OXIDATION STUDY OF AN ULTRA HIGH TEMPERATURE CERAMIC COATINGS BASED ON HFSICN

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ABSTRACT

High temperature fiber-reinforced ceramic matrix composites (CMCs) are important for aerospace applications because of their low density, high strength, and significantly higher-temperature capabilities compared to conventional metallic systems. The use of the SiC_f/SiC and C_f/SiC CMCs allows the design of lighter-weight, more fuel efficient aircraft engines and also more advanced spacecraft airframe thermal protection systems. However, CMCs have to be protected with advanced environmental barrier coatings when they are incorporated into components for the harsh environments such as in aircraft engine or spacecraft applications. In this study, high temperature oxidation kinetics of an advanced HfSiCN coating on C_f/SiC CMC substrates were investigated at 1300°C, 1400°C, and 1500°C by using thermogravimetric analysis (TGA). The coating oxidation reaction parabolic rate constant and activation energy were estimated from the experimental results. The oxidation reaction studies showed that the coatings formed the most stable, predominant $HfSiO_4$-HfO_2 scales at 1400°C. A peroxidation test at 1400°C then followed by subsequent oxidation tests at various temperatures also showed more adherent scales and slower scale growth because of reduced the initial transient oxidation stage and increased $HfSiO_4$-HfO_2 content in the scales formed on the HfSiCN coatings.

1.INTRODUCTION

Ceramic matrix composites (CMCs) such as SiC_f/SiC and C_f/SiC are being considered for use in advanced aircraft and spacecraft applications. CMCs are valued for their light weight, and superior ability to withstand higher temperatures without major losses in mechanical strength as compared to nickel based superalloys. However, CMCs must be protected with ceramic coatings that can withstand aggressive oxidation and corrosive combustion during engine or spacecraft entry, descent, and landing (EDL) in order to be viable candidate materials [1]. Improving oxidation resistance is therefore of great importance for Ultra High Temperature Ceramic (UHTC) substrates and coatings that are designed for the harsh operating environments and long-term durability. In general, the oxidation of the SiC based material system is mostly driven by the diffusion of oxygen into the material, although the diffusion of silicon and hafnium towards the surface also contributes to the scale formation reactions [2, 3, 4]. To resist recession and consumption caused by oxidation, coatings must to be designed to form a layer of oxide scales that are strong and have a low oxygen diffusivity to impede further oxygen and metal ion transfer

[1]. To better understand how coatings can be integrated to protect structural ceramic materials, this study was conducted to investigate the oxidation kinetics of an UHTC HfSiCN coating at high temperatures.

2.EXPERIMENTAL

The coating studied was a silicon doped compound HfSiCN, an UHTC composition. The coating composition, whose design is described in References [1] and [2], included silicon added to a HfCN UHTC to help improve the material's oxidation resistance. The coating was deposited onto C_f/SiC composite or SiC monolithic substrates by the Southwest Research Institute using a Plasma-Enhanced Physical Vapor Deposition process.

To study the kinetics of oxide scale formation on ceramic coatings, a series of thermogravimetric analysis (TGA) tests were conducted similar to the work described in Reference [4]. Each C_f/SiC CMC coupon was fully coated all sides with the HfSiCN coating. Three of these samples were initially tested at 1300°C, 1400°C, or 1500°C under 1 atm of O_2 for 100 hours. To better understand the nature of scale growth after the initial transient state, a subsequent round of tests was conducted on three additional samples. These samples were first 'pre-oxidized' at 1400°C for 20 hours in 1 atm of O_2 to develop a consistent scale layer. The pre-oxidation temperature was selected because the samples tested at 1400°C in the initial round of TGA runs showed the shortest initial transient stage (they best fit the parabolic rate behavior) and good scale adherence. The pre-oxidized samples were then further oxidized in the same atmosphere for 100 hours at either 1300°C, 1400°C, or 1500°C. The weight gain data for the test specimens were continuously recorded for the duration of the tests. After the TGA tests, the samples were characterized and analyzed using a Phenom Pro X Scanning Electron Microscope (SEM) and accompanying Energy Dispersive Spectroscopy (EDS) system. X-Ray Diffraction (XRD) was also used to characterize the phase structures of the coating and scales.

