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A thermogravimetric study of the reactions of tungsten disilicide with anhydrous hydrogen fluoride and fluorine

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ABSTRACT

The thermogravimetric results of a study into the dry fluorination of tungsten disilicide, WSi_2, using hydrogen fluoride and dilute fluorine gas as fluorinating agents, are reported. The reaction between tungsten disilicide and fluorine follows the thermodynamically preferred route, viz. the formation of the volatile tungsten hexafluoride along with gaseous silicon tetrafluoride, with the reaction starting just below 200 °C. The reaction with hydrogen fluoride yields solid tungsten metal and gaseous silicon tetrafluoride, similarly thermodynamically predicted, above 250 °C. No reaction is observed at low temperatures where solid tungsten tetrafluoride is expected to form. The results of a kinetic analysis of the data for the reaction with hydrogen fluoride are reported. At temperatures below 450 °C, the kinetics cannot be reliably determined. In the higher temperature region, mass transport of the reactive hydrogen fluoride through the stagnant gas film surrounding the particle, and penetrating the pitted areas, controls the mass loss rate.

1. Introduction

There are two tungsten silicide phases evident from the W–Si phase diagram, viz. WSi_2 and W_5Si_3 [1]. WSi_2 has a number of applications. For example in the semiconductor industry it is used for manufacturing integrated circuits. It also used as high temperature coating and as a furnace material [2–4]. The focus in this paper is on the fluorine chemistry of tungsten disilicide (WSi_2). The most common fluorides of tungsten are WF_4, WF_5 and WF_6 [5].

Very few articles could be traced that discuss the reactions of WSi_2 with either hydrogen fluoride or fluorine. O'Hare [3] reported on the fluorination of WSi_2 with fluorine gas. His purpose was to determine the standard molar enthalpy of formation of the disilicide using fluorine combustion calorimetry. WSi_2 was treated with F_2 in the presence of tungsten (as an auxiliary substance) and sulphur (as a fuse) to achieve complete conversion. The products obtained were WF_6 and SiF_4. The most frequently reported fluorine reactions are with tungsten metal, especially the direct exothermic fluorination with fluorine, where WF_6 is produced, mostly for the semiconductor industry [6,7]. No data on the reaction between WSi_2 and HF could be found.

In this paper we report on reactions of WSi_2 with both anhydrous HF (AHF) and F_2, investigated using thermogravimetry. Equilibrium thermodynamic calculations predict that stoichiometric ratios of WSi_2 and F_2 produce $WF_6(g)$ and $SiF_4(g)$ at all temperatures from room temperature – above the boiling points of WF_6 and SiF_4, 17 and −86 °C respectively – up to 1000 °C (Eq. (1) below).

$$WSi_2(s) + 7F_2(g) \rightarrow WF_6(g) + 2SiF_4(g) \qquad (1)$$

The thermodynamically calculated species distribution for the reaction between 1 kmol silicide and 12 kmol of AHF, is given in Fig. 1 below. These equilibrium calculations were done with The HSC Chemistry software suite [8].

$WF_4(s)$ is predicted to exist up to about 120 °C. At higher temperatures (>150 °C) the reaction produces tungsten metal as the final product. This corresponds with the stoichiometry of Eq. (2) below.

$$WSi_2(s) + 8HF(g) \rightarrow W(s) + 2SiF_4(g) + 4H_2(g) \qquad (2)$$

The results reported here largely confirm the thermodynamics.

2. Results and discussion

The course of the reaction of the disilicide with 10% fluorine diluted in nitrogen is given by the thermogravimetric curve in Fig. 2. The WSi_2 is fully converted to gaseous WF_6 and SiF_4. The

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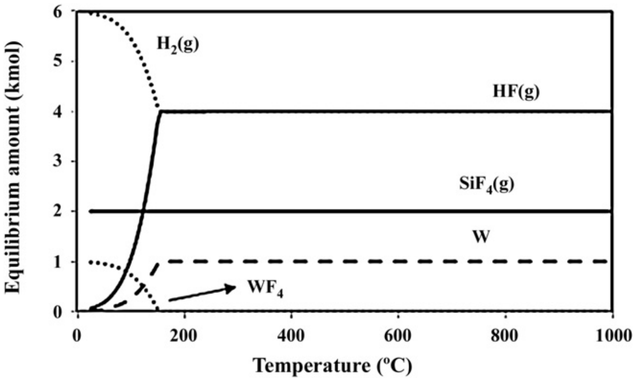

Fig. 1. Equilibrium composition of the reaction between WSi_2 and HF.

