

COMPARATIVE KINETIC STUDY OF THE REACTIONS BETWEEN CuCl AND Si, Cu₃Si OR Cu₅Si POWDERS

H. SOUHA, G. WEBER and B. GILLOT

*Faculté des Sciences Mirande, Laboratoire sur la Réactivité des Solides, associé au C.N.R.S.,
U.A. 23, B.P. 138, 21004 Dijon Cedex (France)*

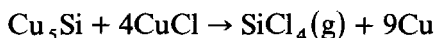
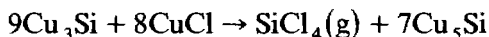
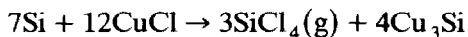
(Received 28 March 1990)

ABSTRACT

Attempts have been made to study the kinetics of the reactions between CuCl and Si, Cu₃Si or Cu₅Si by thermogravimetry (TG). For the three systems it is established that the kinetics of TG in the range 240–290 °C under vacuum are governed by a nucleation–growth mechanism with an activation energy of about 140 kJ mol⁻¹ for the three systems. The effect of the reaction time and of the temperature on the mass change is also discussed, with special emphasis on the presence of Si₂Cl₆.

INTRODUCTION

The reaction of powdered silicon with copper(I) chloride to yield the compound Cu₃Si is a very important process in the production of a variety of silicon polymers from chlorosilanes [1]. Until recently, Cu₃Si was considered to be the result of two successive reactions [2,3]: first, copper chloride is reduced by silicon to produce copper and SiCl₄(g) in small amount, then copper diffuses in the silicon matrix to form Cu₃Si. However, in a previous publication [4], we have established that the reaction between silicon and CuCl produces copper as the final phase, and that this copper results from simultaneous and successive reactions according to the following equations



where Cu₃Si and Cu₅Si are intermediate compounds which react with CuCl, whereas Cu would be the stable end product of the reaction. Moreover, both the reactivity and the solid products of the reaction are significantly affected by certain factors, such as the composition and total pressure of the gas phase, the mixing and grinding operation, the thickness of the SiO₂ film on the grains of Si [5], particle diameter and the proportions of the constituents in the mixture.

The present study was undertaken to investigate further the kinetics of these three reactions, which are associated with a mass loss due to evolution of the silicon tetrachloride occurring during the reduction process. To reach this objective, the experiments were effected under similar conditions (residual pressure, grinding time, silicon oxide layer) throughout this study.

EXPERIMENTAL PROCEDURE

Silicon powder (325 mesh and 99.5% pure), CuCl (300 mesh and 99.999% pure) and Cu₃Si (100 mesh and 99% pure) were obtained from Alfa Products; Cu₅Si (100 mesh) was supplied by Pechiney.

The reaction is followed by monitoring the total mass change of the mixture as a function of temperature or time by means of a MacBain thermobalance with a sensitivity of 0.02 mg. Portions (25 mg) of CuCl + Si (Si/CuCl molar ratio of 0.58), CuCl + Cu₃Si (Cu₃Si/CuCl molar ratio 2.56) or CuCl + Cu₅Si (Cu₅Si/CuCl molar ratio 1.62) mixtures are intimately ground in an agate mortar for 15 min, and 20 mg of the mixture are uniformly spread at the bottom of a scoop suspended from a quartz spring and placed in the reactor of the thermobalance. The reactor is evacuated, outgassed in vacuo (1 Pa) at room temperature for 60 min and preheated at 180°C for 30 min before the sample is heated to the temperature of the experiment. The preheating is useful to remove any moisture present in the sample and to shorten the time required for the sample to reach the selected temperature. The SiCl₄(g) liberated during the reaction is condensed in a liquid-nitrogen trap, and the mass loss is calculated for 100 mg of CuCl.