3.RESULTS AND DISCUSSION

3.1 TGA Kinetics and Analysis

Data from the TGA showed a sharp drop in the mass of all the HfSiCN coated C_f/SiC samples during their first hour of testing. This can be accounted for by the evaporation of moisture that had been absorbed by the sample prior to testing, as well as organic residue that may have built up during processing and handling. The weight gain data from all the samples were made comparable by dividing each sample's change in mass by its surface area (the resulting term is referred to as the specific weight gain). Because the main objective was to study the growth of scales that takes place on the surface of

ceramic materials at high temperatures, the data was adjusted and graphed to show only the mass gain that takes place after the initial burnout. Initially, the sample weight gain rate is relatively high. Once oxide scales cover the original surface, the rate of weight gain decreases because the scales slow the oxygen diffusion rate [3, 4, 5]. The data fit well with the proposed parabolic rate law, which supports the assertion that the reaction is controlled by diffusion and the formation of relatively protective scales [3, 4, 6].

To better characterize the oxidation kinetics of the HfSiCN coatings, plots were made comparing change in specific mass squared versus time. The parabolic nature of the reaction leads to relatively linear trends when graphed using this relationship, which makes it possible to extrapolate the reaction rate constants for longer time. As shown in Figure 1, the first round of TGA tests showed that the sample tested at 1300°C had the highest growth rate, followed by the sample tested at 1500°C and 1400°C, respectively. However, it is unlikely that the 1300°C sample demonstrated the highest growth rate over the course of 100 hours because of a true temperature dependence for a temperature-activated process. Instead, it is believed that this sample had a higher relative growth rate because, at the lower temperature, the formation of the initial continuous protective oxide layer, as expected to be predominantly hafnia silicate or hafnon, is slower. Since the protective oxide scale layer did not form quickly, the sample remained in its transient stage for a longer period of time during the test. The sample tested at 1400°C seemed to have achieved a stable reaction rate the quickest, which is why the samples for the next round of testing were pre-oxidized at 1400°C. The pre-oxidation at 1400°C for 20 hours allowed for the assumption that all samples would have the initial layer of steady-state protective scales already formed when the 100 hour test began, so that the temperature effect on the steady-state reaction rates could be studied for the specimens.

In both rounds of testing, the samples tested at 1400°C proved to have the most stable reaction rates, as shown by their increasingly linear behavior. This is supported by XRD data discussed below. The 1500°C pre-oxidized sample also showed a fairly strong linear behavior, although the overall growth rate quickly slowed, due to the high temperature and quick formation of the protective scales. It is possible that SiO_2-containing scales were more prone to volatility at 1500°C, and thus may have contributed to the relatively lower observed scale growth rate at 1500°C.

Special attention was paid to data from the end of the test, at which point the formed protective scales can effectively control diffusion. In analyzing the last 30 hours of testing for all of the samples, linear regressions were used to estimate the oxidation rate constant k_p of the reactions at various temperatures.
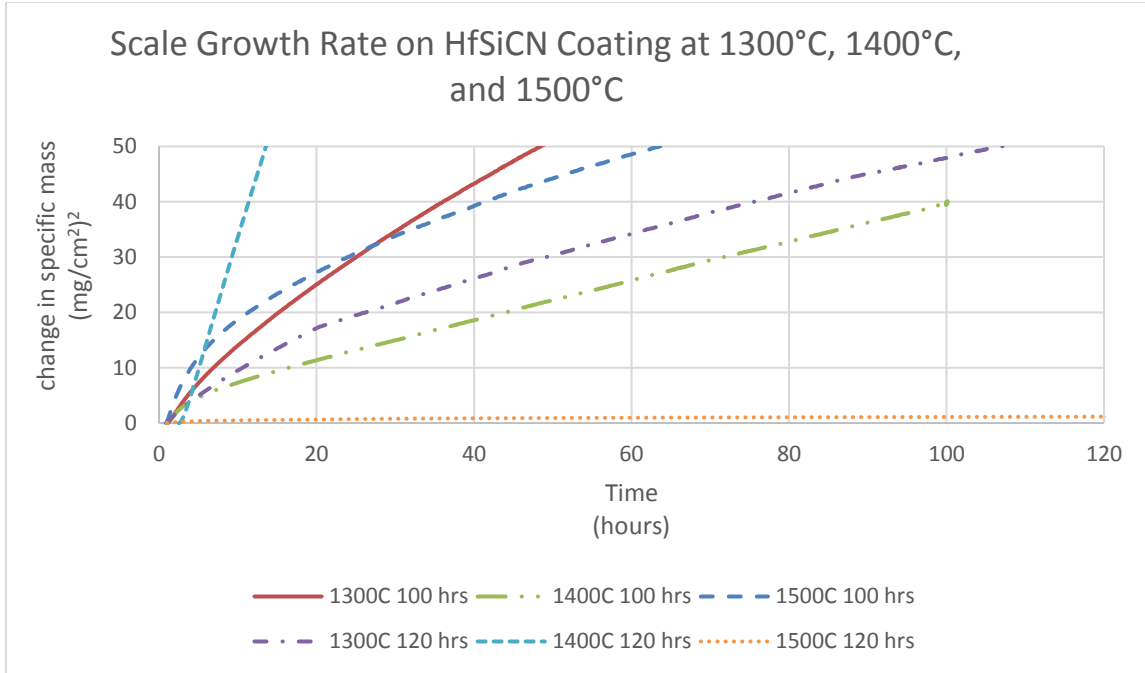
Figure 1. The HfSiCN coating oxidation weight gain squared vs. time. The standard form of a parabolic rate law is $\Delta w^2 = k_p \times t + C$, where Δw is specific weight gain, k_p is parabolic rate constant, C is a constant. As can be seen from the parabolic rate law relation, when the change in specific mass is squared, the graph is linear, and therefore the slope can be treated as an approximation of k_p for the coating system.

