Kinetic study of the reaction between copper(I) chloride and commercial silicon or silicides
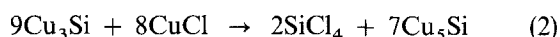
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The reaction of CuCl with silicon containing as impurities Al, Fe, Ca and Ti or with some silicides (Si_2Ca, Si_2Fe, Si_2Ti) has been investigated in the temperature range 250–310 °C. For the reaction between CuCl and commercial Si, it has been found that at 282 °C, the aluminium promotes the reaction between Cu_3Si and CuCl while its rate of consumption is greatly decreased by the presence of iron impurity. The combined action of these two impurities improves the quantity of the copper–silicon alloy formed. In the presence of silicides, the reaction with CuCl leads to copper formation with a high degree of dispersion.

1. Introduction
Chlorosilanes, which are the starting materials in the production of a variety of silicones, are prepared by gas–solid reaction between CH_3Cl and an excess of silicon in the presence of the alloy Cu_3Si (η phase) as catalyst [1]. During the last 40 years most researchers have considered that Cu_3Si formation is accomplished by the reaction between Si and CuCl (CuCl is the result of the reaction between Cu and CH_3Cl) to give finely divided Cu and gaseous $SiCl_4$, Cu then diffusing into the remaining Si matrix to form Cu_3Si [2].

However, we have recently established [3] that the reaction between Si and CuCl leads to Cu_3Si, Cu_5Si and Cu through successive reactions according to the following scheme:

$$7Si + 12CuCl \rightarrow 3SiCl_4 + 4Cu_3Si \qquad (1)$$

$$9Cu_3Si + 8CuCl \rightarrow 2SiCl_4 + 7Cu_5Si \qquad (2)$$

$$Cu_5Si + 4CuCl \rightarrow SiCl_4 + 9Cu \qquad (3)$$

In such a scheme, Cu is the final product of the reaction whereas Cu_3Si and Cu_5Si are intermediates which react with CuCl.

The reactions mentioned above are the overall reactions, and one of the elementary steps involved comprises the reaction between Cu and CH_3Cl to give CuCl which in turn reacts with Si to regenerate the active Cu_3Si alloy according to Reaction 1. It has been reported [4] that, for the synthesis of dimethyldichlorosilane which represents an exceedingly valuable industrial product, the best results were obtained with Cu_3Si prepared at 260–280 °C by pressure-moulding of a mixture of powdered silicon and cuprous chloride. In addition, due to their high mobility the copper atoms, separating in the atomic state, are distributed more uniformly on the silicon surface which assures a good reproducibility of the results obtained with this Cu_3Si alloy.

Owing to the importance of Reaction 1, this paper describes the effects of the purity of the starting mater-

ial, commercial silicon, containing principally as impurities Al, Fe, Ca and Ti, on the kinetics of the formation and decomposition of the intermetallic compound Cu_3Si. Concerning these impurities, it has been reported [5] from the results of an analysis of the microstructure and phase composition of commercial silicon of different grades that Si_2Fe, Si_2Ca and Si_2Ti may be also present as individual inclusions in the matrix of silicon. In distinction from Fe, Ca and Ti, the aluminium in the silicon is distributed uniformly, probably as a result of the fact that this element constituted a solid solution with silicon. Thereby, the kinetics of reaction between silicides Si_2Fe, Si_2Ti and Si_2Ca was also compared with that of commercial silicon of different degrees of purity.

2. Experimental procedure
2.1. Materials
Pulverized silicon with the different grades of composition given in Table I was supplied by Pechiney. All silicon lots used were analysed by atomic absorption spectroscopy. No other elements were present above approximately 10 p.p.m.

Weighed amounts of silicon and Fe, Ca and Ti were induction-melted in recrystallized alumina crucibles under an argon gas atmosphere. Alloys after quenching were subjected to metallographic and X-ray diffraction investigation (Table II). Prior to using it, silicide was ground to a particle size of 2 to 3 μm (Table II).

High-purity (99.999%) copper chloride from Alfa Products was used.

