study for comparison with the lutetium-containing compositions. The Ho–Lu mixture was compacted by hot pressing at 1950 °C under a uniaxial load of 30 MPa. For the Al–Lu and Al–Y samples, densification was achieved by cold isostatic pressing and gas pressure sintering at 2100 °C (Al–Lu)²⁵ or 1990 °C (Al–Y) under a nitrogen overpressure of 10 MPa. In all cases, relative densities >99% were obtained. Subsequently, the ceramics were cut to produce coplanar samples of 1 mm × 10 mm × 17 mm, which were ground and polished on both sides to a 1 μm finish.

The oxidation behaviour of the samples was examined using an experimental setup comparable to Opila's.⁷ All experiments were carried out at 1400 °C with an air flow rate of 60 l h⁻¹, corresponding to a flow velocity of about 3 cm/s at the inlet of the reaction tube. To avoid pollution of the furnace atmosphere with alkaline ions,^{7,26} the 99.7% alumina tubes and crucibles were aged at 1600 °C for 120 h in an argon flow prior to the experiments. The residual sodium content of the

central section of one tube was determined by atomic emission spectroscopy (ICP-OES) to be ≤ 8 ppm. A pre-saturator at 70 °C and a saturator at 50 °C adjusted an absolute humidity of 78 mg deionised water per litre air, corresponding to a partial pressure of water of 0.01 MPa or 10%. For each experiment fresh, non-oxidised samples were used. After oxidation times between 8 and 500 h, the weight change of the samples was measured with an accuracy of 0.01 mg. On the basis of repeated dry oxidation runs with Ho–Lu and Al–Lu samples, the repeatability is estimated as $\pm 0.03 \text{ mg cm}^{-2}$. Additionally, scanning electron microscopy (SEM, Zeiss DSM-982 in backscattered electron mode), energy-dispersive microanalysis (EDX, Link ISIS 400) and X-ray powder diffraction (XRD, Siemens D-5000 in Bragg-Brentano geometry, $\text{Cu K}\alpha$ radiation) were used to monitor structure and phase composition of the oxide layers.

3. Results

In Fig. 1, the square of the weight change of the samples Ho–Lu and Al–Lu is plotted as a function of the oxidation time. Both materials show a persistently increasing weight gain. Fitting a linear function to the Ho–Lu data shows its oxidation kinetics to be parabolic with a rate constant of $k_p = 4.9 \times 10^{-3} \text{ mg}^2 \text{ cm}^{-4} \text{ h}^{-1}$. For comparison, a lower rate constant of $k_p = 7.0 \times 10^{-4} \text{ mg}^2 \text{ cm}^{-4} \text{ h}^{-1}$ is measured in stagnant air.

In contrast, the weight gain of Al–Lu does not obey parabolic kinetics. Curve fitting with a multiple-law model,²⁷ modified to describe parilinear kinetics, yields good agreement:

$$\frac{\Delta m}{A} = \sqrt{(k_p t)} - k_1 t. \quad (4)$$

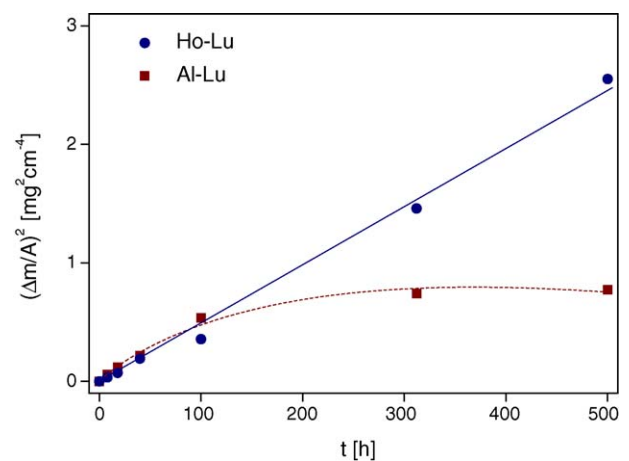


Fig. 1. Square of the specific weight change vs. oxidation time in wet air at 1400 °C for the LPS-SiC materials Ho–Lu and Al–Lu. The lines represent parabolic (full line) and parilinear oxidation behaviour (broken line), respectively.