In Figure 2, data from the 1300°C pre-oxidized sample was plotted alongside data from the 1400°C and 1500°C 100 hour test samples. The activation energy can be estimated, as show from Equations (1a), (1b) and (2) below:

$$k_p = A \cdot exp(-\frac{Q}{RT}) \tag{1a}$$

where A is the pre-exponential factor, Q is the activation energy, R is gas constant. Take the natural logarithm of both sides of Equation (1a),

$$\ln kp = \ln(A) - \frac{Q}{R} \cdot T \tag{1b}$$

where the slope is $-\frac{Q}{R} = -1723.5$, thus the activation energy is

$$Q = -1723.5 \times -1 \times 8.314 \frac{J}{mol\ K} = 14,300\ J/mol = 14.3\ kJ/mol$$
$$(2)$$

This estimation is considered to be extremely rough in that it is only based on a small number of test data points and that those data points were produced by samples tested under varying conditions.
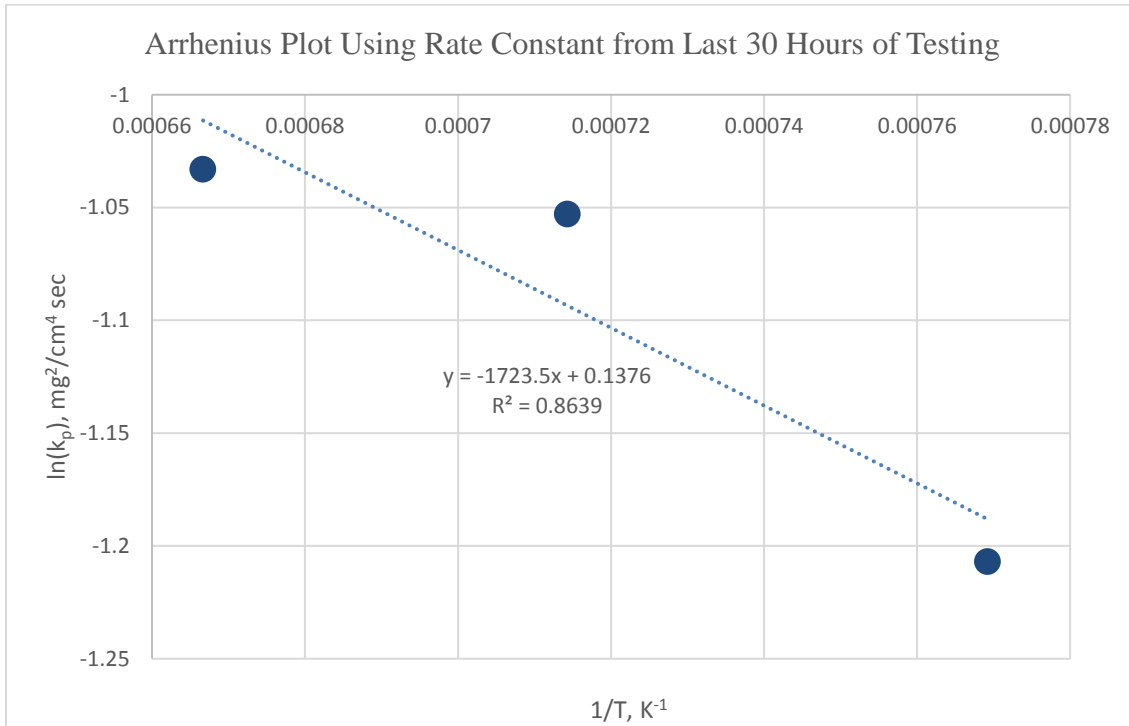