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

RESULTS AND DISCUSSION

Figure 1 shows the thermogravimetric curves for the sublimation of CuCl when it is placed alone in the scoop (curve d) and the thermal reaction of mixtures of Si/CuCl (curve a), Cu₃Si/CuCl (curve b) and Cu₅Si/CuCl (curve c) under vacuum at 3°C min⁻¹ heating rate. It can be seen that, in the presence of Si or copper silicides, the sublimation temperature of CuCl is lowered by ca. 70°C, accompanied by the simultaneous formation of Cu₃Si, Cu₅Si and Cu for the reduction of CuCl by Si, of Cu₅Si and Cu for the reduction of CuCl by Cu₃Si and of Cu for the reduction of CuCl by Cu₅Si.

The maximal experimental mass loss (Δm_{\max}) for the Si/CuCl and Cu₃Si/CuCl systems was slightly greater than that calculated (Δm_{cal}) in considering the total consumption of CuCl. The difference $\Delta m_{\max} - \Delta m_{\text{cal}}$ was associated with the partial sublimation of CuCl, indicating that a

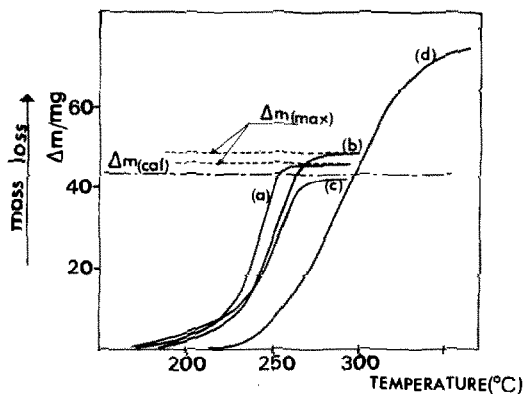


Fig. 1. Thermogravimetric curves in vacuum for: (a) mixture of Si and CuCl (molar ratio 0.58), (b) mixture of Cu_3Si and CuCl (molar ratio 2.56), (c) mixture of Cu_5Si and CuCl (molar ratio 1.62), (d) sublimation of CuCl; Δm_{cal} represents the total consumption of CuCl by silicon or silicides.

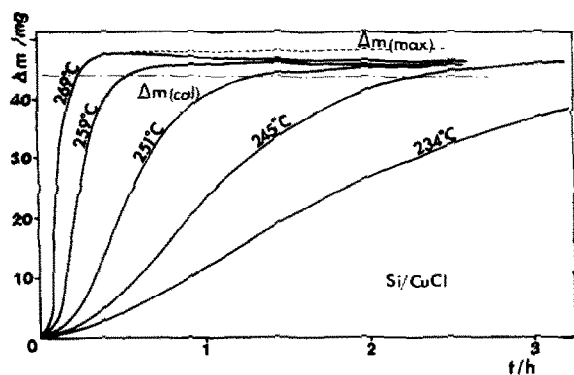


Fig. 2. Mass change Δm with time as a function of temperature for Si/CuCl system.

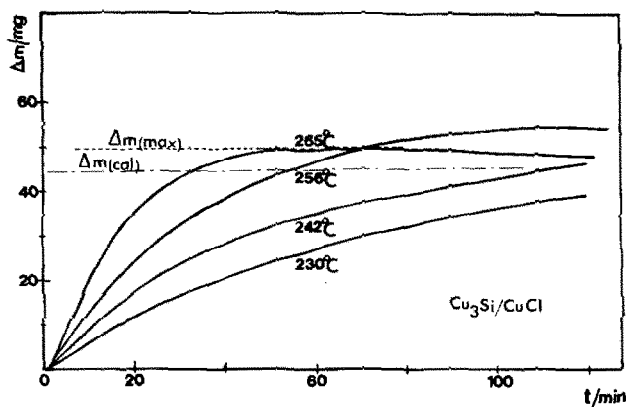


Fig. 3. Mass change Δm with time as a function of temperature for $\text{Cu}_3\text{Si}/\text{CuCl}$ system.