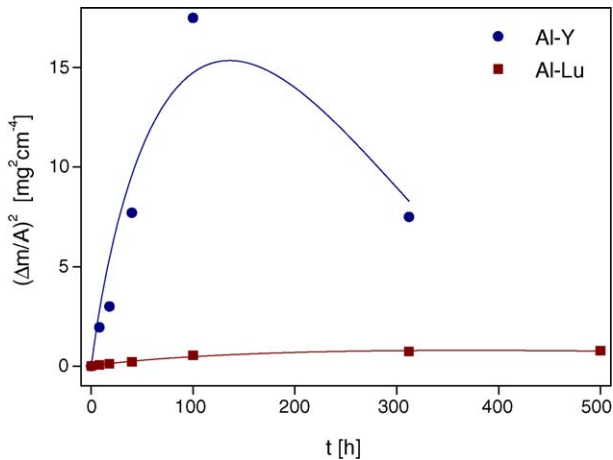


Fig. 2. Time-dependent specific weight change of LPS-SiC materials Al-Y and Al-Lu at 1400 °C in moistened air flowing at 601 h⁻¹. The lines represent parabolic oxidation behaviour.

In Eq. (4), $\Delta m/A$ is the weight change per surface area, t is the oxidation time, and k_p ($=8.4 \times 10^{-3} \text{ mg}^2 \text{ cm}^{-4} \text{ h}^{-1}$) and k_l ($=2.4 \times 10^{-3} \text{ mg cm}^{-2} \text{ h}^{-1}$) are the parabolic and linear rate constants, respectively. This material exhibits parabolic oxidation in ambient air, with $k_p = 3.1 \times 10^{-3} \text{ mg}^2 \text{ cm}^{-4} \text{ h}^{-1}$.

From Fig. 2, it is obvious that wet oxidation also causes parabolic behaviour in the material Al-Y (AlN/Y₂O₃ sintering additive), and that the corrosion is much more severe for Al-Y than for Al-Lu.

According to the fit to the weight gain curve of Al-Lu (Fig. 1), a shallow maximum is expected around $t = 350$ h. Although this is not verified by the measured data (the weight gain after 312 and 500 h is the same within the experimental accuracy), the assumption of two concurrent processes taking place is corroborated by examining polished cross sections of the oxidised samples. Fig. 3 shows the film morphologies after 500 h; up to this oxidation time, a monotonically increasing oxide layer thickness is found for both Ho-Lu and Al-Lu. Although estimating an average thickness from the SEM images is somewhat subjective, the film thickness of Ho-Lu seems to increase proportional to the weight change. Al-Lu shows the same kind of relationship up to 100 h, after which the layer thickness continues to increase while the weight gain levels off. Since a finite oxidation rate necessarily exists, there must be an additional process accompanied by mass loss.

After 500 h in wet air at 1400 °C, the oxide layers contain lanthanide-rich phases which appear as bright grains in the backscattered electron (BSE) images due to atomic number contrast. According to semi-quantitative EDX microanalysis, they are rare earth silicates of a composition close to R₂Si₂O₇, which is corroborated by XRD (Fig. 4). In the case of Ho-Lu, the holmium and lutetium content varies between different silicate grains. The dark phase also present in both kinds of oxide layers is SiO₂ (α -cristobalite). The oxide films on Al-Lu contain one or more additional phases (light grey), which appear to be aluminium silicate according to EDX but

