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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Production of Silicon from Magnesium Silicide

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Abstract—Kinetic methods and thermogravimetry were used to study the oxidation process of magnesium silicide in air in the temperature range 300–1000°C. The reaction products were identified by X-ray phase analysis. It was found that the reaction occurs in the temperature range 510–710°C to give silicon and magnesium oxide. With the temperature increasing further, silicon is oxidized to silicon dioxide.

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The conventional techniques for manufacture of silicon for solar power engineering include a number of stages in which silicon-containing raw materials are purified to remove interfering impurities and then elementary silicon is obtained [1, 2].

Despite being widely used and well developed, methods for production of polycrystalline silicon from metallurgical silicon are technically complex, require substantial capital investment for setting-up production plants, and gross maintenance expenditure in manufacture of commercial products.

Alternative technologies, such as production of silicon from special-purity quartz by its reduction and subsequent additional purification occupy a rather small part of the market; however, the share of polycrystalline silicon produced by these techniques steadily grows annually [3].

A method is known for production of silicon by magnesiothermic reduction of silicon dioxide, followed by separation of reaction products [4]. Silicon and magnesium oxide are separated by acid leaching with hydrochloric acid. Together with dissolution of magnesium oxide, there occurs decomposition of the silicide to give silane (SiH_4) vapor. Interacting with water contained in hydrochloric acid, silane self-ignites with explosive blasts. In the end, SiO_2 is again formed. A loss of this kind is inadmissible in reduction of the pure and rather expensive oxide.

The reduction product is the three-component system composed of silicon, magnesium oxide, and magnesium silicide Mg_2Si:

$$2Mg + SiO_2 = 2MgO + Si, \quad (1)$$

$$4Mg + SiO_2 = 2MgO + Mg_2Si, \quad (2)$$

$$2Mg + Si = Mg_2Si. \quad (3)$$

To remove magnesium silicide, it is suggested to subject magnesiothermy products to thermal calcination in air. The separation is based on the reaction of magnesium silicide with oxygen to give magnesium oxide and silicon. In this way, it is possible to provide the maximum recovery of silicon from silicon dioxide and to preclude any loss of silicon.

The goal of the present study was to examine the interaction of magnesium silicide with oxygen and to identify reaction products.

Thermodynamic calculations of the decomposition of magnesium silicide were performed for the temperature range 298–900 K [5] (Table 1). The equilibria of chemical reactions (4)–(7) were found by the Temkin–Svwartzman method:

$$Mg_2Si + O_2 = 2MgO + Si, \quad (4)$$

$$Mg_2Si + 2O_2 = 2Mg_2SiO_4, \quad (5)$$

$$Mg_2Si + 2O_2 = 2MgO + MgSiO_3, \quad (6)$$

$$Mg_2Si + 2O_2 = 2MgO + SiO_2. \quad (7)$$

Table 1. Values of the standard $\Delta H°$, $\Delta S°$, $\Delta G°$, and log K_p for the reactions of thermal decomposition of magnesium silicide by oxygen at temperatures of 298–900 K

Parameter	Temperature, K						
	298	400	500	600	700	800	900
$Mg_2Si + O_2 = 2\ MgO + Si$							
$\Delta G°$, kJ mol^{-1}	–1062	–1041	–1020	–999	–978	–957	–936
$\Delta H°$, kJ mol^{-1}	–1124.6	–1124.76	–1124.97	–1125.18	–1125.39	–1125.6	–1125.81
K_p	1.07×10^{185}	1.12×10^{136}	4.49×10^{106}	1.13×10^{87}	1.12×10^{73}	3.51×10^{62}	2.36×10^{54}
$Mg_2Si + 2\ O_2 = 2\ Mg_2SiO_4$							
$\Delta G°$, kJ mol^{-1}	202	230	255	278	299	319	337
$\Delta H°$, kJ mol^{-1}	96.28	95.65	94.81	93.97	93.13	92.29	91.16
K_p	5.64×10^{-36}	8.41×10^{-31}	2.09×10^{-27}	5.98×10^{-25}	4.67×10^{-23}	1.56×10^{-21}	2.87×10^{-20}
$Mg_2Si + 2\ O_2 = 2\ MgO + MgSiO_3$							
$\Delta G°$, kJ mol^{-1}	–1003	–967	–932	–898	–864	–830	–797
$\Delta H°$, kJ mol^{-1}	–510.68	–511.23	–511.961	–512.69	–513.42	–514.15	–514.88
K_p	1.233×10^{69}	1.212×10^{51}	8.666×10^{35}	1.16×10^{26}	1.304×10^{19}	9.054×10^{13}	9.428×10^{9}
$Mg_2Si + 2\ O_2 = 2\ MgO + SiO_2$							
$\Delta G°$, kJ mol^{-1}	–1918	–1879	–1840	–1800	–1761	–1721	–1681
$\Delta H°$, kJ mol^{-1}	–2035.5	–2035.5	–2036.03	–2036.74	–2037.45	–2038.16	–2038.87
K_p	1.58×10^{334}	3.43×10^{245}	2.08×10^{192}	6.73×10^{156}	2.94×10^{131}	2.77×10^{112}	4.36×10^{97}

