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Original Article

Oxidation of β -SiC at high temperature in Ar/O₂, Ar/CO₂, Ar/H₂O gas mixtures: Kinetic study of the silica growth in the passive regime

Mathieu Q. Brisebourg, Francis Rebillat, Francis Teyssandier*

Laboratoire des Composites Thermostructuraux (LCTS), UMR-5801, 3 allée de la Boétie, 33000, Bordeaux, France

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ABSTRACT

The kinetics of silica growth during passive oxidation of SiC was studied using an original interferometric method carried out in a reactor specifically designed for that purpose. The influence of various oxidant species, O₂, H₂O, CO₂ as well as their mixtures was investigated in a high temperature domain ranging from 1550 °C to 1850 °C at atmospheric pressure. This method is an efficient way to measure the various oxidation regimes usually described by the Deal-Grove model. Both the linear and parabolic rate constants are found to be independent of gas phase composition above 1700 °C, and to increase with oxygen partial pressure below 1700 °C for P_{O₂} > 20 kPa. In the parabolic growth regime, we observed a transition from a low temperature interstitial-dominant to a high temperature network-dominant oxygen transport in the silica scale. The present results suggest the existence of a similar transition in the linear growth regime.

1. Introduction

Silicon carbide (SiC) is a well-known oxidation-resistant material at high temperatures due to its ability to form a continuous protective oxide scale (SiO₂) under highly oxidative environments (passive oxidation). The silica scale formed under these conditions acts as a diffusion barrier against gaseous oxidant species and limit the kinetics of SiC oxidation. Accordingly, studying the silica growth kinetics during passive oxidation of SiC at high temperature is a critical step to improve its lifetime in high temperature applications. The literature shows that silica growth studies can be classified in two categories: i) studies using macroscopic methods such as thermogravimetric analysis (TGA), which may possibly be coupled with mass spectroscopy, and ii) studies based on oxygen isotopic tracing or in-situ spectroscopic ellipsometry, which are applied to thin oxide scales (a few tens of nanometers) and are usually carried out on single-crystals. Thermogravimetric methods are not very accurate in the case of thin silica scale in the linear growth regime and are difficult to implement above 1600 °C. Isotopic tracing methods or in-situ spectroscopic ellipsometry are more appropriate for the understanding of oxidation mechanisms at the atomic scale.

We have developed a new device that provides an accurate basis for in situ thickness measurement of the growing silica scale in the range 200–2500 nm. Our method, which can be considered as midway between the two above-mentioned categories of studies, is based on optical interferometry applied to silica scales growing on the β -SiC outer surface of a TEXTRON SCS-6 filament. The filament is Joule-heated

thanks to its carbon core. The objective was to investigate the growth kinetics of silica in the temperature range 1550 °C–1850 °C under a large variety of environments: O₂, CO₂, H₂O and their mixtures. Though the originality of our study was to focus on the linear regime that is usually difficult to measure with TGA, both the linear and parabolic regimes were studied. The influence of the volatilization rate of the oxide scale in the presence of water vapor was also studied thanks to the 3-D simulation of our reactor to take into account the reactive volatilization of SiO₂ when being in contact with H₂O.

The following sections are devoted to a literature review on SiC oxidation by O₂, CO₂ or H₂O and the Deal and Grove linear-parabolic model generally used to model the silica growth rate.

1.1. SiC passive oxidation in the presence of O₂

Zheng et al. [1] have studied passive oxidation of SiC by Ar/O₂ gas mixtures in the temperature range 1200 to 1500 °C. The authors have shown that the silica growth rate, which was satisfactorily described by the Deal-Grove model, was composed of a rather short linear regime followed by a parabolic regime rate-controlled by diffusion of oxidant species through the silica scale. Below 1200 °C, the parabolic rate constant (k_p) showed a linear dependence to O₂ partial pressure, thus indicating that O₂ diffusion through the silica scale was rate limiting. In contrast, as temperature increased the dependence to O₂ partial pressure vanished. In a companion article [2] these authors have found that the transition between these dominant mechanisms takes place at

* Corresponding author at: Laboratoire Procédés, Matériaux, Energie Solaire (PROMES) UPR8521, Rambla de la Thermodynamique, Tecnosud, 66000, Perpignan, France.
E-mail address: Teysandier@univ-perp.fr (F. Teysandier).

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1350 °C and is accompanied by an increase of the apparent activation energy from 120 to 260 kJ mol⁻¹. By use of isotopic tracing methods at high temperature oxygen was shown to diffuse preferentially in the form O²⁻ by ions exchange in the silica network. According to this mechanism, silica growth rate should not be dependent on the partial pressure of O₂. This has been confirmed by Goto et al. [3] at 1627 °C using similar initial gaseous mixtures. Transport by vacancies at high temperature is however contested by Doremus [4] because the corresponding activation energy is too low to account for the breaking of the Si-O chemical bond associated with such a mechanism. Doremus [4] as well as Sasse et al. [5] proposed instead that at high temperature the silica growth rate is limited by transport of oxygen from SiC/SiO₂ interface to SiO₂/gas interface by interstitial SiO species. Above 1400 °C the amorphous silica scale is found by some authors [6,7] to transform into the cristobalite allotropic form, mainly under the influence of impurities. The change of transport mechanism from interstitial type to network type that is observed by Zheng et al. [2], is no longer observed at high temperatures when SiO₂ is in the form of cristobalite [8].