2.2. Equipment
Thermogravimetric analysis (TG) was used to first determine the main kinetic factors of the reaction by investigating the mass loss of the sample during the reduction process. To reach this objective, the total

TABLE I Characteristics of commercial silicon samples

Run number	Impurities (wt %)				Particle size (nm)
	Al	Ca	Fe	Ti	
1	0.0046	0.0073	0.082	< 0.002	4
2	0.32	0.0067	0.059	0.003	3.5
3	0.29	0.38	0.17	0.003	3.7
4	0.18	0.20	0.39	< 0.002	4

TABLE II Characteristics of silicide samples

Run number	Compound	Structure	Particle size (nm)
5	Si_2Ca	Rhombohedral $a = 1.040$ nm, $\alpha = 21.5°$	3.61
6	Si_2Fe	Orthorhombic $a = 0.987$ nm, $b = 0.779$ nm, $c = 0.784$ nm	2.84
7	Si_2Ti	Orthorhombic $a = 0.826$ nm, $b = 0.479$ nm, $c = 0.855$ nm	2.95
8	$SiCu_3$	Orthorhombic $a = 7.676$ nm, $b = 0.700$ nm, $c = 2.194$ nm	1.5

mass changes, Δm, were measured as a function of time by means of a Mac Bain thermobalance with a sensitivity of 5×10^{-2} mg for various CuCl and Si (or silicide) loadings subjected to a vacuum. Powders were intimately mixed for a molar ratio $Si:CuCl = 18$. 25 mg of the mixture was then spread as a thin layer on the balance arm and the reactor evacuated (1 Pa) for 60 min at room temperature, then for 30 min at 205 °C, before the sample was heated to the temperature of the experiment.

The experiments were also performed in the glass reactor shown in Fig. 1. A glass tube of diameter 20 mm and length 200 mm was closed at one end while the other end was provided with a liquid nitrogen trap for $SiCl_4$ (g) to condense. Beside the trap, the glass vessels were heated at 70 °C to prevent condensation of $SiCl_4$ (g). The reactor was placed in a

horizontal tubular furnace heated with electrical resistance wire. The temperature was monitored through a calibrated millivoltmeter using a copper–constantan thermocouple. The vacuum was maintained at 10^{-1} Pa by using an oil diffusion pump. In performing an experiment, Si (0.4262 g) and CuCl (0.0738 g) were intimately mixed in an agate mortar. The sample was spread in a small boat made of glass (15 mm × 30 mm × 6 mm) and placed at one end of the tube. The reactor was firstly evacuated (10^{-1} Pa) at room temperature for 3.5 h before sample heating to the temperature of the experiment under vacuum. The preheating was useful to remove any moisture present in the sample and to shorten the time required for the sample to reach the selected temperature. For each reaction time, the $SiCl_4$ (g) was condensed in a liquid nitrogen trap and thereafter hydrolysed in distilled water,
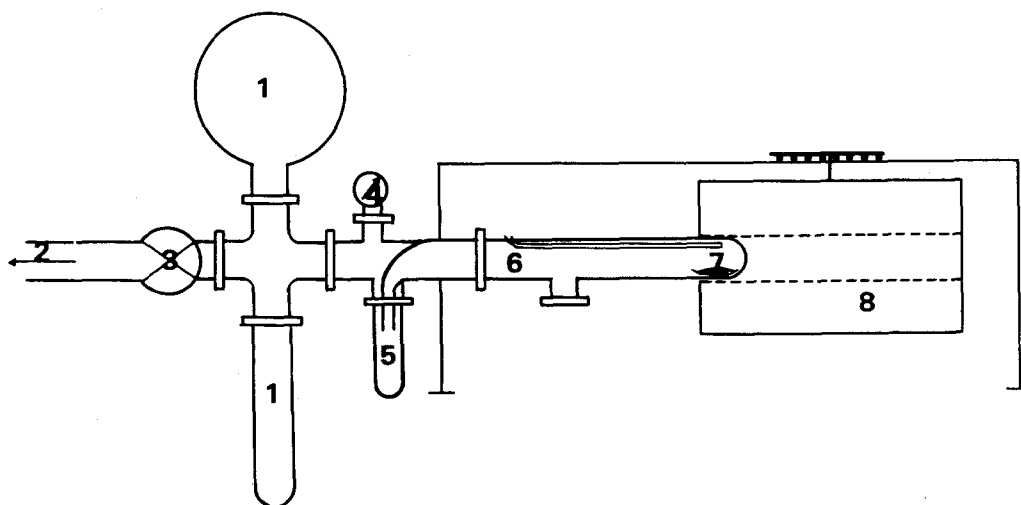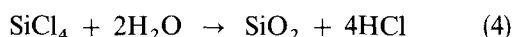