The standard Gibbs energies are negative for all the reactions and have large values in the whole temperature range 298–900 K, i.e., these reactions may occur spontaneously and their equilibrium is irreversibly shifted toward formation of reaction products. The reactions of thermal decomposition of magnesium silicide are exothermic and occur with a substantial release of heat. With increasing temperature, the probability of oxidation of magnesium silicide to silicon and magnesium oxide becomes lower, with a simultaneous decrease in the probability of side reactions in which magnesium meta- and orthosilicate and silicon dioxide are formed. However, the equilibrium constants of the decomposition reactions remain large in the whole variation range of the given parameter.

EXPERIMENTAL

Differential scanning calorimetry and thermogravimetric and differential-thermal analyses were performed in a flow of air on a SDT Q600 combined analyzer with software processing of thermal analysis data (Instruments Universal V4.2E). The heating was made at a rate of 5 deg min^{-1} in corundum crucibles in the temperature range 20–1000°C. In the study, a set of three runs was performed with a calorimetric reproducibility of ±2% and gravimetric reproducibility of ±0.1 μg; the reagents used were of analytically pure grade.

The kinetic experiment was performed by the method of continuous weighing of a reacting weighed portion with automatically recording of its mass. The conversion was found from the gain in mass, resulting from the formation of solid products in the course of oxidation of the weighed portion. The temperature was maintained constant to within ±2°. A 1-g portion of the Mg_2Si powder in a platinum crucible was placed in a reactor electrically heated to a prescribed temperature. After the decomposition process was complete, which was judged from the attainment of a constant mass, the heating was switched off and the crucible was removed from the reactor. The solid residue formed upon the thermal decomposition of magnesium silicide, constituted by silicon and undecomposed magnesium silicide, was weighed on an analytical balance. To rule out a methodological experimental error, five runs were made at each temperature. The average deviation of the experimental data was 3–5%. The reproducibility of the

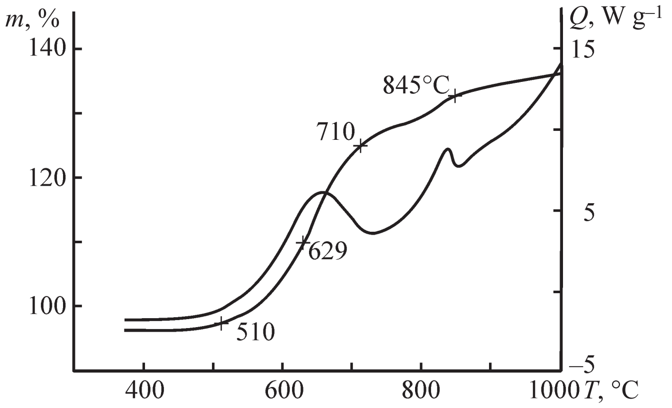

Fig. 1. Thermogram of the process of Mg_2Si interaction with atmospheric oxygen. (m) Mass, (Q) heat flux, and (T) temperature.

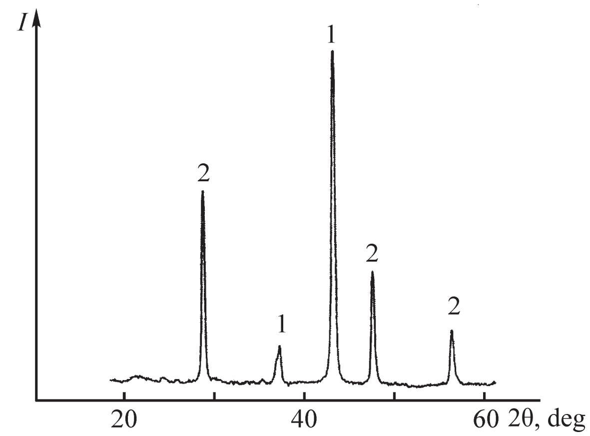

Fig. 2. XPA spectra of products formed in interaction of Mg_2Si with atmospheric oxygen at a temperature of 650°C. (I) Intensity and (2θ) Bragg angle.

experiments indicates that the temperature dependence of the decomposition rate, obtained in the study, is reliable and can be used to find kinetic parameters of the decomposition process.