Figure 2. Arrhenius plot of $\ln(k_p)$ versus inverse temperature (1/T) for HfSiCN oxidation. The fitted line has a slope -1723,5 mg^2/cm^4sec-K

3.2 X-ray analysis

XRD analysis conducted on the samples from the first round of testing revealed differences in scale compositions between the samples tested at different temperatures. The X-ray phase analyses for the phase fractions after the oxidation are shown in Figure 3, and results are also summarized in Table 1. Hafnia (silicon doped) is considered chemically and thermally more stable than silica. In addition, hafnon ($HfSiO_4$) is known to have a low oxygen diffusivity, which makes it a more protective oxide scale component [7]. Based on this information, the ratio of hafnia to silica present in each sample by weight percent was used to evaluate the stability of the oxide layers that formed. The sample tested at 1400°C

had the highest ratio of hafnia to silica, suggesting that the coating material has a higher stability at this temperature.
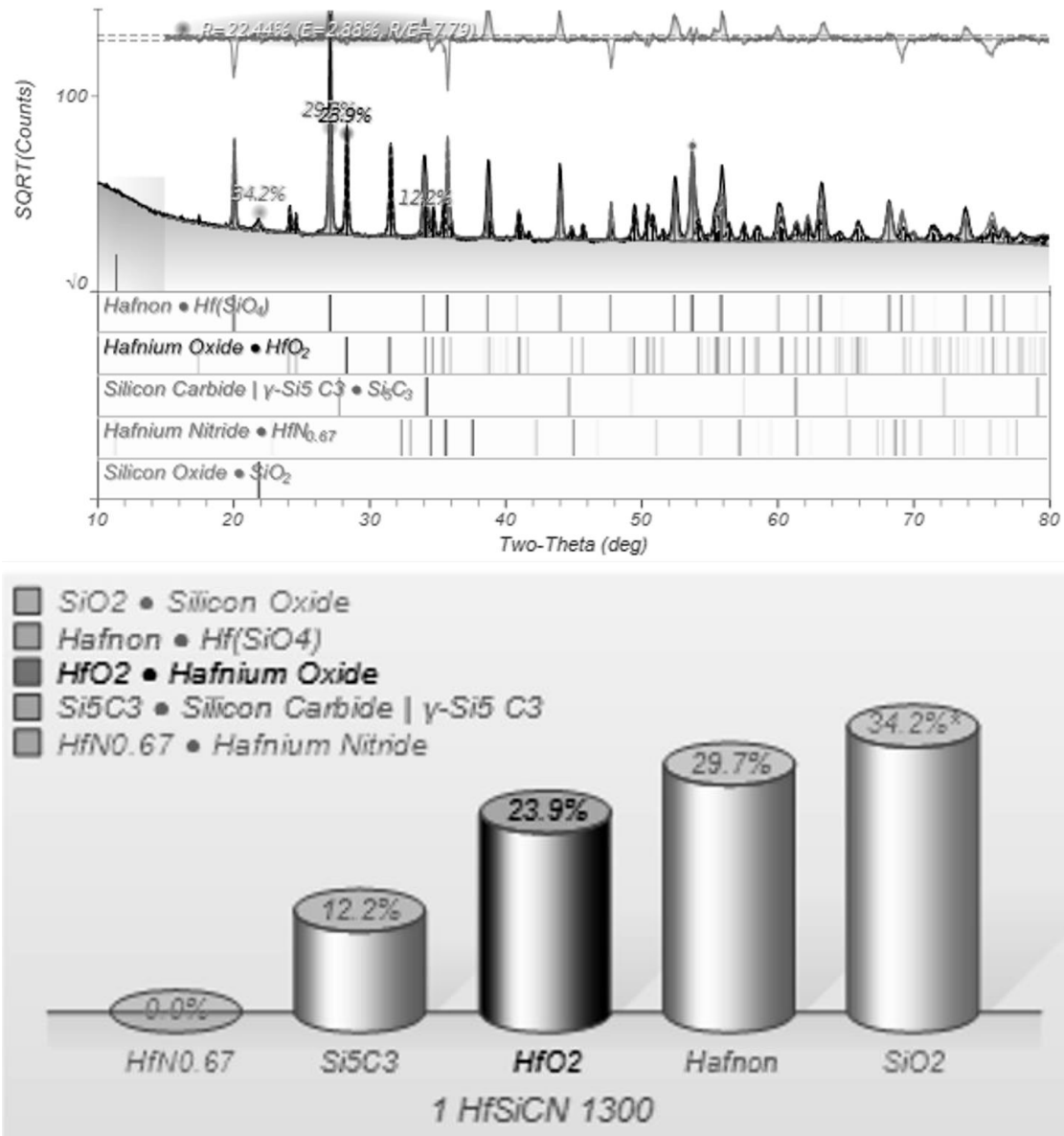
(a) 1300°C

