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Vaporization and condensation in the Al_4C_3-SiC system

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ABSTRACT

Al_4SiC_4 is a refractory ceramic with a reported band gap of about 2.5 eV, making it an interesting semiconductor material for various applications in the field of energy. However, the synthesis of Al_4SiC_4 single crystals has so far not been investigated. In this study, the sublimation growth method is explored as a potential route for getting high quality single crystals. Combining a thermodynamic analysis with an extensive experimental approach, the vaporization and condensation phenomena in the Al_4C_3 – SiC system are described. Experimental conditions, such as initial composition, baking temperature and temperature gradient, are investigated and demonstrated regarding the crystallization of Al_4SiC_4. From the results obtained, a condensed phase diagram at equilibrium is established for the molar fraction $X_{Al4C3/(Al4C3+SiC)} < 0.5$, which corresponds to the suitable condition for the Al_4SiC_4 condensation. Indeed, Al_4SiC_4 single phase could be experimentally condensed either by self-nucleation or as oriented film on SiC substrates.

1. Introduction

The Al-C-Si chemical system contains a family of aluminum-silicon ternary carbides that can be identified by the general formula $(Al_4C_3)_x(SiC)_y$. The first mention of such a compound appeared in a letter issued in 1961 by Barczak, who briefly reported on the synthesis of Al_4SiC_4 and the corresponding X-ray diffraction data of two of its polymorphs, namely the α- and β-phases [1]. Thoroughly reconsidered by Schoennahl et al. the basic knowledge on Al_4SiC_4 was refined [2]. The authors detailed the possibility to synthesize small Al_4SiC_4 crystals by firing at high temperature, either as an Al_4SiC_4 sintered body or a mixture of Al_4C_3 and SiC raw materials. They also pointed out the extremely narrow temperature window for getting crystals, of about 30 °C between 1950 °C and 1980 °C, conditions under which small yellowish transparent platelets were obtained. Recently, different synthesis routes have been explored, such as solid state reaction and carbo-thermal reduction [3,4].

After these first investigations, Al_4SiC_4 has been extensively studied as a high-temperature structural material and thermal coating for high temperature applications [5–8]. It combines advantageously some interesting ceramic properties, such as high melting point (2080 °C), low density (3.03 g/cm^3) and excellent oxidation and corrosion resistance. It is only recently that its electronic structure has been investigated theoretically through ab initio calculations, predicting semiconducting properties with an indirect bandgap of 1.05 eV and a strong anisotropy of the transport properties due to a very high c/a ratio in the lattice cell, close to 6.62 [9].

At first glance, the bandgap computed by Hussain et al. is not compatible with the transparency of the platelets reported by Schoennahl et al. This discrepancy was the starting point of our investigation of Al_4SiC_4 materials. High quality single crystalline small platelets have been synthesized in order to measure the UV–vis absorption spectrum of Al_4SiC_4. An optical bandgap of about 2.5 eV [10] was found to be in good agreement with the one computed more recently by Pedesseau et al. [11]. According to the calculated band structure, Al_4SiC_4 exhibits both indirect and direct band gap energies of 2.5 and 3.2 eV, respectively. Slightly higher than the bandgap of 3C-SiC (cubic polytype of SiC), Al_4SiC_4 could be an interesting material for applications such as high temperature electronics, photovoltaic or photo-electrochemical water splitting. Semiconductor based applications usually require high quality, high purity crystals. The crystal growth process implemented must be also compatible with further upscaling, i.e. compatible with the current technologies, which is far from being straightforward for a refractory ternary carbide. In order to assess the applicability of the sublimation growth process, which has been developed for silicon carbide ingots production (see for instance [12,13]), we investigate in the present paper, as a preamble, vaporization and condensation

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phenomena in the Al_4C_3-SiC binary system. Both thermodynamic calculations and experiments are confronted, in order to propose a vapor phase route for the synthesis of Al_4SiC_4 single crystals.

2. Material and methods

2.1. Thermodynamic calculation

Thermodynamic calculations of the ternary Al-Si-C were performed with the Factsage 6.0 package, using a set of coherent data from SGTE and SGPS, compiled from the refinement of the ternary Al-Si-C system proposed by Gröbner et al. [14]. The different species considered in the present work are gathered in Table 1.

Before discussing the gas phase composition, the validity of the compiled database has been assessed by computing an isothermal section at 1800 °C and the pseudo-binary Al_4C_3-SiC section. The calculations were found in perfect agreement with the experimental works of Oden et al. [15]. The pseudo-binary section is characterized by the existence of two ternary carbides Al_4SiC_4 (also denoted as Al_4C_3SiC or AS) and Al_8SiC_7 (also referred as $(Al_4C_3)_2SiC$ or 2AS). The first one would exhibit a congruent melting at about 2080 °C and the second one a peritectic decomposition at 2085 °C.