The X-ray phase analysis was made on a DRON-3M instrument with a copper anticathode (current 25 mA, voltage 35 kV). The results of processing of the X-ray data were compared with the NBSCR database for the crystal structures of inorganic compounds.

According to gravimetric analysis data (Fig. 1), heating of a weighed portion containing magnesium silicide results in the onset at 510°C of an exothermic reaction between magnesium silicide and atmospheric oxygen to give silicon and magnesium oxide. At 710°C, the already formed silicon is oxidized to silicon dioxide:

$$Mg_2Si + O_2 \rightarrow 2MgO + Si,$$
$$Si + O_2 \rightarrow SiO_2.$$

An X-ray diffraction pattern of the product formed in thermal decomposition of Mg_2Si in air at a temperature of 650°C demonstrated that its main components are silicon and magnesium oxide. No other phases were found (Fig. 2).

The study of the oxidation of magnesium silicide in the temperature range 520–600°C and the mathematical processing of kinetic data demonstrated that the conversion of magnesium silicide nonlinearly varies with time (Fig. 3). The conversion grows to the greatest extent during the first 3 min after the beginning of the process for al of the temperatures studied. During this interval of time, the conversion was 30 to 60 wt %, respectively, at temperatures in the range from 520 to 600°C. During the following 10 min, the rise in conversion becomes slower and then it linearly varies until the end of a run, slowly growing by, on average, 5%. An increase in the decomposition temperature from 520 to 600°C results in a significant rise in the conversion of magnesium silicide. At a temperature of 600°C, the conversion reaches a value of 70% in 15 min.

The kinetic data on the interaction of magnesium silicide with oxygen were mathematically processed by the contracting-sphere equation (correlation coefficients 0.95–0.98):

$$\alpha = 1 - [1 - 6.311\tau \exp(-58253\pm158.3/RT)]^3,$$

where α is the conversion (fraction units).

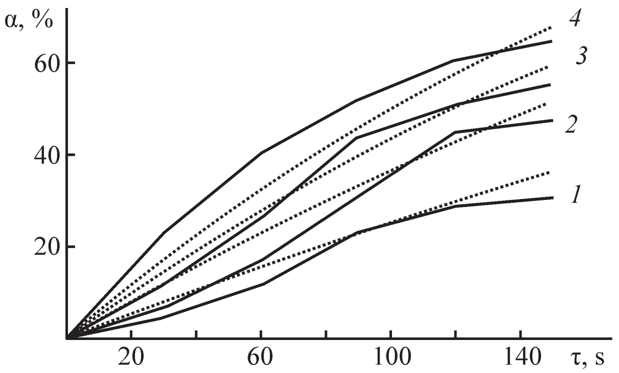

Fig. 3. Conversion α of magnesium(II) silicide vs. time τ for the oxidation process. T (°C): (*1*) 520, (*2*) 560, (*3*) 580, and (*4*) 600.

The activation energy of the process was 58.25 kJ mol^{-1}. The process occurs under kinetic control, with the rate of the overall process governed by the true kinetics of the chemical reaction on the surface and little dependent on the diffusion conditions. The process can be intensified by raising its temperature.

To determine the extent to which magnesium silicide reacts with oxygen, we performed a set of experiments on thermal decomposition under static (in an electrically heated furnace) and dynamic (in a hindered-settling reactor) conditions.

Decomposition of magnesium silicide under static conditions. A 2-g portion of magnesium silicide was placed in a ceramic crucible, with its layer uniformly distributed over the surface so that its thickness was 1–2 mm. Then the crucible was placed in the furnace electrically heated to a prescribed temperature. After the run duration ended, the crucible with decomposition products was removed from the furnace.

The powder containing magnesium silicide decomposition products (magnesium oxide, silicon, silicon oxide) was dissolved in hydrochloric acid. The solution was filtered and the solid residue was dissolved in hydrofluoric acid to remove the silicon oxide formed. The remaining precipitate (elementary silicon) was washed with twice-distilled water, filtered-off, and dried at 200°C.