Figure 3. X-ray diffraction spectra and analysis for phase fractions on oxide scales for HfSiCN coating oxidation at various temperatures. (a) 1300°C; (b) 1400°C; (c) 1500°C.
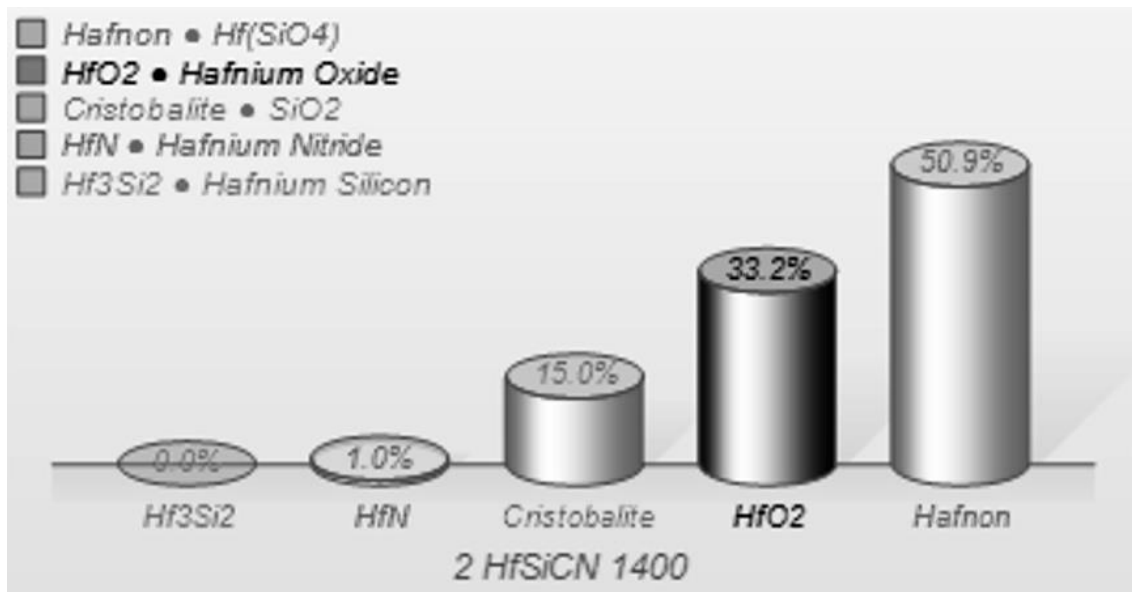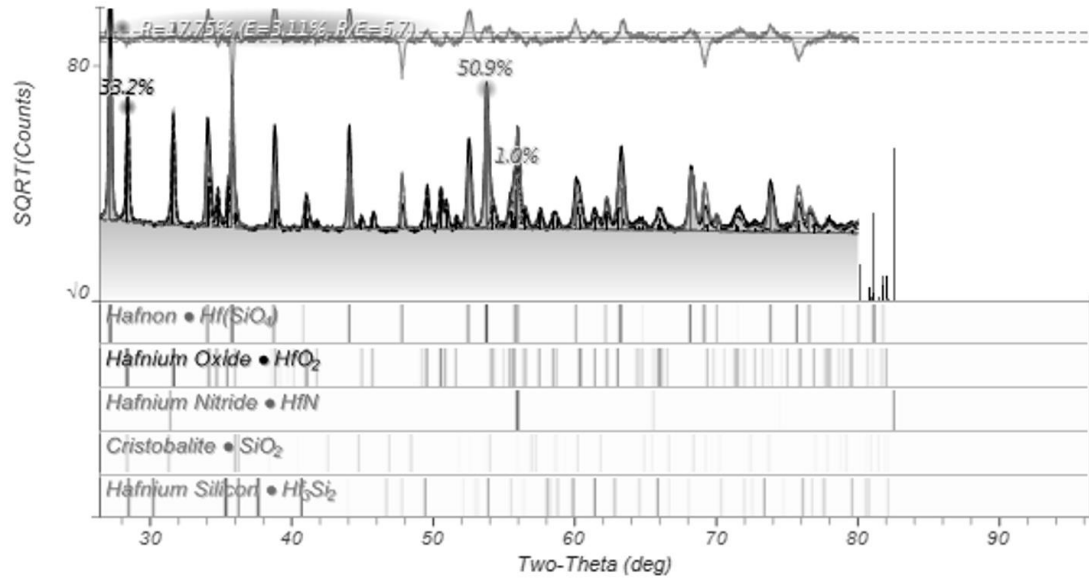
(b) 1400°C