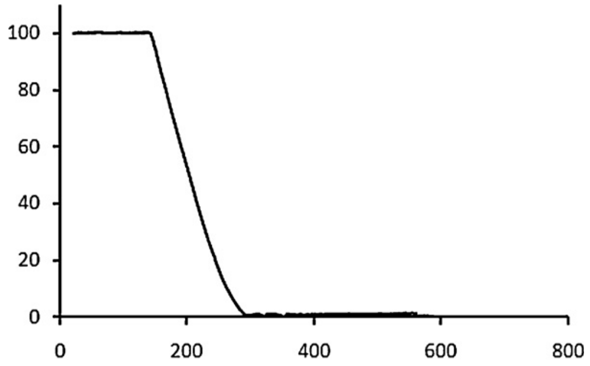

Fig. 2. Dynamic thermogravimetric curve of the reaction between WSi_2 and 10% F_2 in nitrogen.

reaction starts below 200 °C and full conversion is achieved before reaching 350 °C. Once the ignition temperature has been achieved, the reaction follows the thermodynamically predicted course.

The reaction with 10% AHF in nitrogen is given in Fig. 3. The reaction starts at roughly 250 °C, and nearly full conversion (23.4% mass loss) is achieved at 800 °C. The reaction gives tungsten metal as the final product, with a small amount of silicon. These results were obtained with X-ray fluorescence (XRF) analysis, and X-ray diffraction (XRD).

When the HF reactions were conducted isothermally (Fig. 4) in the temperature range of 200–700 °C, tungsten metal was the final product in the range of 250–400 °C. At temperatures higher than 450 °C, further volatilisation was observed (see Fig. 4).

Scanning electron microscope (SEM) images of the final products are given in Fig. 5. Nearly parallel cracks are observed on the surface of the particles. Evidently after the removal of the silicon from the crystalline matrix, the more dense tungsten metal forms, leaving unoccupied strips in the particles. This becomes more pronounced with temperature.

The mass loss curve in Fig. 3 strongly suggests that two kinetic mechanisms are relevant. The first mass loss trend lies between 200 and 450 °C. Beyond that, the curve flattens out suggesting a second mechanism. Three models, the full derivation of which can be found in e.g. Levenspiel [9], were fitted to the data. For simplicity the particles are assumed to be spherical. The algebraic expressions describing α, the fractional residue, as a function of time, are given below.

For the case of rate control by the chemical reaction itself, the rate expression is

$$1-\alpha^{1/3}=\frac{t}{\tau} \tag{3}$$

with τ, the time to full conversion, given by

$$\tau=\frac{\rho_B R}{bk''C_g} \tag{4}$$

For the case where diffusion through the stagnant gas film surrounding each individual particle controls the reaction rate, the expression is