The calculations have been conducted at constant volume for a temperature varying from 1500 to 2200 °C. The vapor phase is assumed to behave as a perfect gas. As initial conditions, we set a mixture of SiC and Al_4C_3 with various compositions, an argon atmosphere and an excess of solid carbon. These conditions have been selected because they are close to the experimental ones which are presented in the next section. To simulate the sublimation growth process, i.e. a growth cavity submitted to a temperature gradient, we used the following procedure: first, the equilibrium vapor phase composition is calculated at a given temperature (T_{POWDER} which is the hot point) for a set of initial conditions. Then, all the gaseous phases are selected and injected as input conditions in a second calculation, at a lower temperature (T_{SEED}). With such an approach, it is possible to describe on a pure thermodynamic footing, the nature and composition of the phases condensing at the seed side, which is the "cold point".

2.2. Experiments

Experiments have been performed in a high temperature furnace, developed for the seeded sublimation growth of SiC. General description of the growth cell is given in Fig. 1(a). More details are available, for instance, in Ref. [16] together with a typical temperature distribution obtained by numerical simulation. Basically, it consists of an inductively heated graphite crucible placed in a water-cooled quartz chamber. The whole crucible was made of graphite and insulated with graphite felts. Pressure and temperature were controlled during the process. Temperature was measured with a bichromatic optical pyrometer, from the back side of the crystallization area. Growth temperature was varied from 1900 to 2000 °C, and the growth pressure was fixed at 150 or 300 mbar using argon atmosphere. Source materials were composed of a mixture of high purity powders of Al_4C_3 (Alfa Aesar, 99 +% purity) and SiC (Sika tech E301) with a molar ratio X_{Al4C3} defined as $X_{Al4C3} = nAl_4C_3/(nAl_4C_3 + nSiC)$. 4° off-axis (to ⟨11–20⟩) 4H-SiC wafers with a chemo-mechanical polished silicon or carbon face were used as seed substrates. SiC substrates were stuck at the top of the crystallization area using graphite glue.

Reactor was manually heated up with a constant power until 1000 °C, the detecting range temperature of the used pyrometer. Afterwards, the heating rate was fixed at 30 °C/min until the growth temperature at high pressure (≈800 mbar) in order to prevent the sublimation of raw materials. At the beginning of the annealing, the pressure was decreased to the growth pressure. During the growth, all parameters were stable. At the end of the annealing, the pressure was increased to 800 mbar to prevent any sublimation, and the reactor was cooled down by turning off the power. The schematic description of the process parameters is presented in Fig. 1.

Inner temperature distribution of the reaction cell has been assessed by numerical simulation using the Finite Element Method (FEM) software, COMSOL Multiphysics. The simulation, coupling induction heating and heat transfers was performed in a two-dimensional axisymmetric geometry. The production and consumption of heat related to the chemical reactions in the powder and at the condensation area are neglected. We will mainly use hereafter four computed temperature points, as indicated in Fig. 1(a) and plotted as a function of the input induction current in Fig. 1(b) for a reference position of the induction coil with respect to the crucible. Two important temperature differences were defined as follow:

$$\Delta T_1 = T_{P\_TOP} - T_{SEED} \quad \text{(i)}$$

$$\Delta T_2 = T_{P\_BOT} - T_{P\_TOP} \quad \text{(ii)}$$

The adjustment of the temperature distribution in the seeded sublimation growth process of SiC has been extensively studied using numerical simulation. More specifically, the effect of the induction coil's position and the design of the heatsink on the temperature has been examined [17–19]. Based on a similar approach, and fixing the crucible design, we controlled the axial temperature gradients ΔT_1 and ΔT_2 by simply moving up and down the induction coil. As a rule, moving up the coil with respect to the reference position gives rise to a decrease of the temperature gradients. Conversely, by moving down the coil, the temperature gradients increase.

Phase analysis has been conducted by X-Ray Diffraction (XRD) using a Bruker D8 Advance diffractometer with the Cu Kα1 radiation in the Bragg-Brentano configuration. Refinement using the Rietveld treatment has been carried out to analyze phases on a quantitative footing. For more local identification, such as, for instance, for a single grain, we used a Jobin Yvon/Horiba LabRam Raman spectrometer equipped with a liquid nitrogen cooled coupled charge device detector. The green laser excitation (λ = 514.5 nm) was focused to a spot size in the range of 1 μm^2 on the sample. Raman spectra were calibrated by using a silicon single crystalline wafer at room temperature.

3. Results and discussion

3.1. Thermochemistry of the gas-solid system

Table 2 gives the computed equilibrium partial pressures of the different gaseous species at 2000 °C for an initial composition of $X_{Al4C3} = 0.5$. The partial pressures clearly spread over a large range of values, which are distributed on ten orders of magnitudes. Some species can thus be neglected. The system can be described accurately by considering only 7 species, namely Al(g), Al_2(g), AlC_2(g), Al_2C_2(g), Si(g), C_2Si(g) and CSi_2(g). The evolution of the partial pressures of these species as a function of temperature is plotted in Fig. 2(a). The corresponding atomic ratios C/Si and Al/Si in the gas phase are plotted in Fig. 2(b). On this latter figure, we added two grey, thick horizontal lines which represent the stoichiometry of the two solid compounds Al_4SiC_4 and Al_8SiC_7, encountered in the pseudo-binary section. These two ternary carbides have atomic ratios of Al/Si = C/Si = 4 for Al_4SiC_4, and Al/Si = 8 and C/Si = 7 for Al_8SiC_7.

As expected, vaporization of Al_4C_3-SiC ceramics strongly increases with temperature. The vapor composition is character-