

Calorimetry of Si-C-O Polymer Derived Ceramics

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Silicon oxycarbides are one family of a new class of materials that has recently been synthesized and possesses unusual high-temperature properties. These materials, called polymer derived ceramics (PDCs), are prepared by pyrolysis of a polymer and exhibit the following characteristics: (i) they retain their amorphous structure to very high temperatures, (ii) they show very high creep resistance and (iii) despite of the excess carbon they contain, their resistance to oxidation is extremely high. Understanding of the microstructure and energetics of the PDCs is essential for the interpretation of their unusual properties. High-temperature oxidative solution calorimetry in a molten oxide solvent was used to measure the energetics of SiO_xC_y samples as a function of composition and short-range order and/or microstructure. The amorphous SiO_xC_y materials are energetically stable with respect to a mixture of crystalline SiO₂, SiC, and C. There is a strong correlation between the enthalpies of formation of the samples and the C content: the stability increases as the C:O ratio increases. Our calorimetric results provide strong evidence for short-range order and favorable bonding, perhaps at interfaces, and are consistent with the conceptual model that describes the PDCs as nanodomains constructed from silica tetrahedra, which are surrounded by mixed Si-C-O bonds and embedded in a graphene network.