Figure 3. X-ray diffraction spectra and analysis for phase fractions on oxide scales for HfSiCN coating oxidation at various temperatures. (a) 1300°C; (b) 1400°C; (c) 1500°C (Continued).

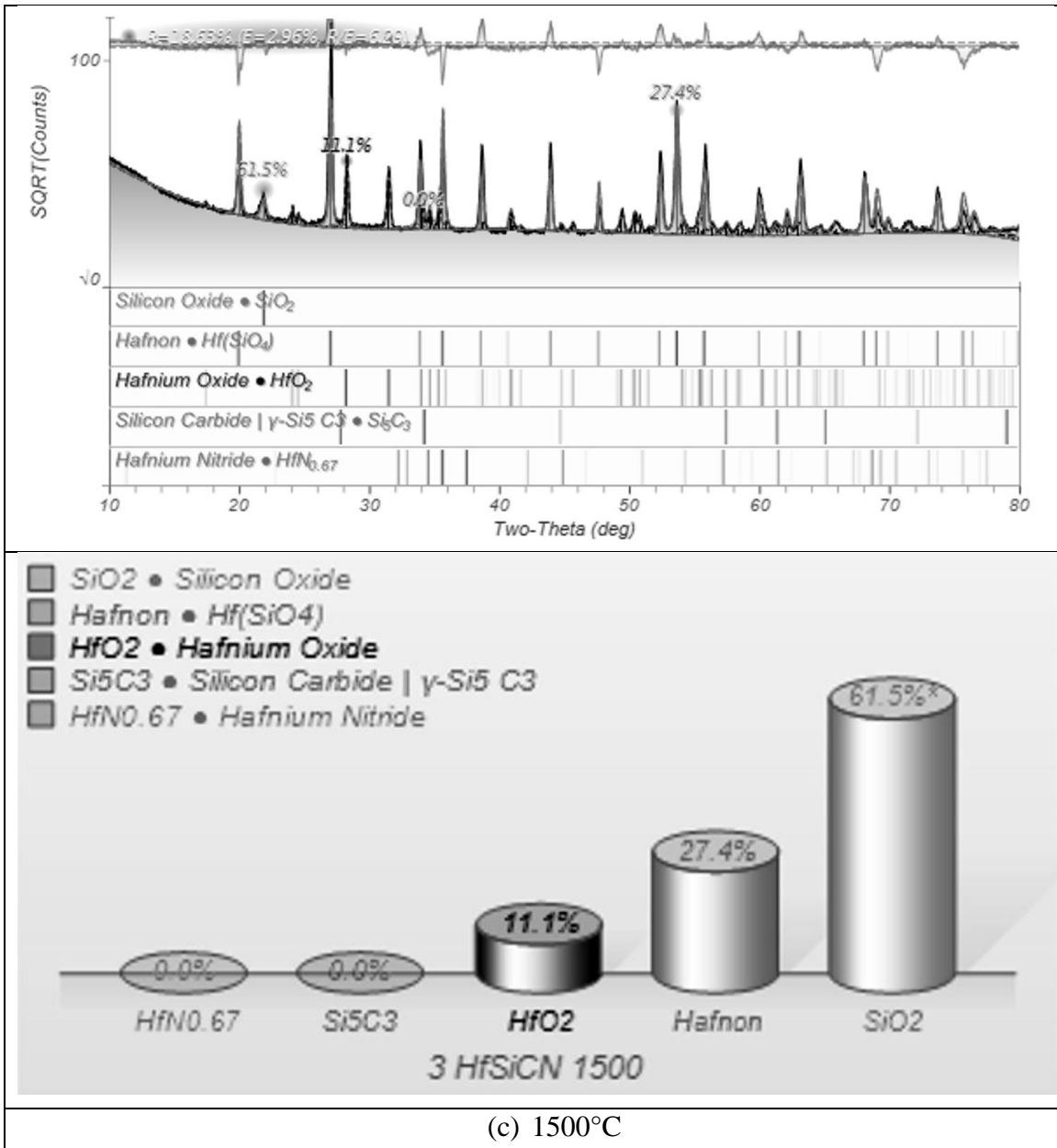Figure 3. X-ray diffraction spectra and analysis for phase fractions on oxide scales for HfSiCN coating oxidation at various temperatures. (a) 1300°C; (b) 1400°C; (c) 1500°C (Continued).

