



High temperature monitoring of silicon carbide ceramics by confocal energy dispersive X-ray fluorescence spectrometry



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ABSTRACT

In the present work, we presented an alternative method for monitoring of the oxidation situation of silicon carbide (SiC) ceramics at various high temperatures in air by measuring the Compton-to-Rayleigh intensity ratios (I_{Co}/I_{Ra}) and effective atomic numbers (Z_{eff}) of SiC ceramics with the confocal energy dispersive X-ray fluorescence (EDXRF) spectrometer. A calibration curve of the relationship between I_{Co}/I_{Ra} and Z_{eff} was established by using a set of 8 SiC calibration samples. The sensitivity of this approach is so high that it can be easily distinguished samples of Z_{eff} differing from each other by only 0.01. The linear relationship between the variation of Z_{eff} and the variations of contents of C, Si and O of SiC ceramics were found, and the corresponding calculation model of the relationship between the ΔZ and the ΔC_C , ΔC_{Si} , and ΔC_O were established. The variation of contents of components of the tested SiC ceramics after oxidation at high temperature was quantitatively calculated based on the model. It was shown that the results of contents of carbon, silicon and oxygen obtained by this method were in good agreement with the results obtained by XPS, giving values of relative deviation less than 1%. It was concluded that the practicality of this proposed method for monitoring of the oxidation situation of SiC ceramics at high temperatures was acceptable.

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1. Introduction

SiC ceramics have many excellent properties, such as high strength, high hardness, high corrosion and wear resistant and so on. Thus, SiC ceramics are widely used in many fields, like mechanical manufacturing, metallurgy, chemical engineering, electronics, and nuclear structural, and so on [1–7]. In extreme environments, especially under the conditions of high temperature and high oxygen concentration, silicon carbide ceramic is oxidized to form a surface oxide (SiO_2) layer. Thus, the various properties of silicon carbide ceramic, such as mechanical properties and thermal properties are changed, and can finally lead to component failures. To prevent the active/passive oxidation of SiC ceramics one should gain an in-depth and comprehensive understanding of the processes proceeding during the silicon carbide oxidation. Therefore, it is of great significance for material science to develop a rapid detection method with high sensitivity for detecting the variation

of contents of components (e.g., carbon, oxygen, and silicon) of SiC ceramics.

Energy dispersive X-ray fluorescence (EDXRF) is a well-established multi-element and nondestructive analytical technique and is widely reported in the literature for the qualitative and/or quantitative determination of trace, minor, and major elements in a large variety of matrices [8–11]. The quantitative determination of trace or ultra-trace levels of higher-Z elements in samples is difficult, due to the low-Z “dark matrix”, which enhances the matrix absorption effects and gives rise to a high spectral background [12–15]. Furthermore, the determination of low-Z elements by conventional XRF is an even more difficult task and is sometimes even impossible (e.g., hydrogen). Especially for EDXRF, some of the problems and challenges are involved in measuring light elements, because of the low fluorescence yields of the characteristic analytical X-ray lines, strong absorption of the fluorescent radiation in the beam pathway and sample matrix as well as in the spectrometer components, and the low efficiency of the detector [16]. Total reflection X-ray fluorescence has a better potential and is more sensitive for the determination of low-Z elements than EDXRF [16,17], but it involves sophisticated instrumentation, like synchrotron radiation [18] or a vacuum chamber

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[19,20]. In these cases, to achieve a satisfactory signal-to-noise ratio, the irradiation times must be long, but even then they usually have a low precision and low accuracy.