Figure 1 Schematic diagram showing the experimental set-up for studies on the system of commercial Si with CuCl. (1) Glass vessels heated at constant temperature, (2) pump, (3) valve, (4) pressure gauge, (5) liquid nitrogen trap, (6) reactor, (7) powered mixture, (8) oven.

where it reacted instantaneously at room temperature according to the reaction

$$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl \qquad (4)$$

The liberated HCl was estimated at known intervals of time. Thus plots from the HCl titrated with NaOH (Δm_{cal}) versus time describe the progress of the reaction. In both cases, the mass change Δm or Δm_{cal} was calculated for 100 mg of CuCl.

X-ray diffraction analysis was used to identify the solid products formed during the course of the reaction.

3. Results and discussion
3.1. Commercial silicon

Fig. 2 shows the thermogravimetric curves $\Delta m = f(T)$ for the sublimation of CuCl when it is placed alone in the scoop (curve S) and the thermal reaction of mixtures of commercial Si and CuCl (curves 1, 2, 3 and 4) under vacuum at $3\,°C\,min^{-1}$ heating rate. It can be seen that, in the presence of commercial Si, the sublimation temperature of CuCl is lowered by ca. 70 °C. As a result, the temperature at which CuCl begins to react with silicon can serve as a criterion for the reactivity of the mixture. A lower initiation temperature is obtained with a mixture containing a greater amount of aluminium (Fig. 2, sample 2). On the other hand, the activity is decreased by the presence of calcium as principal impurity (Fig. 2, sample 3).

The kinetic curves at temperatures ranging from 250 to 310 °C, $\Delta m_{cal} = f(t)$ (Fig. 3a) for samples 1 and 2, have an S-shape indicating a nucleation and growth mechanism, i.e. the rate initially increased, reached a maximum and then decreased. Tamhankar et al. [6] studied the effect of temperature on this reaction and have reported a contribution of two steps acting simultaneously, autocatalytic and non-catalytic, with a shift in the controlling mechanism. However, when the induction period corresponds to a low degree of conversion, the sigmoidal nature of the reaction is best explained by considering the Prout–Tompkins equation [7]. The plausibility of this is supported by the fact that Cu_3Si and Cu_5Si are intermediate compounds and copper the final phase. The $d(\Delta m_{cal})/dt$
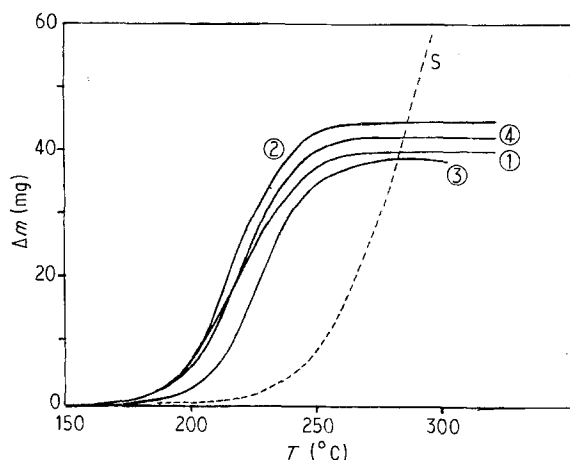
Figure 2 (1–4) Thermogravimetric curves, $\Delta m = f(T)$, obtained in a vacuum for different degrees of purity of silicon (Table I) to study the reactivity of the Si–CuCl system; (S) sublimation of CuCl.
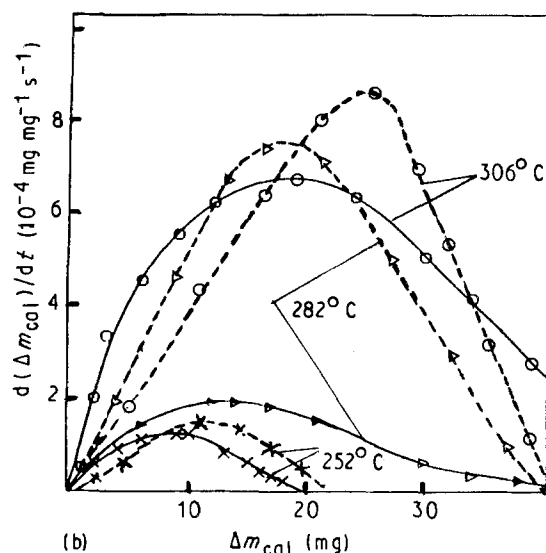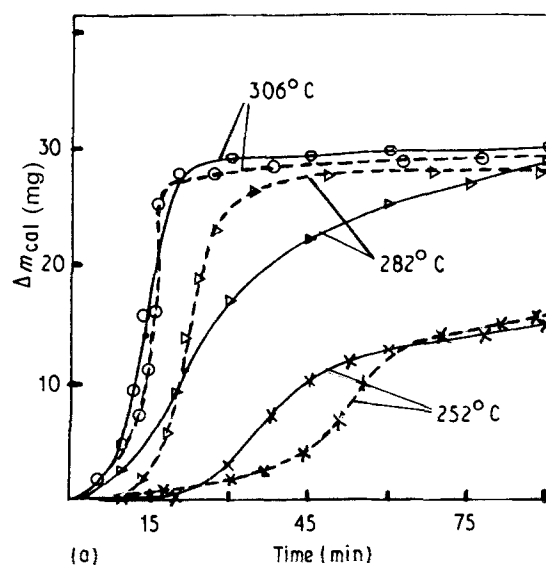
Figure 3 (a) Mass change (Δm_{cal}) with time and (b) rate $d(\Delta m_{cal}/dt)$ as a function of Δm_{cal} at different temperatures: (———) sample 1, (— — —) sample 2.