Table 1. XRD Phase Analysis of Samples Tested at 1300°C, 1400°C, and 1500°C for 100 hours, in flowing Oxygen

1300°C		1400°C		1500°C	
Phase Chemical Formula	Weight Percent	Phase Chemical Formula	Weight Percent	Phase Chemical Formula	Weight Percent
$Hf(SiO_4)$	29.7	$Hf(SiO_4)$	50.9	$Hf(SiO_4)$	27.4
SiO_2	34.2	SiO_2	15.0	SiO_2	61.5
HfO_2	23.9	HfO_2	33.2	HfO_2	11.1
Si_5C_3	12.2	HfN	1.0		

3.3 Optical and Microscopic Analysis

After TGA testing, all of the samples showed spalling, as shown in Figure 4. The samples that were tested at a lower temperature had worse spalling that those tested at higher temperatures, which supports the hypothesis that at a lower temperature, continuous, strong protective scales are slower to form. Images from SEM analysis showed the beginnings of spallation at a magnification of 500x (Figure 5). In addition to spalling, SEM analysis also showed differences in the two sides of the sample. On each sample, the 'smooth' side had better fine spherical grains, while the 'rough' side showed parallel linear shaped morphologies that are possibly a result of the more porous or detached SiC fibers underneath the coating. The EDS analysis showed that there was less carbon and nitrogen present on the rough side, which implies that the differences in texture might have caused different oxidation rates, and higher amounts of material recession on the rough side as gaseous oxides formed.