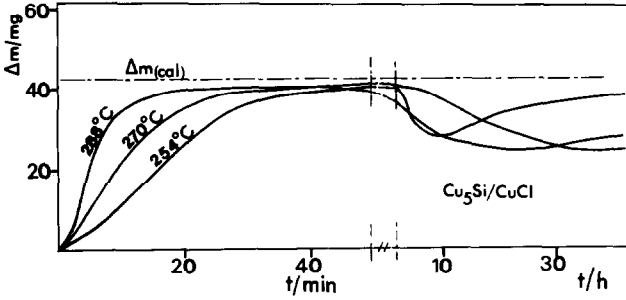


Fig. 4. Mass change Δm with time as a function of temperature for $\text{Cu}_5\text{Si}/\text{CuCl}$ system.

fraction of CuCl in the gaseous state does not react. These observations enabled the study of these reactions by the isothermal mass loss method.

The kinetic curves of the reduction $\Delta m = f(t)$ at different temperatures in respect of the three systems are shown in Figs. 2, 3 and 4. For reaction times below about 1 h, the curves revealed the typical S-shape characteristic of the nucleation growth mechanism of the product phases at the active sites in the crystal, i.e. the rate initially increased, reached a maximum and then decreased. The $d(\Delta m)/dt = f(\Delta m)$ curves represented only for the Si/CuCl system (Fig. 5) allows us to determine the maximum rate $\zeta_i = \Delta m_i / \Delta m_{\max}$ for each system (Table 1) where Δm_i corresponds to the Δm value at which the rate $d(\Delta m)/dt$ is maximum. The kinetic data have been considered

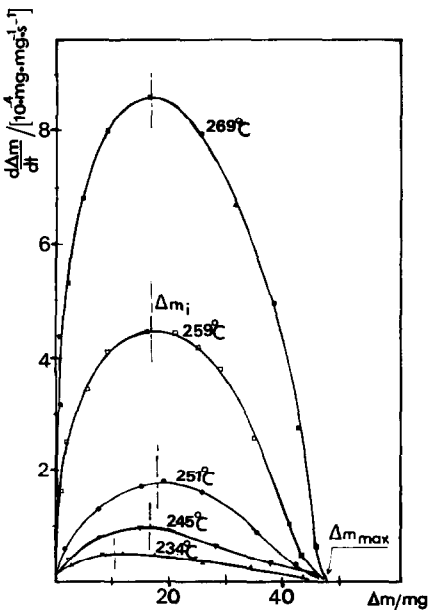


Fig. 5. Rate $d(\Delta m)/dt$ as a function of Δm for Si/CuCl system.

TABLE 1

Maximum rate and activation energies for the reduction of CuCl by Si and the silicides

System	ζ_i	E (kJ mol ⁻¹)
Si/CuCl	0.33	135
Cu ₃ Si/CuCl	0.34	152
Cu ₅ Si/CuCl	0.31	143

solely where ζ_i shows no change with the temperature because a change of ζ_i with temperature indicates a shift in the controlling mechanism of reaction. In a previous study some observations were made regarding the effect of a few more factors, such as grain size, purity and proportion of reactants, and grinding time, that affect the kinetic behaviour [4]. It is evident from Fig. 5 that ζ_i can be considered as constant in the temperature range 240–270 °C. For CuCl/Cu₃Si and CuCl/Cu₅Si systems, the temperature ranges are 240–280 °C and 250–290 °C, respectively.

The isotherms were best fitted with the equation $\log \zeta/(1 - \zeta) = kt$ between $0.30 < \zeta < 0.80$, where ζ represents the transformation degree defined by $\zeta = \Delta m_t / \Delta m_{\max}$ and k is the temperature dependent proportionality constant. This equation is the integrated form of the Prout–Tompkins equation [6]. The apparent activation energies, E , calculated by plotting $\log k$ against $1/T$ at different constant values of ζ are listed in Table 1. For the Si/CuCl system the value agrees reasonably well with the values ranging from 127 to 173 kJ mol⁻¹ reported in the literature for purified Si samples [2,7] but differs from that obtained by Tamhankar et al. [3] when leached ferrosilicon (with 5% of Fe) is used (210 kJ mol⁻¹) instead of pure silicon.

The similar values of the activation energies found for the reaction of CuCl with copper silicides, in spite of granulometric differences between Si, Cu₃Si and Cu₅Si, may conceivably be explained if the rates of decomposition of Cu₃Si and Cu₅Si to give Cu are comparable.