$= f(\Delta m_{cal})$ curves (Fig. 3b) allow us to determine the maximum rate $\alpha_i = \Delta m_i / \Delta m_{cal}$ for each system where Δm_i corresponds to the Δm value at which the rate $d(\Delta m_{cal})/dt$ is maximum.

As already observed in the $\Delta m = f(T)$ curves (Fig. 2), the presence of aluminium as principal impurity promotes the reaction between Si and CuCl at 282 °C, while at higher temperatures it showed the converse effect. In the phases obtained during the course of the reaction, X-ray diffraction patterns indicate the presence of copper, Cu_3Si and Cu_5Si compounds. Fig. 4 shows the evolution of R_1, R_2 and R_3 ratios of the peak heights corresponding to these different phases with reaction time at 282 °C, where R_1, R_2 and R_3 are defined as

$$R_1 = \frac{I_{Cu(0.209\,nm)} + I_{Cu(0.181\,nm)}}{I_{Cu_5Si(0.207\,nm)} + I_{Cu_5Si(0.197\,nm)}}$$

$$R_2 = \frac{I_{Cu(0.209\,nm)} + I_{Cu(0.181\,nm)}}{I_{Cu_3Si(0.203\,nm)} + I_{Cu_3Si(0.197\,nm)}}$$

$$R_3 = \frac{I_{Cu_5Si(0.207\,nm)}}{I_{Cu_3Si(0.203\,nm)}}$$
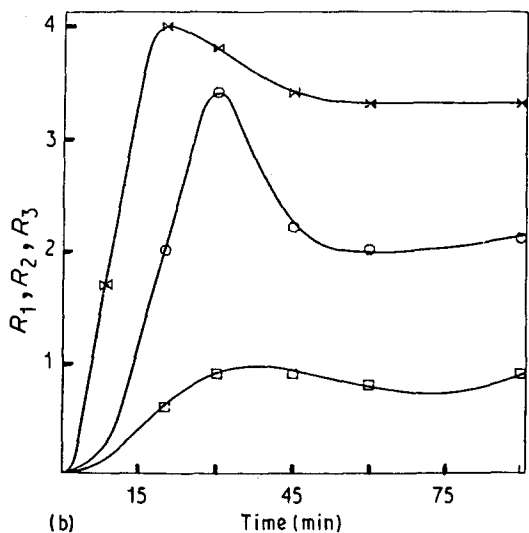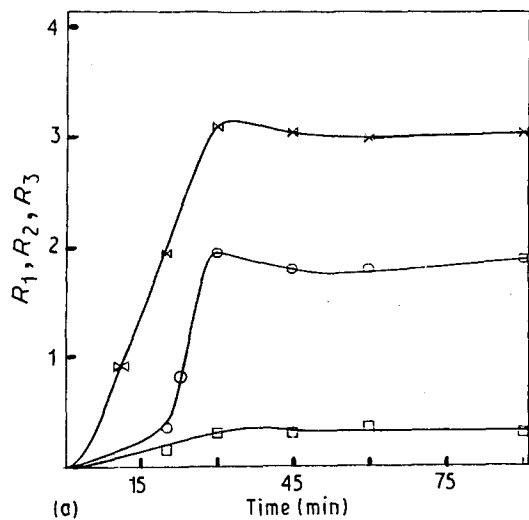
Figure 4 Evolution of ratios (⋈) R_1, (○) R_2 and (□) R_3 as a function of time for (a) sample 1 and (b) sample 2 at 282 °C.