Figure 4. Photo images of oxidation tested specimens. (a) A pristine sample. (b) Sample tested for 100 hours at 1300° C. (Note that coating loss on the sides of the sample is due to handling after the test). (c) Sample tested at 1400°C for 100 hours. (d): Sample tested at 1500°C for 100 hours. The images illustrate the different amounts of spalling that occurred on the surface of samples tested at different temperatures. Even after taking into account the damage that was cause by handling, the sample tested at 1300°C had the worst spallation, followed by the sample tested at 1400°C. The sample tested at 1500°C had relatively little spalling.
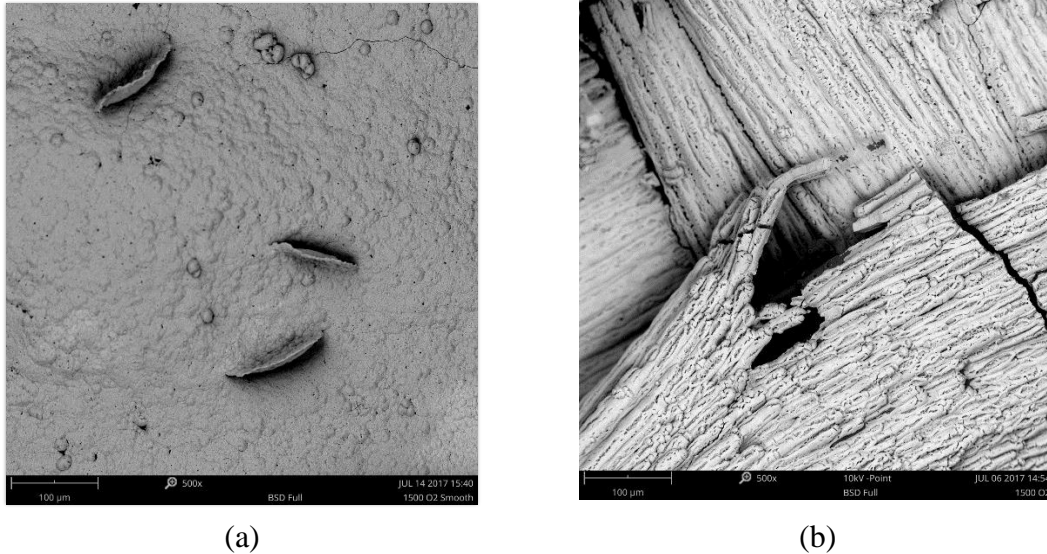
| (a) | (b) |

Figure 5. Scanning Electron Microscope (SEM) images of a 1500°C oxidation tested specimen. Image (a) shows the 'smooth' side of the sample tested at 1500°C for 100 hours, while image (b) shows the 'rough' side of the same sample. One can note the difference in grain texture, as well as the beginnings of spallation on the 'smooth' side.

It is important to discuss possible error in the EDS system, as it is not always the most accurate method for composition analysis, particularly for light elements such as carbon and nitrogen. The EDS system counted larger than expected atomic percent of silicon even when directed at hafnia grains, which may be due to the fact that EDS emissions penetrate the surface of the sample, and may have been incorporating the silicon present in the substrate below the scales. Finally, while it is believable that boron detected by the EDS system could have escaped from the CMC (boron is used in the processing of the CMC), the atomic percent estimated by the system is not. This could be another effect of the EDS recording composition below the surface, or error cause by a flaw in the calibration of the system and a lack of standard available for comparison. To get better data, it will be necessary to conduct other spectrometry tests that measure only on-surface composition, perhaps using an Auger or X-ray Photoelectron Spectroscopy (XPS) system, and using a quantitative Wavelength Dispersive Spectroscopy (WDS) system where better peak resolutions can be obtained and also with composition standards and calibrations.

4. CONCLUSION

A series of TGA tests were conducted to study the oxidation kinetics of a composition series of HfSiCN ceramic coating systems on C_f/SiC CMCs. Results showed that the reactions follow an approximate parabolic rate law, where the reaction rate is initially more rapid and then slows down, when more protective oxide scales form and

reduce further diffusion fluxes of oxygen and metal hafnium and silicon through the coating scales. Samples tested at lower temperatures showed greater recession and spalling because, at lower temperatures, the formation of the more protective oxide scales was slower. Data collected from these tests was used to estimate the activation energy of the oxidation reaction (approximately 14.3 kJ/mol). However, a higher activation energy is possible when considering possible scale volatility at 1500°C. SEM, EDS, and XRD analyses were also done after the TGA testing to characterize the coatings' microstructures and collect data on the composition of the oxide scale phases. The SEM/EDS system revealed recession as constituents of the coating formed gaseous oxides, as well as the spalling of the mechanically weaker oxide scales. XRD analysis showed that the samples tested at 1400°C had the most favorable ratio of hafnia to silica scales, which, along with the steadier reaction rate of samples tested at this condition, suggests that the material is able to maintain stability at this temperature.

Further testing could be conducted using methods of spectroscopy more accurate than EDS to characterize the oxide scale composition. In addition, identical TGA tests should be conducted to improve the statistical integrity of calculated reaction constants and activation energies.

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