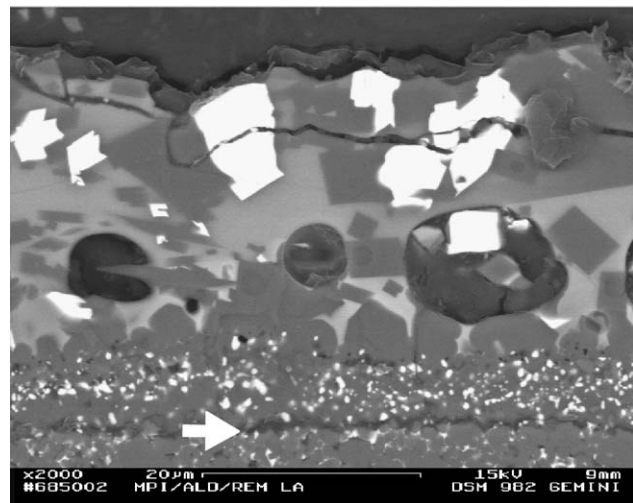
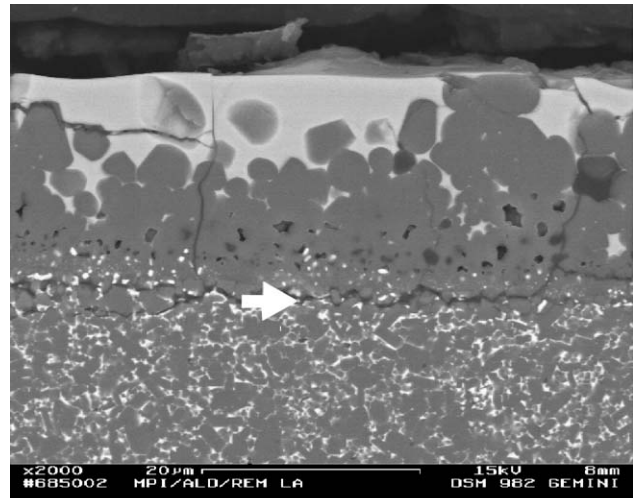


Fig. 3. BSE images of the oxide films on Ho-Lu (upper) and Al-Lu (lower) after 500 h in wet air at 1400 °C. Both films contain SiO₂ (dark grey) and rare earth silicates (bright). The oxide layer on Al-Lu also contains one or more aluminium silicate phase(s) (light grey). The arrows indicate the base material-oxide interface.

could not be identified unambiguously by XRD. The phase inventory according to XRD is very similar for all experimental conditions (dry as well as wet oxidation).

4. Discussion

The oxidation resistance of the present lutetium-containing ceramics is much higher than that of liquid phase sintered SiC materials containing various other additives, such as Y₃Al₅O₁₂ and combinations of AlN or Al₂O₃ with Y₂O₃ or Er₂O₃.^{28,29} They exhibit parabolic rate constants in excess of 10⁻² mg² cm⁻⁴ h⁻¹, a limit which was confirmed in our lab for a similar set of additives and also for combinations of two rare earth oxides other than Lu₂O₃ (e.g., Dy₂O₃, Y₂O₃, Er₂O₃, Ho₂O₃). In one study of dry oxidation

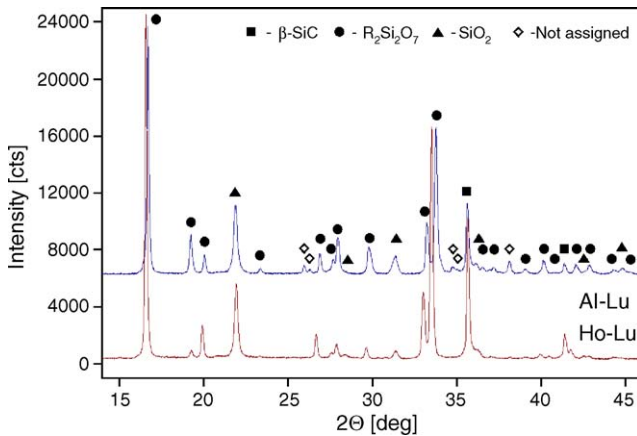


Fig. 4. XRD scans of oxidised surfaces of Ho–Lu and Al–Lu materials after 100 h in wet air at 1400 °C. Both surface layers contain SiO₂ (α-cristobalite) and monoclinic R₂Si₂O₇, the latter with a strong texture judging from its measured Bragg intensities. The XRD pattern of Al–Lu has unidentified reflections of a phase possibly related to mullite (Al₆Si₂O₁₃) or silimanite (Al₂SiO₅). The SiC reflections belong to the base material.