$$1-\alpha=\frac{t}{\tau} \tag{5}$$

with

$$\tau=\frac{\rho_B R}{3bk_g C_g} \tag{6}$$

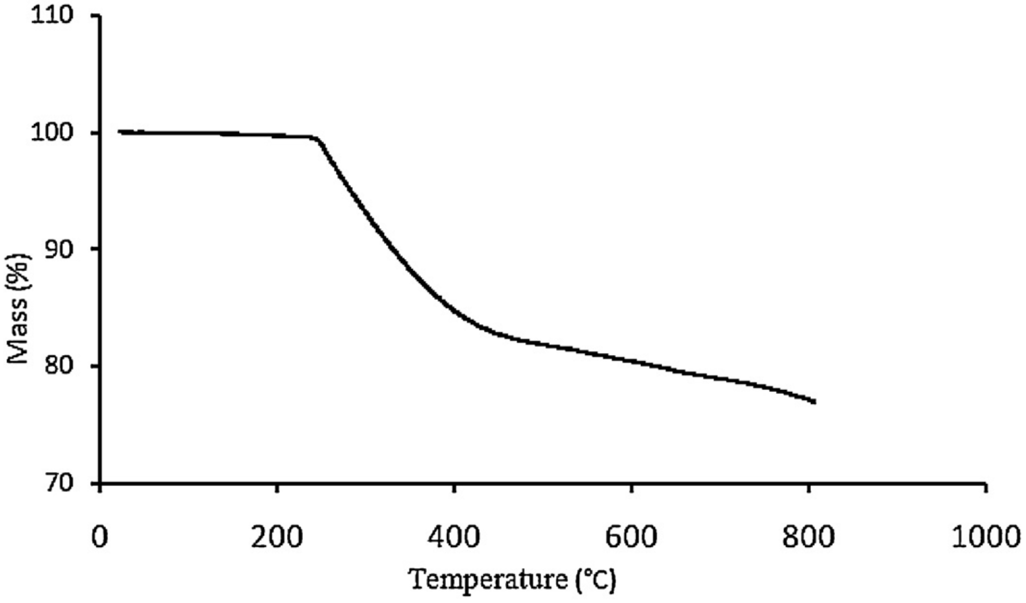

Fig. 3. Dynamic thermogravimetric curve of the reaction between WSi_2 and 10% HF in nitrogen.

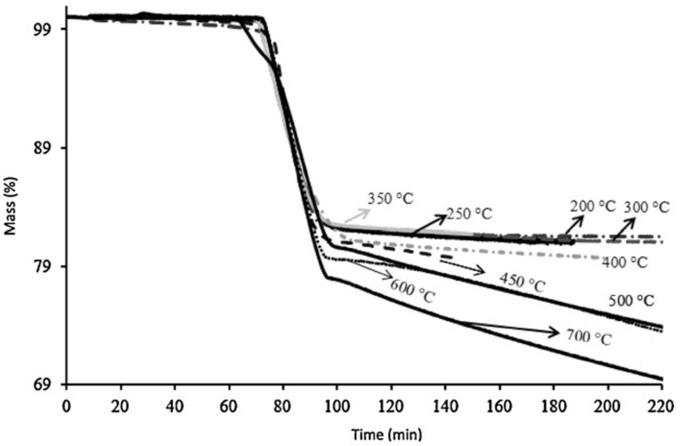

Fig. 4. Isothermal reactions between WSi_2 and HF.

In the case where diffusion through the product layer is rate limiting, the expression is

$$1 - 3\alpha^{2/3} + 2\alpha = \frac{t}{\tau} \tag{7}$$

with

$$\tau = \frac{\rho_B R^2}{6bD_e C_g} \tag{8}$$

In the above equations ρ_B is the molar density of the solid reactant, R is the initial particle size (assuming full sphericity), C_g is the reactant gas concentration, k'' is the chemical reaction rate constant, k_g is the mass transport coefficient through the stagnant gas film, and D_e is the effective diffusion constant through the product layer. The symbol b is the stoichiometric coefficient for the general gas–solid reaction:

$$A(g) + bB(s) \rightarrow \text{Products} \tag{9}$$

Plots of the left-hand side of the three rate expressions, i.e. Eqs. (3), (5) and (7) against time should yield straight lines for a model to be valid. The best least squares fit allows selection of a model. From the slopes of these plots, $1/\tau$, the relevant constant at each temperature, which are k_g, D_e, and k'', can be calculated. The three constants all display Arrhenius behaviour, and their temperature dependence can be determined from simple Arrhenius plots.

The general conclusions drawn from the kinetic analysis are as follows. Poor model fits are obtained at 200 °C. This suggests that the reaction only fully develops somewhat above 200 °C. From 250 to 450 °C, highest R^2 values are obtained for the chemical reaction control model, i.e. Eq. (3), but the calculated activation energy is improbably low (7.2 kJ mol^{-1}, with a pre-exponential factor of 0.032 m s^{-1}). It is likely that in this temperature region there are competing mechanisms that makes kinetic analysis impossible with the method used here. In the high-temperature region, 450–700 °C, the best data fit is obtained for the gas-film diffusion control model, Eq. (5). One could argue that the SiF_4 diffusing away