The rate of formation of the first Cu nuclei would depend on the rates of Cu_3Si formation and Cu_5Si consumption and therefore on the presence of aluminium in the starting silicon (Fig. 4a and b). This interpretation agrees with the evolution of R_1 and R_2. Indeed, with aluminium, R_1 and R_2 ratios present a marked maximum (Fig. 4b), Cu being preferentially formed in the first minutes of the reaction. Thus the decrease can be ascribed to the high rate of formation of Cu_3Si. The most obvious advantage of the presence of aluminium as an impurity in the starting silicon is the increase in silicon consumption when the temperature approaches 280 °C.

This is probably connected with the fact that at this temperature the aluminium promotes the consumption of Cu_3Si. Similar results have been obtained by adding $AlCl_3$ to fused CuCl in the reaction with a single crystal of silicon when the Cu_3Si nuclei are pitted in the centre [8]. The formation of cavities inside the Cu_3Si nuclei was thought to be caused by the additive, which promotes the reaction between Cu_3Si and CuCl to form copper. Moreover, the aluminium (> 3 mol %) increased both nucleation rate and lateral growth of Cu_3Si nuclei but decreased slightly the growth rate of the continuous layer of Cu_3Si.
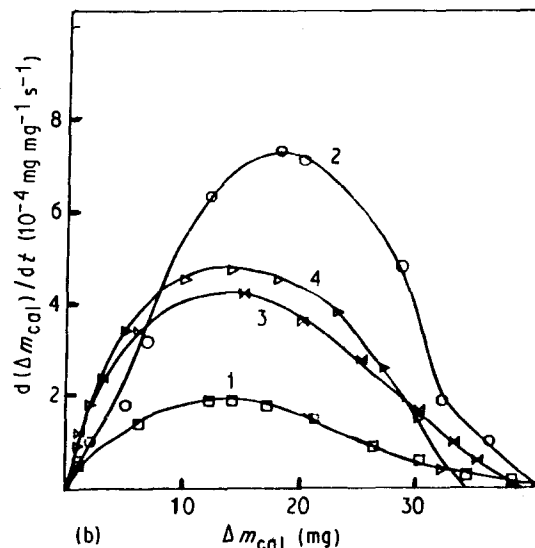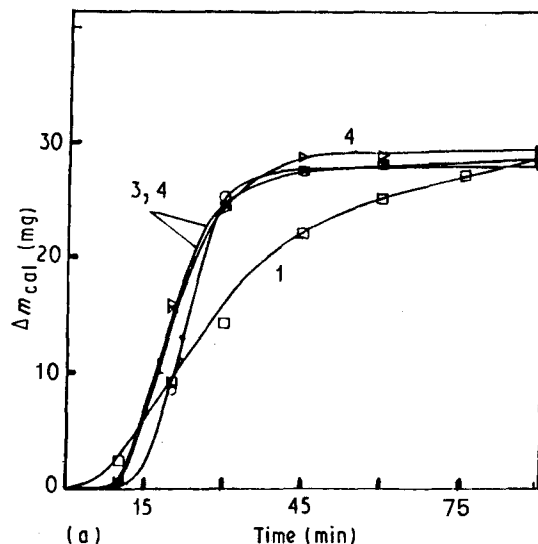
Figure 5 (a) Mass change Δm_{cal} with time and (b) rate $d(\Delta m_{cal}/dt)$ as a function of Δm_{cal} for samples (□) 1, (○) 2, (⋈) 3 and (▷) 4 at 282 °C.

