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Air and chlorine gas corrosion of different silicon carbides analyzed by nano-Fourier-transform infrared (nano-FTIR) spectroscopy

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ABSTRACT

The present study shows the potential of high-resolution imaging and nano-Fourier-transform infrared (nano-FTIR) spectroscopy for corrosion science. The protective oxidation layers of different chlorine-gas treated silicon carbides (SiCs) were characterized with these techniques. A nitrified SiC showed the highest resistant strength against chlorine corrosion at 1000 °C compared to the other SiCs. Nano-FTIR spectroscopy with a lateral resolution below 40 nm detected differences in the crystallinity of the bulk-SiC and in the transitional region to the protective layer. Furthermore, high-resolution imaging provides deep insight in the interfacial layer between bulk-SiC and the protective oxidation layer on sub-micrometer scale.

1. Introduction

Previously, we developed a thermochemical process using chlorine-donors [1–3] at approx. 1000 °C to separate toxic heavy metals from sewage sludge ash (SSA) and to increase the plant-availability of phosphorus (P) in the SSA in order to produce P-based fertilizers.

Because of the oxidative corrosive atmosphere (chlorine and/or hydrochloric acid gas in air) in the thermochemical process and abrasive properties of the SSA an appropriate construction material is required to perform this process in a rotary kiln at a temperature of approx. 1000 °C. A potentially suitable material is silicon carbide (SiC). Silicon-based ceramics, including SiC and silicon nitride (Si_3N_4) have many applications in high-temperature technologies because of their high-temperature stability and oxidation resistance [4–6]. The oxidation resistance of these materials is due to the formation of a protective oxidation film composed of silicon oxide (SiO_2). This limits the access of oxygen/chlorine to the carbide or nitride. Consequently, investigations on the corrosion resistance of different types of SiC materials were carried out.

This article focuses on the analysis of the protection layer of different SiCs by nano-Fourier-transform infrared (nano-FTIR) spectroscopy. Nano-FTIR spectroscopy [7–11] is performed on an apertureless scanning near-field optical microscope (SNOM). This technique overcomes the diffraction limit by scattering incident light on the tip of an atomic force microscope (AFM) scanning in nanometer proximity to the sample surface. Thereby the AFM is operated in the tapping mode at the mechanical resonance frequency Ω of the cantilever. The exponential dependence of the near-field signal on the tip-surface distance causes the corresponding detector signal to be modulated at higher harmonics of Ω. Demodulation at higher harmonics thus allows the separation of the weak near-field signal from the intensive far-field background contribution. A lateral spatial resolution below 40 nm limited by the tip apex can be obtained in the mid-infrared region (4000–700 cm^{-1}).

The nano-FTIR experiments were performed at the low-energy electron storage ring Metrology Light Source (MLS) [12] enabling the use of ultra-broadband synchrotron radiation at the IR beamline as well as tunable CO_2 laser sources. The use of synchrotron radiation (SR) allows the acquisition of IR spectroscopic information over a wide spectral range while the tunable monochromatic sources enable imaging of the material distribution [9,13,14] (see schematic in Fig. 1). In this article we show the potential of this approach for the characterization of corrosion of materials.

2. Materials and methods

2.1. Materials

Different types of SiC (C-SiC, Si-SiC and N-SiC; Schunk Kohlenstofftechnik GmbH, Heuchelheim, Germany) were used for the thermochemical experiments. The N-SiC was different from the other

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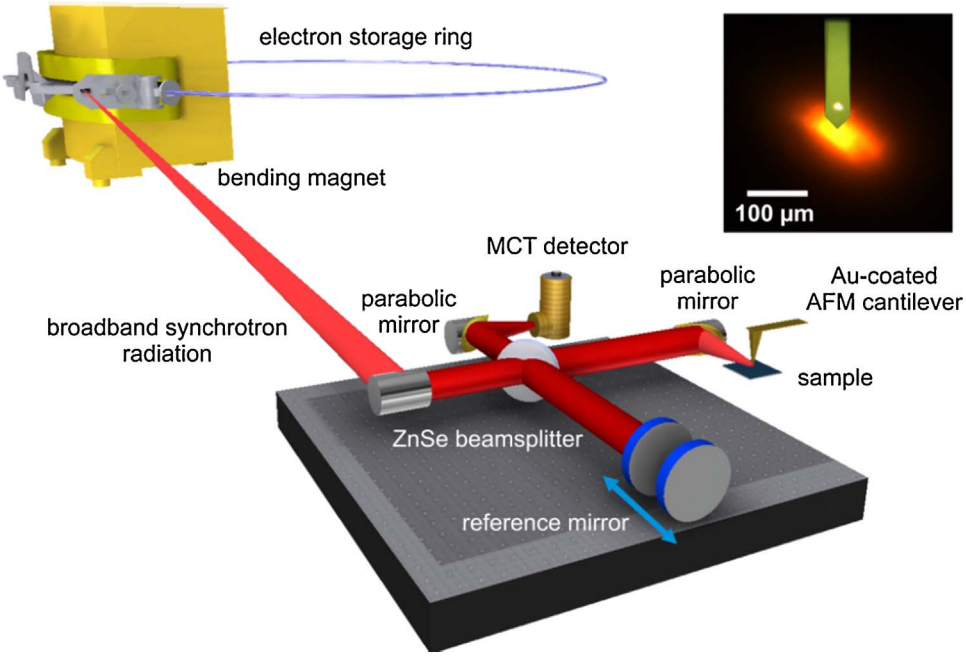

Fig. 1. Schematic diagram of the experimental s-SNOM setup using broadband synchrotron radiation in the IR regime from the electron storage ring MLS, from [13].