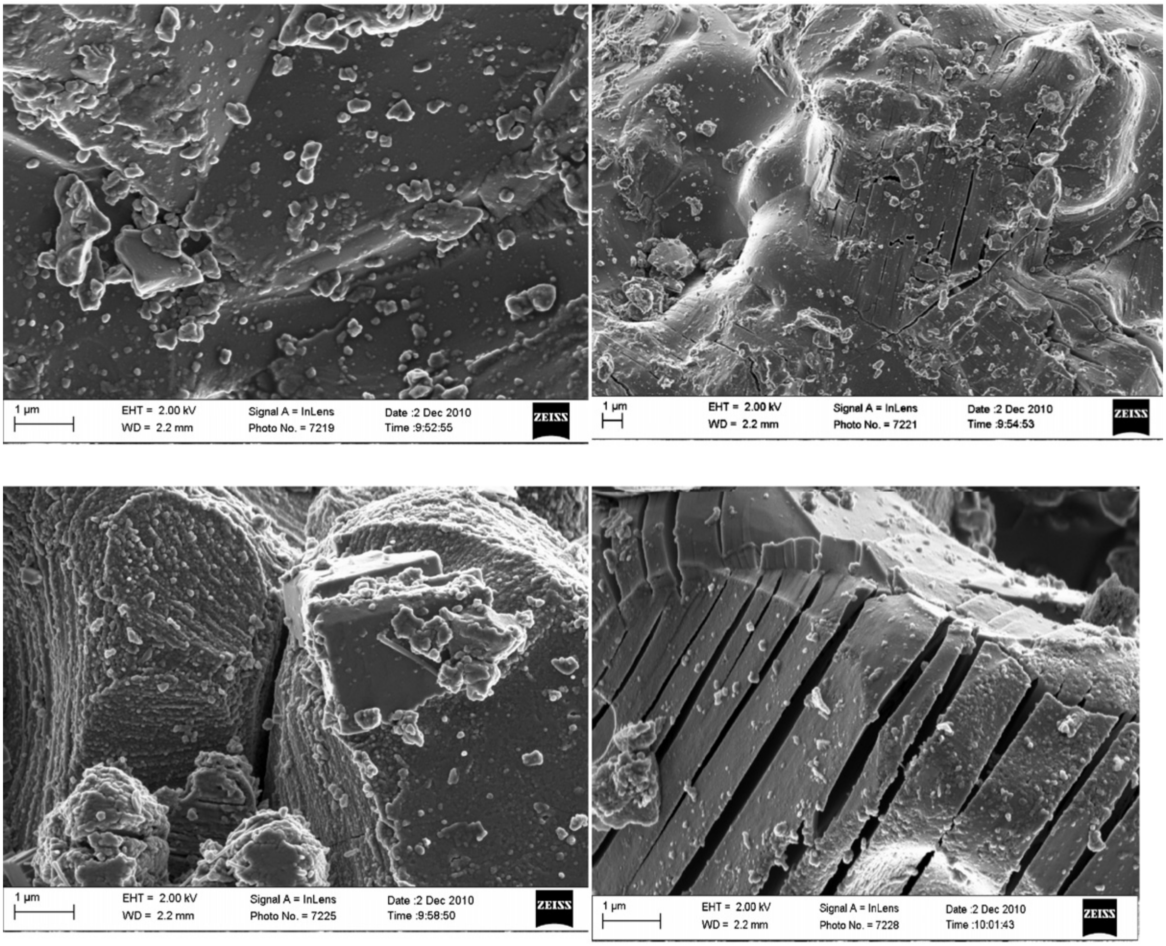

Fig. 5. SEM micrographs of WSi_2, untreated and after reaction with HF at different temperatures.