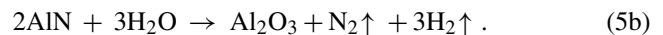
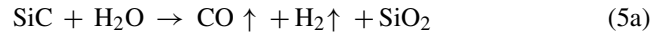
at 1400 °C, a low k_p value of $1.1 \times 10^{-3} \text{ mg}^2 \text{ cm}^{-4} \text{ h}^{-1}$ was also reported for a SiC material hot-pressed with AlN–Yb₂O₃ additive.²⁸

When compared to SiC materials without oxidic additives, the dry oxidation resistance of the Lu₂O₃-containing ceramics is found to be on the same order of magnitude as that of chemically pure CVD-SiC. In wet atmosphere, $k_p \approx 5 \times 10^{-4} \text{ mg}^2 \text{ cm}^{-4} \text{ h}^{-1}$ was reported for CVD-SiC under a similar set of experimental parameters (1400 °C, 90% O₂:10% H₂O, gas flow velocity 0.4 cm s⁻¹).^{7,8} The mass gain was close to parabolic, but inspection of Fig. 7 of Ref.⁷ reveals a deviation in the direction of parabolic kinetics for the most clean conditions investigated. From data measured at the higher temperature of 1500 °C,²⁴ an inferior wet oxidation resistance can be deduced for SiC ceramics solid-state sintered with B and C additions.

The low oxidation rate of Ho–Lu and Al–Lu may be attributed to the high cationic strength of Lu³⁺ in silicates,²⁵ which has a large influence on the diffusivity of oxygen in the oxide films. For Al–Lu, there is no pronounced weight loss up to 500 h. Thus, although Al–Lu does not possess long-term stability in terms of passive oxidation kinetics in the presence of moisture, it may qualify for a range of high-temperature applications based on its comparatively small rate of corrosion. On the other hand, the differences in the oxidation behaviour of Ho–Lu and Al–Lu may be attributed to the structure and phase composition of the oxide layers formed (Fig. 3).

It is quite obvious that gaseous reaction products at the interface between oxide and silicon carbide substrate, which are likely to result from reactions such as (2), (5a) and (5b), lead to much larger pores in the case of Al–Lu. Note that these reactions have exemplary character—in particular, the intergranular phase of Al–Lu does not contain free AlN according to XRD analysis (Fig. 4). The actual decomposition reactions

of the Al- and N-containing silicates will be more complicated than it is suggested by these equations:



The porosity is likely to interfere with the protective capacity of the oxide film. This may also be the case for the through-thickness cracks perpendicular to the film surface, which are equally visible in SEM images of as-prepared oxide layers and form a mudflat crack pattern. They are thought to be due to thermal expansion mismatch. As the oxide films on both base materials exhibit good adherence in tape tests with an adhesive force of 70 N cm⁻², cracks parallel to the surface (Fig. 3) are regarded as artifacts of a uniaxial warm pressing step which is required during the preparation of the cross-sectional specimens.

In the Ho–Lu samples, the SEM cross sections indicate formation of a more or less continuous surface layer of rare earth di-silicates. Formation of the corresponding monosilicates (RSiO₅) was not observed. Similar to yttrium silicates, which are already being examined as environmental barrier coatings,^{30,31} the parabolic kinetics of Ho–Lu during wet oxidation up to 500 h suggest that the silicates Lu₂Si₂O₇ and Ho₂Si₂O₇ exhibit a high degree of stability in moist air. In the oxide films on Al–Lu, on the contrary, the lutetium silicate grains are randomly distributed and offer less protection to the SiO₂ and Al-silicate phases.

Recent studies on novel silicon nitride ceramics containing circa 7 mass% of lutetium in oxidic form (SN 281/282, Kyocera, Japan) revealed parabolic oxidation kinetics. However, the rate of volatilisation was substantially decreased in comparison to more conventional Si₃N₄ materials.^{21,22} Oxide layers on SN 282 exhibited a morphology of spherical Lu₂Si₂O₇ particles dispersed in a silica matrix,^{22,23} and even though Lu₂Si₂O₇ was chemically stable in comparison to silica,²³ the silicate grains were partially spalled off during corrosive attack on the film. In the light of these results, the reason for the favourable wet oxidation behaviour of Ho–Lu may be that its higher content of rare earth oxide additive (24 mass%) enables the formation of a more closed cover layer of lutetium and holmium silicates.

5. Conclusion

The results obtained in the present study show that the oxidation resistance of LPS-SiC ceramics can be improved substantially as compared to the sintered SiC materials available to-date. When Lu₂O₃ is added as a sintering aid, the oxidation rate is appreciably reduced. When the sintering additive is aluminium-free in addition, parabolic oxidation kinetics can be achieved in wet air under the conditions investigated. In comparison to CVD-SiC, a reference material showing excellent performance in oxidising atmospheres, the oxidation rate is on the same order of magnitude.

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