In an XRF spectrum, not only can the characteristic fluorescent lines be seen, but also the Rayleigh and Compton scattered lines can also found together. These two scattering modes are always considered as a drawback, except in cases when they are used to correct for the matrix effects [21,22]. Nonetheless, when determining the content of low-Z elements in materials, the use of scattered radiation could be advantageous. The total mass absorption coefficient consists of two parts of the mass scattering coefficient and photoelectric coefficient. For low-Z elements, the mass scattering coefficient becomes increasingly larger part of the total mass absorption coefficient. Because the total mass absorption also decreases with decreasing Z, the photoelectric coefficient will become very small, which is, of course, one of the problems with XRF. Therefore, scattering intensity has a sensitive change with the variation of contents of light elements in the scatterer, and scatter regions may yield more information for the quantitative analysis of low-Z elements. Even compounds without any characteristic X-ray fluorescent lines can still be extracted and exploited to complete the results of the analyses [23–25]. In particular, Dwiggins proposed a method for utilizing the intensity ratio of coherent to incoherent scattering of X-rays to determine hydrogen and carbon in hydrocarbons, petroleum, and in a matrix containing additional elements [23]. This method shows a high precision and accuracy in the determination of low-Z elements. It relies on the fact that both coherent (or Rayleigh) and incoherent (or Compton) scattered peak intensities are sensitive functions of sample matrix compositions; in particular, samples with high contents of low-Z elements provide very intense scattering processes.

It has long been known that very low-Z elements produce more Compton scattering, while elements with higher-Z produce a larger proportion of Rayleigh scattering. Therefore, the Compton-to-Rayleigh intensity ratio (I_{Co}/I_{Ra}) should be sensitive to small changes in the composition of samples. The I_{Co}/I_{Ra} is not directly dependent on the physical density of materials, but dependent on Z. For a compound matrix (of light elements), the concept of effective atomic number (Z_{eff}) can be employed to replace the compound by a single analogous element with the same impact upon the scattering line intensities. The Z_{eff} helps to visualize many physical characteristics of a sample with a single number, and has been efficiently employed for the analysis of liquids, biological samples, powders, and polymers, where the non-measuring unknown elements could not be easily analyzed by conventional XRF technique. The Z_{eff} is an intrinsic characteristic of each compound, and due to this unique advantage, a large number of literatures have reported the measuring of Z_{eff} of samples [26–30].

In the present work, we presented an alternative method of measuring the Compton-to-Rayleigh intensity ratios and effective atomic numbers of the scatters against Mo-K α line to quantitative analyses of the variation of contents of components of SiC ceramics after oxidation at various high temperatures in air by employing a confocal EDXRF spectrometer.

2. Experimental procedure

2.1. Theoretical basis of X-ray scattering

In this subsection, a short overview is presented of the fundamental parameter equations. The general expressions of primary Rayleigh-scattered radiation (I_{Ra}) and the Compton-scattered radiation (I_{Co}) can be written, respectively, as:

$$I_{Ra} = I_0 k \frac{d\sigma_{Ra}}{d\Omega} \frac{1 - \exp[-\rho d \mu(E_0)(csc \theta_1 + csc \theta_2)]}{\mu(E_0)(csc \theta_1 + csc \theta_2)} \quad (1)$$

$$I_{Co} = I_0 k \frac{d\sigma_{Co}}{d\Omega} \frac{1 - \exp[-\rho d (\mu(E_0)csc \theta_1 + \mu(E_{Co})csc \theta_2)]}{\mu(E_0)csc \theta_1 + \mu(E_{Co})csc \theta_2} \quad (2)$$

where I_0 is the primary X-ray beam intensity, and k is a constant corresponding to the given geometric parameters of the confocal instrument and the detector efficiency. θ_1 and θ_2 , respectively corresponding to the incident angle of primary beam and the exit angle of scattered radiation. $\frac{d\sigma_{Ra}}{d\Omega}$ and $\frac{d\sigma_{Co}}{d\Omega}$, respectively corresponding to the Rayleigh differential scattering cross-section and Compton differential scattering cross-section. $\mu(E_0)$ and $\mu(E_{Co})$ respectively corresponding to the mass absorption coefficient at energy E_0 and E_{Co} . The relationship between E_0 and E_{Co} is the well-known Compton kinematic equation:

$$E_{Co} = \frac{E_0}{1 + (E_0/m_0c^2)[1 - \cos(\theta_1 + \theta_2)]} \quad (3)$$