1.2. SiC passive oxidation in the presence of H₂O

In the presence of water vapor, provided that the influence of the silica vaporization by reaction with water vapor is low, the Deal-Grove model can also describe the silica growth. In contrast, at high temperature, vaporization of the silica scale, which follows a linear rate, has to be taken into account using a modified Deal-Grove model named parilinear model by Opila et Hann [9]. Passive oxidation in the presence of H₂O is characterized by a much longer linear regime than in the case of O₂ [10,11]. Diffusion of oxidant species in silica is indeed so fast in the presence of H₂O-containing atmospheres that transition towards a parabolic regime where diffusion is rate limiting, is observed for thicker silica scale than in the case of O₂ gaseous mixtures. As a consequence, k_p is increased by an order of magnitude in the presence of water vapor because of the enhanced solubility of H₂O molecules into silica [12]. Given the similarity between the k_p values measured at 1100 °C either in O₂+H₂O gas mixtures or in Ar+H₂O mixtures [12], it can be concluded that in the presence of H₂O, O₂ has a marginal influence on the oxidation mechanism of SiC. Passive oxidation of SiC in H₂O atmospheres is also enhanced because of the modification of the silica structure by formation of Si–OH bonding. Such a structural transformation causes a decrease of the silica density, which leads to i) a lower ability of the silica scale to protect SiC from further oxidation [13], and ii) formation of an increased quantity of bubbles because of the enhanced production of gaseous species by the oxidation reaction [12].

1.3. SiC passive oxidation in the presence of CO₂

Opila and Nguyen [14] have shown in the temperature range 1200 °C–1400 °C that oxidation of SiC in the presence of CO₂ no longer follows the Deal-Grove model. It is instead characterized by an initial weight increase according to a parabolic law followed, several hours later, by a linear decrease. This kinetics seems to be independent of temperature in the domain studied, which suggests that diffusion of oxidant species through the silica scale is no longer rate limiting when CO₂ is the oxidant species. Dissociation of the CO₂ molecule at the surface of SiO₂ may in that case be rate limiting [14]. When using CO₂ as oxidant species, the measured oxidation rates are always much lower than those measured when using O₂ or H₂O. Goto et al. [3] have revealed in the range 1600 °C–1700 °C that k_p is highly temperature dependent and varies linearly as a function of oxygen chemical activity. Such a behavior is characteristic of a network diffusion of oxygen through the silica scale.

Regarding the diffusion of species inside the silica layer, it can be concluded that at least two basic mechanisms are identified. The oxidant molecule (O₂ or H₂O) can dissolve and diffuse as molecular species

through the porosity of the structure, this process is usually named interstitial diffusion. Oxygen can also diffuse in the form of O²⁻ ions in the silica network. These two transport processes take place simultaneously, however their relative importance varies according to the temperature domain. Transport by molecular species will be named type 1 mechanism henceforth in this text. It is dominant at low temperature and high oxygen partial pressure and characterized by i) low activation energies for both k_i and k_p (typically about 100 kJ/mole), and ii) a linear dependence to the partial pressure of the oxidant species. The second transport process will be named type 2 mechanism. It is dominant at high temperature and low oxygen partial pressure. In this case, the growth rate constant is independent of gas phase composition and has a high activation energy.

1.4. The Deal & Grove model

The growth of SiO₂ during passive oxidation of SiC is usually described by the Deal and Grove model [15]. The model was initially developed to describe the kinetics of passive oxidation of silicon in the presence of either O₂ or H₂O. It can be extended to silica growth during oxidation of SiC, the major difference being in this case that a large amount of carbon is released at the SiO₂/SiC interface. The following steps describe the growth of SiO₂ in the modified model:

- Adsorption of gaseous oxidant species at the surface of the silica scale,
- Diffusion of oxidant species through the silica scale towards the SiC/SiO₂ interface,
- Oxidation reaction at the interface SiC/SiO₂ interface,
- Diffusion of the reaction products through the silica scale towards the SiO₂/gas interface,
- Desorption of the gaseous products from the silica surface

According to the Deal-Grove model, the steady-state kinetics of the SiO₂ growth is given by the following linear- parabolic equation:

$$X^2 + AX = B^*(t + \tau) \quad (1)$$

where X is the thickness of the oxide layer and t is the oxidation time. τ corresponds to a shift in the time coordinate, to account for the presence of an initial oxide layer. The model predicts that for short oxidation times or thin oxide scales, the oxide growth rate is linear with time and limited by reactions between SiC and the oxidant species at the SiC/SiO₂ interface. For longer oxidation times, as the oxide scale grows thicker, the model predicts that diffusion of oxidant species through the oxide scale towards the SiC/SiO₂ interface eventually becomes rate limiting. B and B/A are respectively the parabolic and linear rate constants. The model is based on several assumptions: steady-state conditions, flux of the oxidant species across the oxide layer given by Fick's law, and formation of SiO₂ by oxidation reaction at the interface between SiC and the oxide scale expressed by a first-order kinetic reaction.

At high temperatures or in the presence of water vapor, the silica scale can decompose or vaporize. Such processes are characterized by linear reaction rates. When oxidation in the parabolic regime and volatilization occur simultaneously, the Deal and Grove model no longer apply. The overall kinetics is in this case described by the more complex parilinear kinetics that has been proposed and detailed by Opila and Hann [9]. Such kinetics is characterized by the occurrence of a limiting oxide scale thickness at long oxidation times.

If a growth rate limited by diffusion of oxidant species through the silica scale is a sound interpretation of the parabolic regime, in contrast, in the linear regime there is no direct evidence for reactions taking place at the interface between SiC and the oxide scale to be slow enough to control the oxidation rate, especially at high temperature. Several authors have shown that the presence of a thin extra layer of constant

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