Fig. 5a compares the kinetic curves at 282 °C for samples 1, 2, 3 and 4 and Fig. 5b illustrates the rate curves versus Δm_{cal}. When iron and calcium are added to aluminium (samples 3 and 4) the reactivity of the mixture is decreased after 15 min of reaction but remains greater than that of sample 1 (Fig. 5b). In the case of the reaction between samples 3 or 4 and CuCl (Fig. 6) the evolution of the R_3 ratio is similar to that of R_3 for samples 1 and 2 (Fig. 5). On the other hand, spectacular changes are caused in the evolution of R_1 and R_2, which exhibit a maximum at about 30 min of reaction for sample 3 and 45 min for sample 4. Moreover, as the value of R_1 for sample 3 is 90% greater than that for sample 4, it can be predicted that the rate of Cu_3Si consumption by CuCl is larger for sample 3 and in consequence the copper content increases with the presence of calcium as principal impurity. For sample 4, the R_2 ratio is low and the formation rate of copper is not altered by iron as principal impurity. This behaviour may indicate that the rate of consumption of Cu_3Si is greatly decreased by the presence of this impurity.

(a)

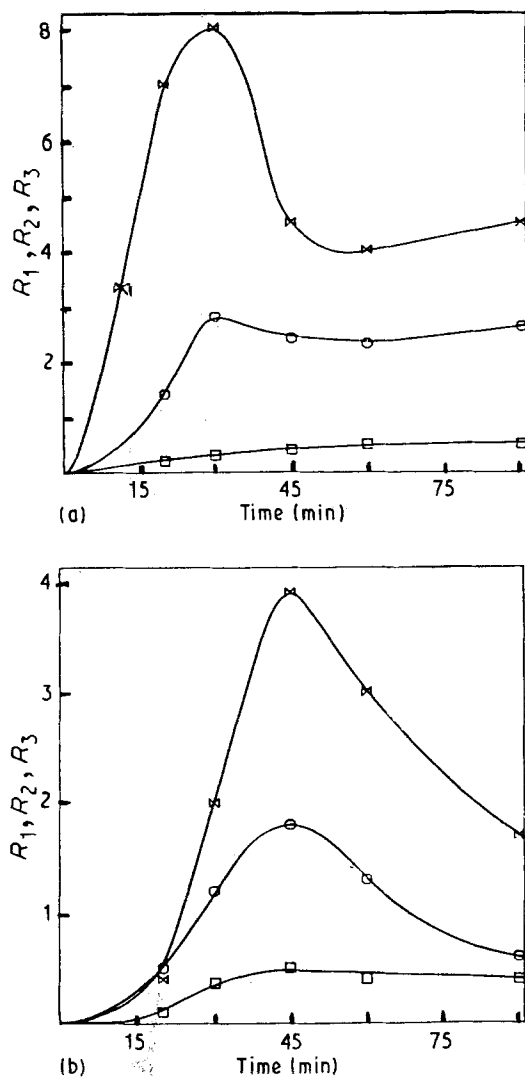*Figure 7* Thermogravimetric curves, $\Delta m = f(T)$, obtained in a vacuum for different silicides: (5) Si_2Ca, (6) Si_2Fe, (7) Si_2Ti, (8) $SiCu_3$; (S) sublimation of CuCl.

(b)

Figure 6 Evolution of ratios (⋈) R_1, (○) R_2 and (□) R_3 as a function of time for (a) sample 3 and (b) sample 4 at 282 °C.

