Identification of silicon oxycarbide bonding in Si-C-O-glasses by EELS

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The formation of silicon oxycarbides, i.e. SiO\textsubscript{x}C\textsubscript{y} compounds, is being indicated in a number of materials: For example, in the high-performance Nicalon® fibres, an incomplete transformation of the polymeric precursor is supposed to generate some amount of oxycarbide by “remembering” the C-Si-O bond-complex of the initial precursor [1]. Within the interlayer system of Nicalon® fiber reinforced glass matrix composites indications of SiO\textsubscript{x}C\textsubscript{y} have been found by several authors [2–6]. Here, the occurrence of SiO\textsubscript{x}C\textsubscript{y} is the result of almost complex oxidation processes of the fibers. Furthermore, oxycarbides have formed in amorphous and oxygen-rich grain boundaries of sintered SiC powders [7] and, particularly, in novel compact glasses containing Si, C, O produced via the pyrolysis of polycarbosiloxanes or similar preceramic precursors at temperatures around 1000 °C. At higher temperatures, however, these materials usually crystallize as a mixture of SiC and SiO\textsubscript{2} [8–11]. In all these examples, the existence of silicon oxycarbides, their structure and composition influence the materials properties. Hence, they are important tools for the effective microstructural tailoring of these materials.

In all the references given the presence of SiO\textsubscript{x}C\textsubscript{y} has been deduced most straightforwardly via X-ray photoelectron spectroscopy (XPS). In [1] the energy of the Si-2p core level of the SiO\textsubscript{x}C\textsubscript{y} component indicates an atomic charge of the silicon atom (influenced by its bonding partners), which is intermediate between those of silicon in SiC and SiO\textsubscript{2}.

Likewise, electron energy loss spectroscopy (EELS) yields information on the chemical bonding state of the elements of interest by analyzing the near edge structure (ELNES) up to about 20 eV above the onset which can be attributed to transitions of core-shell electrons into unoccupied states above the Fermi level. For glasses containing Si, C, O, the spectra usually seem to be more or less similar to those of a mixture of SiC and SiO\textsubscript{2} (cf. spectrum (III) in Fig. 2), depending on the composition of the materials. In particular, a non-ambiguous correlation between the measured spectra and appropriate quantum-mechanical calculations is still missing. First approaches made in [7] and [11] show that the partial density of unoccupied states is being shifted according to the electronegativity of the bonding partners of silicon.

The present study is a contribution to the detection of silicon oxycarbide specific details in the ELNES of the Si-L\textsubscript{2,3}-edge, where polymethylsiloxane (CH\textsubscript{3}SiO\textsubscript{1.5}) pyrolyzed at 1000 °C to form a glassy sample is used as a model system.
correlation effects the degeneration of the Si-2p levels is partly cancelled and therefore split into some levels with energy differences up to 0.2 eV. These levels shift from ~93.7 eV below the Fermi level (Si-carbide) down to ~95.9 eV (silicon dioxide) with increasing oxygen amounts bonded to the silicon atom. For silicon dioxide and oxy carbide, there are two groups of unoccupied molecular orbitals (MO’s) with s-like (a), d-like (e) and mixed p and d-like symmetry (t). These results are in line with SCF (self consistent field)-Xα-calculations performed in [14]. In addition, note that for tetrahedrally coordinated silicon, transitions are possible following the optical selection rules (p → d*, p → s*) as well as usually forbidden p* ones (parity selection rule) (cf. [15]).

Fig. 2 shows a typical Si-L2,3 edge (background subtracted) measured for the pyrolyzed polymethylsioxane material (spectrum IV) as well as for SiC (spectrum I) and SiO2 standards (spectrum II). At first sight, the spectrum (IV) looks very similar to that of the SiO2 standard (II), comprising of the two distinct peaks at about 108 and 114 eV, related to 2p* transitions, the energy differences in Fig. 1 were calibrated to match the two main peaks of SiO2 by adding 3 eV to each. This was done to compensate possible systematic errors due to the saturation of dangling bonds in the simple clusters used for the DFT calculations with hydrogen atoms, leading to an additional potential influencing the energy position of the calculated eigenvalues. In Fig. 2 the resulting transition energies are inserted as dashed lines, clearly showing that the first two peaks of spectrum (V) (the measured spectrum (IV), with its SiO2 and SiC components subtracted) most probably fit the energy values calculated for the SiO2-C2 cluster, i.e. with silicon atoms bonded to oxygen and carbon as well.

In conclusion, one can say that the EELS results prove the investigated glassy material to contain not only SiO2 and SiC but also a certain amount of O-Si-C units, viz. oxy carbide.

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References

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