The thus obtained data on the yield of silicon are listed in Table 2 in relation to the variable technological parameters (temperature range 600–720°C and run duration 10–30 min).

At a temperature of 600°C, the highest yield of silicon relative to the theoretical value was 72.61% after 30 min of heating in air. During the following 1.5 h, the oxidation of magnesium silicide did not stop, with the maximum yield of silicon at this temperature being 98%. At 720°C, the maximum yield (97.87%) was reached during the first 10 min of a run, with the content of elementary silicon decreasing during the following 20 min due to the intensification of the process of its oxidation to silicon dioxide. The largest yield of silicon relative to the theoretical value (98.11%) was reached at a temperature of 660°C and experiment duration of 30 min.

Table 2. Yield of silicon in decomposition of magnesium silicide in air under static conditions

Run duration, min	Yield of Si relative to the theoretical value, %, at indicated temperature, °C		
	600	660	720
10	60.35	83.12	94.87
20	66.98	92.20	93.21
30	72.61	98.10	91.67

Decomposition of magnesium silicide under dynamic conditions. The hindered-falling reactor is a vertically mounted cylinder with a diameter of 40 mm and a heated reaction zone of 300 mm. The reactor is electrically heated to a prescribed temperature. A screw feeder and a pipe for discharge of gases from the reactor are mounted in its upper part. The reactor has in its bottom part a receiving bin for decomposition products and a pipe for delivery of oxygen into the reactor.

To determine the optimal parameters of the magnesium silicide decomposition process, we performed experiments at temperatures of 660 and 720°C. Data on the yield of silicon in relation to the variable technological parameters (temperature range 660–720°C, amount of powder repeatedly passed through the reactor) were obtained.

After a single passage of the starting powder through the reactor, the content of silicon in the product was 34.8% at 660°C and 44.3% at 720°C. After the powder was passed through the reactor three times, the contents of silicon in the product were 73.9% and 89.6%, respectively. The content of silicon dioxide in the product obtained at 72°C exceeded that or 600°C, which is due to the intensification of the process of silicon oxidation to silicon dioxide.

The thermal decomposition products were subjected to an X-ray phase analysis. It was found that the products are mostly composed of silicon and magnesium oxide. The decomposition reaction occurs at 720°C simultaneously with the oxidation of silicon, which is indicated by the high content of silicon dioxide in the samples under study.

Magnesiothermic reduction of silicon dioxide (Fig. 4) yields a three-component system composed of magnesium oxide, magnesium silicide, and silicon. Magnesium silicide is removed via the oxidation stage, in whose process silicon and magnesium oxide (both solid) are formed. Silicon and magnesium oxide can be separated by acid leaching. Magnesium chloride can be used to recover metallic magnesium [6].

CONCLUSIONS

(1) The oxidation of magnesium silicide by

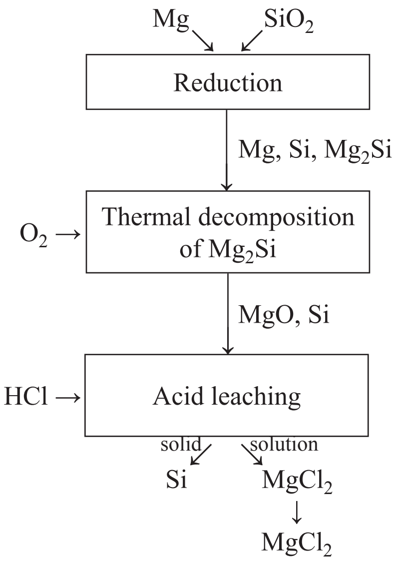

Fig. 4. Scheme of the process for magnesiothermic production of silicon from silicon dioxide, including the stage of thermal decomposition of magnesium silicide.

atmospheric oxygen starts at 510°C to give magnesium oxide and silicon, with silicon oxidized to silicon dioxide at a temperature of 710°C.

(2) The activation energy of the process is 58.25 kJ mol^{-1} in the temperature range 520–600°C.

(3) Magnesium silicide can be decomposed (oxidized with atmospheric oxygen) under static or dynamic conditions. The optimal temperature for the process in which silicon is obtained from magnesium silicide under static and dynamic conditions is 600°C.

(4) A process scheme is suggested for production of silicon via the stage of magnesium silicide oxidation. This scheme will make it possible to raise the yield of the finished product and to preclude loss of pure silicon in the form of silanes in the acid leaching stage.

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