(a)

(b)

3.2. Metal silicides

Generally, the reaction of CH_3Cl with metal silicides (Cu_3Si, Si_2Fe, Si_2Ca, Si_2Ti) has been considered as being determined by the electrostatic interactions between the methyl chloride dipole and the polar metal–silicon surface [9]. As a result of the experiments performed it was established that the place of the copper silicide, as judged from the products of its reaction with CH_3Cl, should be between calcium silicide, titanium silicide and iron silicide. An investigation of the effect of the nature of the silicide on the kinetics of reaction with CuCl was carried out in the temperature range 250–310 °C.

Some heating curves are shown in Fig. 7 for different silicides. Under the applied conditions CuCl starts reacting with Si_2Fe (sample 6) at about 200 °C. Mixing with Si_2Ti (sample 7) or Cu_3Si (sample 8) reduces this temperature for CuCl to 170 °C. Because Si_2Ca (sample 5) is very sensitive to CuCl at room temperature, direct transfer without intermediate exposure to air in a closed system was necessary [10]. When the mixture Si_2Ca–CuCl was made at room temperature, the transformation is effective (Fig. 6) according to the
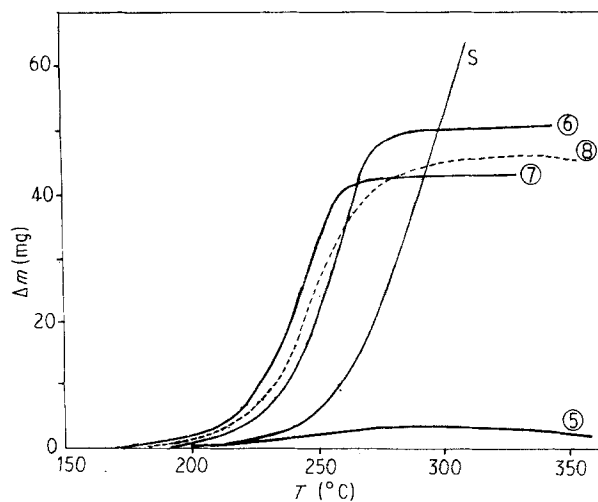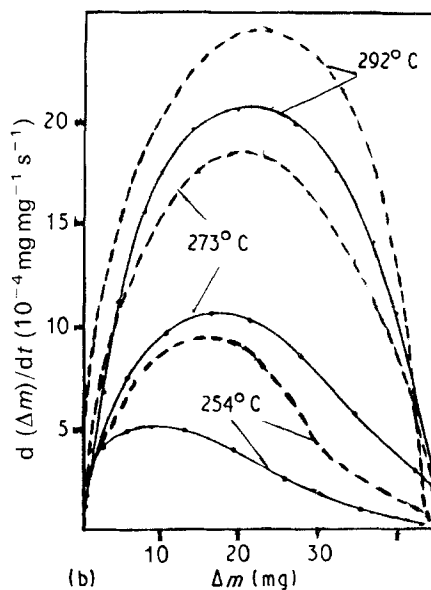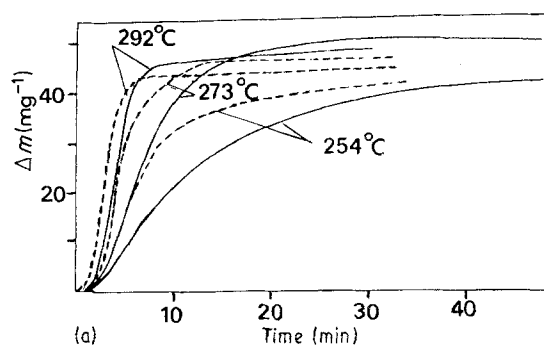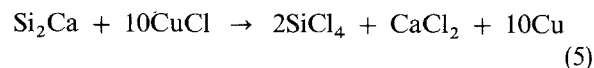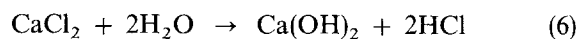
Figure 8 (a) Mass change Δm with time and (b) rate $d\Delta m/dt$ as a function of Δm for (——) sample 6 and (———) sample 7 at different temperatures.

