ESRF	**Experiment title: Phase separation in $Si_{1-x}C_{1+x}$ nanocomposites**	**Experiment number**: HS 1606
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Report:

It is well-known fact that a crystalline silicon carbide slightly changes its stoichiometric composition. Recent work on a synthesis of silicon carbide using thermal exfoliated graphite as an initial carbon reagent has demonstrated an existent possibility of a significant substitution of silicon atoms by carbon atoms in the silicon sub-lattice of the silicon carbide crystal structure [1]. This compound has been called SiC-C solid solution. It has been also established that both the structural state of the carbon component in the reagent mixture and non-equilibrium conditions of the combustion reaction between elemental silicon and carbon are responsible for the formation of the SiC-C solid solution. Further results of laboratory high resolution XRD measurements supported by results of solid state NMR spectroscopy pointed to a simultaneous formation of at least two different crystal structures of silicon carbide by the mentioned synthesis [2]. In this ESRF experiment an attempt has been made to resolve diffraction patterns of these silicon carbides to obtain their structural parameters and microstructure characteristics.

Diffraction patterns of 10 samples amongst which three as-synthesised samples and the rest after high-temperature treatments either in vacuum or under high pressure have been recorded using Debye-Scherrer geometry. Internal standard, silicon powder SRM640c, has been admixed to the samples over all experiments to control angular position of silicon carbide diffraction peaks. All samples were composed of silicon carbide phases and few percent of impurity phases such as α-, β-Si_3N_4 and Si_2N_2O. As a result of grinding all samples treated under high pressure were also including impurity of agate mortar (in particular, SiO_2-low quartz) used for their grinding. A pseudo-Voigt function or, where appropriate, two independent pseudo-Voigt functions have been used to fit each diffraction peak relating to the silicon carbide phases. The obtained peak positions have been used for a least-square refinement of the lattice parameters. Other parameters of the fitting functions (full width at half-maximum and mixing factor of a Lorentzian and a Gaussian) have been taken to extract physical broadening of the diffraction peaks (β_f) to carry out Williamson-Hall analysis, in this case parameters of the instrumental resolution function determined in accordance with [3] have been used for the deconvolution.

It has been found that at the lowest temperature possible for an ignition of this synthesis (1473K) only one silicon carbide phase, characterised by a high concentration of stacking faults, is formed (see the Table). Silicon carbide synthesised at a higher temperature (1573K) has a complicated diffraction pattern, which can be successfully decomposed into two patterns relating to two cubic silicon carbide phases, one is similar to standard cubic silicon carbide (SiC) and another is SiC-C solid solution (see the Table). Probably, the presence of superctoichiometric carbon atoms and their distribution in the structure of the SiC-C is the main cause of a higher microstarin parameter evaluated for this phase then for the standard SiC (see both the Table and the Figure). Thus, it has to be expected that a higher concentration of carbon atoms in the structure of synthesised SiC-C should produce a higher amount of microstrains. Indeed, this conclusion is supported by the results obtained for the SiC-C synthesised at the lowest temperature. This SiC-C has the highest concentration of superstoichiometric C atoms (the lowest lattice parameter) and the highest microstrain parameter.

A vacuum annealing of the powder synthesised at 1573K transforms SiC-C solid solution into standard SiC. There is a distinct growth of SiC/SiC-C ratio and an increase of the SiC-C lattice parameter dependent on a temperature of the annealing, however, this process is not accompanied by a significant change of microstructural characteristics (see the Table). On the contrary, the powder treated under high pressure (4GPa, 2073K) demonstrates transformation of SiC into SiC-C solid solution, which is somewhat unexpected result. A significant overlapping area of peaks of silicon carbide phases on diffraction patterns of samples sintered under higher pressures (6GPa and 8GPa) does not allow a decomposition of these peaks to be carried out properly.

Table. Lattice parameters (a), crystallite sizes (D), Williamson-Hall strain parameters (e_{WH}) of cubic silicon carbides (SiC and SiC-C solid solution) and a ratio of their fractions (q = SiC/SiC-C) in the investigated samples.

Sample	SiC			SiC-C solid solution			q
	a, Å	D, Å	$e_{WH}x10^3$	a, Å	D, Å	$e_{WH}x10^3$	
Synthesised at 1473K	-	-	-	4.3511(5)	588(183)	1.2(2)	0
Synthesised at 1573K	4.35890(5)	1211(56)	0.24(1)	4.35342(8)	1602(333)	0.84(4)	0.24(2)
Annealed at 1673K	4.3584(1)	1019(70)	0.24(3)	4.3533(2)	1445(343)	0.73(7)	0.40(4)
Annealed at 1873K	4.3588(1)	1066(54)	0.24(2)	4.3542(2)	1621(217)	0.71(3)	0.55(5)
Annealed at 1973K	4.35941(5)	1213(49)	0.18(2)	4.3553(2)	1766(294)	0.72(4)	0.90(9)
Annealed at 2173K	4.36051(6)	1134(43)	0.13(1)	4.3580(4)	1225(249)	0.85(7)	1.2(2)
Sintered at 4GPa,2073K	4.3551(2)	1357(153)	0.37(3)	4.35235(4)	1569(69)	0.21(1)	0.32(1)

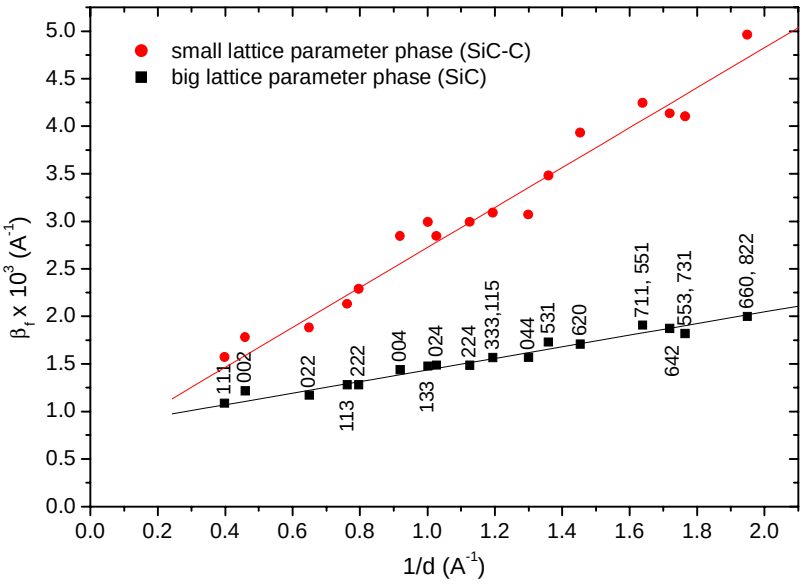

Figure. The Williamson-Hall plot (integral width β_f versus reciprocal d) of silicon carbide phases (SiC-C and SiC) synthesized at 1573 K, hkl indexes presented for reference.

References:

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