SiCs because it contained in addition to 65% SiC also 27% Si_3O_4/Si_2ON_2 and some oxides [15].

The thermochemical treatments of the SiCs were carried out using a quartz glass reactor in a gastight lab-scale rotary furnace (Carbolite HTR 11/150, Ubstadt-Weiher, Germany). For all experiments sticks of SiC samples (45 × 4 x 3 mm^3) were added to an amount of 100 g SSA. The used SSA contained approx. 21% SiO_2 (quartz), 16% Fe_2O_3 (hematite), 16% CaO and 21% P_2O_5 (mainly as whitlockite), 11% Al_2O_3, 3% MgO, 1% Na_2O and 1% K_2O [16] with a grain size of < 400 µm. Afterwards the SSA was heated to 1000 °C with a rate of 20 K/min. This temperature was held stable for 168 h. The quartz glass reactor was continuously moved during thermal treatment (alternating rotation of 315° in both directions). Every 12 h the glass reactor was flushed with an air/chlorine gas mixture composed of 10% and 50% Cl_2, to completely renew the gas atmosphere in the reactor (volume of flushing several times higher than volume of reactor). The SiC samples were weighted before and after treatment.

After the thermochemical experiments the SiC sticks were cut into pieces and parts of it embedded into high purity epoxy resin. These samples were ground down to a height of approx. 5 mm and the surface polished with a 1 µm diamond polishing paste.

2.2. Near-field infrared nanospectroscopy

The measurements described in the following were performed on a commercial scattering-type scanning near-field optical microscope (s-SNOM) (Neaspec GmbH, Germany). It consists of an AFM which was operated in tapping mode and an asymmetric Michelson interferometer with optical components adapted for the mid-IR range. For the near-field measurements on the various SiC samples Au-coated Si-probes with a resonance frequency in the range between 76 kHz and 263 kHz and a typical tip diameter of less than 50 nm were used. The tapping amplitude was set to around 80 nm. The experiments were performed at the IR beamline of the MLS [17]. In the standard operation mode the MLS is operated with 80 electron bunches providing a pulse repletion rate of 500 MHz and a bunch length of 25 ps. The ring current decays during the measurements from 200 mA to 85 mA with a lifetime of 6 h. The IR radiation is coupled out from the storage ring at a bending magnet. A set of diamond windows at the end of the beamline separates the ultra-high vacuum from the ambient conditions under which the s-SNOM system was operated. A periscope-like mirror arrangement aligns the linear polarization of the SR along the tip axis thus providing a strong field-enhancement around the tip apex of the near-field probe. The incident radiation power at a ring current of 100 mA was approx. 2 mW in the mid-IR range. The light backscattered from probe and sample is collected by a parabolic mirror and was analyzed by the asymmetric Michelson interferometer (Fig. 1). One arm contains the planar reference mirror which can be translated over a distance of up to 1500 µm. This corresponds to a spectral resolution of about 3 cm^{-1}. The other arm contains near-field probe and sample. The IR radiation is focused onto the tip and sample by a parabolic mirror under an angle of about 65° thus providing a focal spot with a diameter of about 80 µm.

For recording near-field spectroscopic data the planar mirror in the reference arm of the Michelson interferometer was moved over a distance of 800 µm at each measurement point. The recorded interferogram was obtained as a superposition of the sample and the reference beam. The resulting signal was detected by a liquid nitrogen cooled Mercury-Cadmium-Telluride (MCT) detector (Teledyne Judson Technologies, United States) with a sensitivity range from about 2 µm to 13.5 µm corresponding to wavenumber range from 740 cm^{-1} to 5000 cm^{-1}.

For near-field imaging at a specific excitation wavelength a monochromatic light source is required. As a corresponding IR radiation source, a continuous wave, grating-tuned CO_2 gas laser (PL5, Edinburgh Instruments, UK) was used.

3. Results and discussion

3.1. Thermochemical treatment of SiCs with chlorine gas

Table 1 shows the mass changes of the different types of SiC samples

Table 1
Mass change of various SiC samples during abrasive thermochemical treatment with 10% and 50% chlorine gas at 1000 °C.

	Relative mass change with 10% Cl	Relative mass change with 50% Cl
N-SiC	+1.3% ± 0.1%	−34.0% ± 2.2%
C-SiC	−1.9% ± 0.8%	−100.0%
Si-SiC	−3.0% ± 0.2%	−100.0%