reactions

$$Si_2Ca + 10CuCl \rightarrow 2SiCl_4 + CaCl_2 + 10Cu \quad (5)$$

and

$$CaCl_2 + 2H_2O \rightarrow Ca(OH)_2 + 2HCl \quad (6)$$

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X-ray investigation of the Si_2Ti–CuCl and Si_2Fe–CuCl systems during the course of the reaction indicated only the formation of copper, for example

$$Si_2Ti + 12CuCl \rightarrow 2SiCl_4 + TiCl_4 + 12Cu \quad (7)$$

and

$$Si_2Fe + 11CuCl \rightarrow 2SiCl_4 + FeCl_3 + 9Cu \quad (8)$$

From Fig. 7 it can be seen that the heating curve for Cu_3Si has an intermediate position between Si_2Ti and Si_2Fe. This has to be considered as being determined by the electrostatic interaction between copper chloride dipoles and the polar metal–silicon surface [11]. Also, in this reaction, the reduction or polarization of CuCl may be involved as an elementary step while the rate may be controlled at low temperature.

The kinetic curves of the reduction, $\Delta m = f(t)$ (Fig. 8a), at temperatures ranging from 250 to 310 °C with respect to Si_2Ti–CuCl and Si_2Fe–CuCl systems have an S-shape indicating a typical nucleation and growth mechanism. The corresponding rate curves are represented in Fig. 8b. Thus, in the reduction of CuCl by silicides, the presence of titanium was found to increase the copper formation rate, particularly at 282 °C. It has been reported that a high amount of free copper (not bound to silicon) is harmful to the main reaction, leading to the formation of highly chlorinated silanes [6]. This is attributed to the copper formed, which covers the silicide surface and acts as a barrier for further contact between reactants. In view of the above results it appears that a decrease of the copper content may provide an opportunity to convert a larger part of the silicon before the rapid slow-down of the reactivity starts.

4. Conclusion

A comparison of the reactivity of CuCl with silicon containing as impurities Al, Fe, Ca and Ti revealed that in accordance with kinetic data and X-ray analysis, the most active silicon for the formation of Cu_3Si during a long period is that in which both aluminium and iron are present. A study was made of the qualitative and quantitative composition of the reaction products and of its change during the course of the reaction at 282 °C.

For the reaction of CuCl with silicides such as Si_2Ca, Si_2Fe and Si_2Ti, the results of the kinetic runs, when plotted as mass change versus time, showed a typical S-shape, indicating also a nucleation and growth mechanism but in this case only the copper was detected.

References

1. R. J. H. VOORHOEVE, "Organohalosilanes: Precursors to Silicones" (Elsevier, Amsterdam, 1967) p. 253.
2. R. J. H. VOORHOEVE, J. A. LIPS and J. C. VLUGTER, J. Catal. 3 (1964) 414.
3. G. WEBER, D. VIALE, H. SOUHA, B. GILLOT and P. BARRET, Solid State Ionics 32/33 (1989) 250.
4. A. L. KLEBANSKY and U. S. FIKHTENGOLTS, J. Gen. Chem. 26 (1956) 2535.
5. N. P. LOBUSEVICH, L. A. MALYSHEVA, P. A. PINCHUK, M. I. TAYPIN, L. I. KLEIMENOVA, L. P. SPORYKHINA and L. G. STREKALOVA, J. Appl. Chem. USSR (English translation) 49 (1976) 2194.
6. S. S. TAMHANKAR, A. N. GOKARN and L. K. DORAISWAMY, Chem. Eng. Sci. 26 (1981) 1365.
7. B. GILLOT, H. SOUHA and G. WEBER, Thermochim. Acta 17A (1990) 215.
8. G. WEBER, N. GOURGOUILLON, D. VIALE, B. GILLOT and P. BARRET, React. Solids 6 (1988) 75.
9. R. J. H. VOORHOEVE and J. C. VLUGTER, J. Catal. 4 (1965) 220.
10. H. SOUHA, thesis, University of Dijon, Dijon (1989).
11. B. H. KOLSTER, J. C. VLUGTER and R. J. H. VOORHOEVE, Recueil 83 (1963) 737.