Based on Eqs. (1) and (2), the I_{Co}/I_{Ra} has the following form:

$$\frac{I_{Co}}{I_{Ra}} = \frac{\frac{d\sigma_{Co}}{d\Omega} \frac{1 - \exp[-\rho d (\mu(E_0)csc \theta_1 + \mu(E_{Co})csc \theta_2)]}{\mu(E_0)csc \theta_1 + \mu(E_{Co})csc \theta_2}}{\frac{d\sigma_{Ra}}{d\Omega} \frac{1 - \exp[-\rho d \mu(E_0)(csc \theta_1 + csc \theta_2)]}{\mu(E_0)(csc \theta_1 + csc \theta_2)}} \quad (4)$$

When choosing available primary X-ray beam E_0 and scattering angle θ , the mass attenuation coefficients, $\mu(E_0)$ and $\mu(E_{Co})$, are roughly equal, which can be validated from the XCOM database [31]. Therefore, the I_{Co}/I_{Ra} is given by:

$$\frac{I_{Co}}{I_{Ra}} = \frac{d\sigma_{Co}}{d\Omega} / \frac{d\sigma_{Ra}}{d\Omega} \quad (5)$$

The differential scattering cross-sections for Rayleigh and Compton scattering are [32]:

$$\frac{d\sigma_{Ra}}{d\Omega} = \frac{d\sigma_T}{d\Omega} F^2(\chi, Z) \quad (6)$$

$$\frac{d\sigma_{Co}}{d\Omega} = \frac{d\sigma_{KN}}{d\Omega} S(\chi, Z) \quad (7)$$

where $\frac{d\sigma_T}{d\Omega}$ and $\frac{d\sigma_{KN}}{d\Omega}$ are the Thomson and Klein–Nishina cross sections, respectively. $F(\chi, Z)$ constitutes the scatter form factor of element Z, and $S(\chi, Z)$ is the incoherent scattering function. χ is the momentum transfer and is related to the scatter angle θ and E_0 by:

$$\chi = \frac{E_0}{hc} \sin\left(\frac{\theta}{2}\right) \quad (8)$$

where h and c are the Planck's constant and the speed of light in a vacuum, respectively. For compounds, they contain various elements, and thus, Eqs. (6) and (7), can be written, respectively, as:

$$\frac{d\sigma_{Ra}}{d\Omega} = \frac{d\sigma_T}{d\Omega} \sum_{i=1}^n a_i^{at} F^2(\chi, Z_i) \quad (9)$$

$$\frac{d\sigma_{Co}}{d\Omega} = \frac{d\sigma_{KN}}{d\Omega} \sum_{i=1}^n a_i^{at} S(\chi, Z_i) \quad (10)$$

where a_i^{at} is the atom percentage of the i th element. Therefore, the I_{Co}/I_{Ra} can be expressed as:

$$\frac{I_{Co}}{I_{Ra}} = \frac{d\sigma_{Co}}{d\Omega} / \frac{d\sigma_{Ra}}{d\Omega} = \frac{\frac{d\sigma_{KN}}{d\Omega} \sum_{i=1}^n a_i^{at} S(\chi, Z_i)}{\frac{d\sigma_T}{d\Omega} \sum_{i=1}^n a_i^{at} F^2(\chi, Z_i)} \quad (11)$$

If substituting a compound matrix by a single element of Z_{eff} , then, Eq. (11) can be simplified as the following form:

$$\begin{aligned} \frac{I_{Co}}{I_{Ra}} &= \frac{d\sigma_{Co}}{d\Omega} / \frac{d\sigma_{Ra}}{d\Omega} = \frac{\frac{d\sigma_{KN}}{d\Omega} \sum_{i=1}^n a_i^{at} S(\chi, Z_i)}{\frac{d\sigma_T}{d\Omega} \sum_{i=1}^n a_i^{at} F^2(\chi, Z_i)} \\ &= \frac{\frac{d\sigma_{KN}}{d\Omega} S(\chi, Z_{eff})}{\frac{d\sigma_T}{d\Omega} F^2(\chi, Z_{eff})} \end{aligned} \quad (12)$$

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