THERMODYNAMICAL MODELING OF SILICON CARBIDE SYNTHESIS IN THERMAL PLASMA

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Abstract
The synthesis process of solid SiC in thermal plasma was investigated theoretically by computing the equilibrium composition of the gas mixtures involving silicon and carbon in the presence of argon and hydrogen at various silicon/carbon amounts and at two different total pressures in the system, in the temperature range between 1000 and 6000 K. Use is made of the fact that a thermal plasma, by definition, is a plasma in (local) thermodynamical equilibrium, which makes possible the theoretical determination of its equilibrium composition at definite temperature by employing Gibbs free energy data for the compounds present in the system. From the calculated compositions of the investigated gas systems the temperature-composition phase diagrams were obtained. Using these data the temperature zones with saturated and/or oversaturated vapour of SiC as well as of Si and C were determined and the possibility of the formation of SiC in the solid state via different reaction routes was analyzed.

Keywords: SiC synthesis, thermal plasma, thermodynamics of SiC

Introduction
Silicon carbide (SiC) is a mineral that was first discovered in fragments of the meteorite found at Diablo Canyon in Arizona. It was named Moissanite in honor to its discoverer Nobel Prize winner Henry Moissan. Silicon carbide does not occur naturally; it is produced by high temperature chemical reactions. Commercially, SiC is produced in Acheson furnace [1, 2] where a mixture of high-quality sand and low-sulphur petroleum coke with addition of common salt and sawdust is packed around a graphite core. The mixture is then heated to reach a maximum temperature of approximately 2700°C, after which the temperature is gradually lowered. SiC particles produced in this process are large agglomerates with a wide range of particle sizes. The sintered or hot pressed parts of SiC are usually porous.

Two solid phases of SiC, SiC (β) (cubic 3C diamond-like structure) and SiC (α) (hexagonal) are known but intermediate between cubic and hexagonal are also found in the various polytypes of SiC. Silicon carbide is a very hard material, at Mohs hardness...
scale 9.25 (diamond is 10), and high refractive, with index of refraction of 2.6–2.7 (diamond’s index is slightly lower, 2.42); it has high thermal conductivity (~5 W cm⁻¹ K⁻¹) and is chemically resistant. As semiconductor, that can be operated at temperatures higher than 600°C (silicon devices are limited to operation temperature below 300°C), and in chemically hostile environments, SiC is material of choice for high temperature, high voltage and high frequency applications. Because of these characteristics, different modern techniques have been applied for the synthesis of silicon carbide, for example Chemical Vapour Deposition (CVD) method, where the precursors used for growth of SiC (usually silicon and propane), transported by a carrier gas to a hot zone and decomposed into atoms and radicals, diffuse down onto a (cooled) substrate, producing epitaxial film of SiC [3]. Molecular beam epitaxy [4] method has also been applied to obtain silicon carbide. A very promising method for the synthesis of the high purity ultra-fine powder (in size range 10–100 nm) of silicon carbide is thermal plasma method [5–7]. Reactants as elemental silicon with methane as a source of carbon, are introduced into Ar/H₂ (thermal) plasma [7]; They evaporate and depending on temperature partially dissociate into atoms and ionize producing ions and electrons. The formation of molecules and radicals stable at higher temperatures is also possible. In the plasma zones with lower temperatures, or by rapid cooling (quenching) of this system under controlled conditions, saturated or supersaturated vapor is formed, and the formation of ultra-fine (solid) particles can be achieved.

In this paper the synthesis process of solid SiC in thermal plasma is investigated theoretically by computing the equilibrium composition of the gas mixture involving silicon and carbon in the presence of argon and hydrogen at various silicon/carbon amounts, at different ratios of silicon and carbon amounts, and at two different total pressures in the system, in the temperature range between 1000 and 6000 K. Use is made of the fact that a thermal plasma, by definition, is a plasma in (local) thermodynamical equilibrium, which makes possible the theoretical determination of its equilibrium composition at definite temperature by employing Gibbs (free) energy data for the compounds present in the system, and assuming that the equilibrium of the system corresponds to its minimum energy state.

We point out here that thermodynamical calculation can be very useful for understanding the basic processes in particular plasma processing, but they can not explain all the details arising during experiments, because some steps in plasma synthesis are, or can be, far from equilibrium. Additional information about structure modifications of SiC during heating (or cooling), obtained for example from Thermal Analysis experiments [8, 9], are very useful for the optimization of the synthesis process.

**Method of calculation of equilibrium composition**

Two basic approaches are used to determine the composition of the complex mixtures at high temperatures. In the first one the thermodynamic equilibrium constants for the decomposition and ionization reactions together with the mass conservation law and electrical neutrality are employed to determine equilibrium composition [10]. The second method, based on minimization of the Gibbs free energy, is used in this paper.