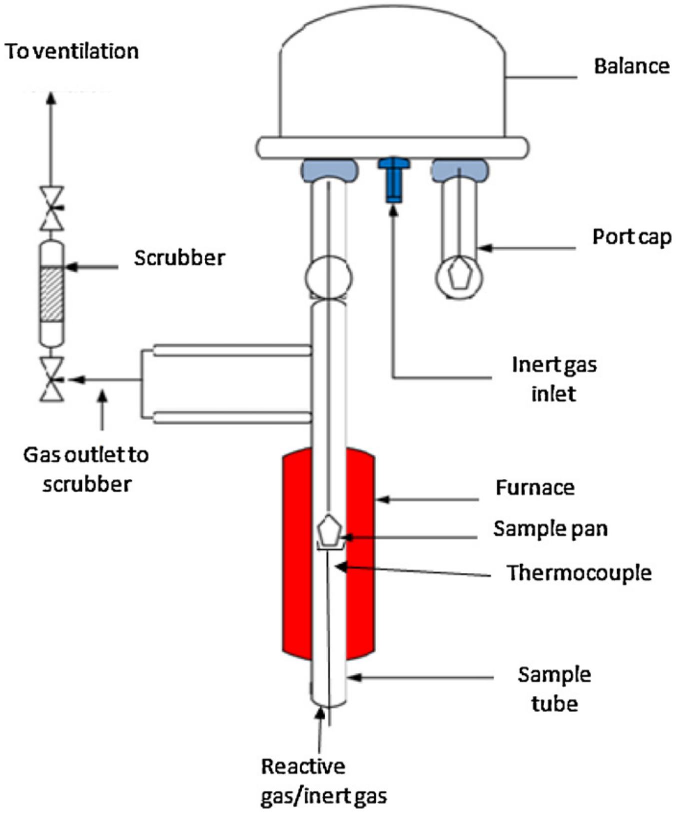

Fig. 6. Schematic diagram of the modified TGA instrument used.

Table 1
Arrhenius parameters for the WSi_2 reaction in the range of 450–700 °C.

	E_a (kJ mol^{-1})	Pre-exponential factor (m s^{-1})	R^2	Temperature range (°C)
k_g	13.4	0.353	0.970	450–700

from the surface contributes to this effect since at higher temperature the mass loss is more rapid, and the generation of SiF_4 similarly more significant. The ash-layer model, Eq. (7), fitted poorly in all cases. This is expected given the open morphology of the final tungsten product.

The Arrhenius parameters (activation energies and pre-exponential factors) are given in Table 1.

The fact that gas film diffusion dominates the kinetics indicates that thermogravimetric analysis is not suitable to determine chemical reaction kinetics for this reaction. An alternative experimental setup will have to be constructed that will allow for higher flow rates so that turbulent flow, impinging onto the sample, can be achieved.

3. Conclusion

The reaction of tungsten disilicide with fluorine follows the route predicted by thermodynamic equilibrium calculations. The silicide is completely volatilised with the formation of SiF_4(g) and WF_6(g). When the fluorination is done with anhydrous HF at temperatures above 250 °C the thermodynamically predicted products (W metal and SiF_4(g)) are once again obtained. The reaction kinetics changes with temperature with possibly competing mechanisms below 450 °C and mass transfer (gas film diffusion) limitation being dominant above 450 °C. At temperatures below 250 °C the thermodynamically predicted WF_4(s) is not observed.

4. Experimental

4.1. Materials

The tungsten disilicide was purchased from Sigma–Aldrich. The dilute anhydrous hydrogen fluoride and fluorine gas (10% HF or F_2 diluted in N_2) were obtained from Pelchem (Pty) Ltd. All reagents had a purity of >99%.

4.2. Experimental procedure

An adapted thermogravimetric analyzer (TGA), schematically depicted in Fig. 5, was used for conducting the experiments. The instrument was modified to handle the corrosive gases HF and fluorine (see Fig. 6).

Details of the instrument and materials of construction are discussed by Van der Walt et al. and Rampersadh [10,11]. General information regarding thermogravimetric analysis can be found in e.g. Brown [12]. A starting mass of 40–60 mg WSi_2 was used for each set of experiments. The WSi_2 was stored in a glove box under nitrogen and treated with special consideration to minimize the oxygen present, even though WSi_2 is known as a reasonably oxidation resistant. Two thermogravimetric methods were used: non-isothermal (dynamic) and isothermal. For isothermal experiments the sample was first heated to the predetermined temperature and then maintained at this constant temperature to equilibrate before introducing the reactive gas. For non-isothermal experiments the reactive gas was introduced at the beginning of each reaction. Isothermal experiments were only carried out with HF(g), since the fluorine reaction was considered basic. The isothermal reactions were done at temperatures ranging between 200 and 700 °C. The samples were placed and heated in a small TG pan (inside diameter of 5.63 and a height of 1.64 mm) to the desired temperature using a rate of 10 °C/min. The diameter of the furnace tube was 10 mm. The thermocouple was inserted through the inlet of reactive gas, and positioned just underneath the TG pan to accurately measure the temperature. The reactive gases were introduced at a flow rate of 60 mL/min. The products obtained from these reactions were analysed using Bruker A-D8 Advanced XRD for phase identification, FEI QUANTA 200 3D SEM for image analysis and EDX and Panalytical Axios XRF spectrometer for elementary analysis.

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