The X-ray investigations on the Cu₅Si/CuCl system during the course of the reaction indicate only the formation of copper, which confirms the reduction of CuCl by Cu₅Si in a single step. The reaction of CuCl with Cu₃Si leads to Cu₅Si and Cu, these two phases being formed simultaneously. In the phases obtained during the reduction of CuCl by Si, X-ray diffraction patterns indicate the presence of Cu, Cu₃Si and Cu₅Si. Figure 6 presents the evolution of spectrum as a function of reaction time, which shows that Cu₃Si and Cu are the only reaction products for $t < 30$ min (curves a and b) whereas, for $t > 30$ min, Cu₅Si was also formed. It was found that the quantitative ratio of Cu₅Si to Cu₃Si increases with increase of the reaction time.

As shown in Figs. 2, 3 and 4, the $\Delta m = f(t)$ curves are identical in shape so long as the temperature does not rise above 260 °C and the reaction time

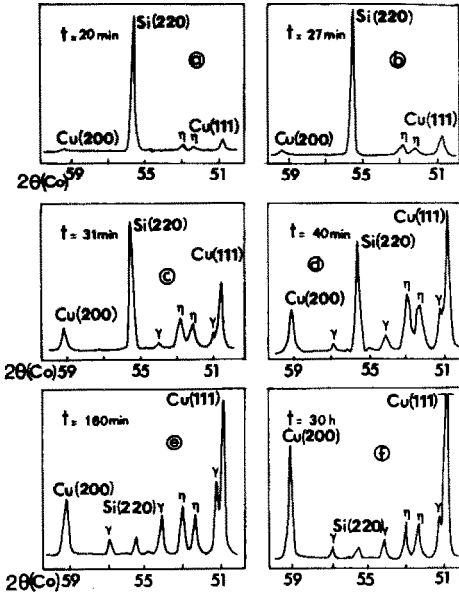


Fig. 6. X-ray diffraction patterns of Si/CuCl system at 251°C showing the evolution of formed phases for different times of reaction: η , Cu_3Si ; γ , Cu_5Si .

is less than 1 h. From a comparative study of the isotherms obtained at 288°C (Fig. 7), it can be observed that, for reaction times above about 50 min, the $\Delta m = f(t)$ curves exhibit a mass gain and then against a mass loss for long reaction times; this behaviour is particularly marked for the $\text{Cu}_5\text{Si}/\text{CuCl}$ system (Fig. 7, curve c).

This behaviour can be ascribed to a small amount of $\text{Si}_2\text{Cl}_6(\text{g})$ which forms as well as SiCl_4 . As suggested by Kohlschutter and coworkers [8,9] for

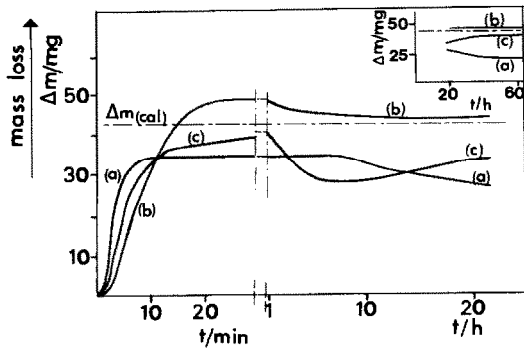


Fig. 7. Comparative reactivity at 288°C of the Si/CuCl (a), $\text{Cu}_3\text{Si}/\text{CuCl}$ (b) and $\text{Cu}_5\text{Si}/\text{CuCl}$ (c) systems.

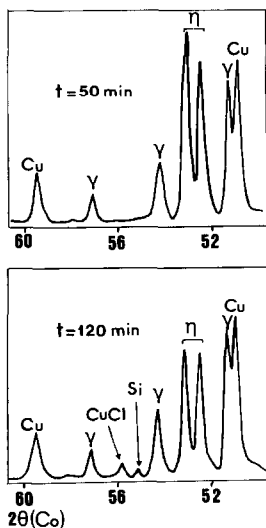
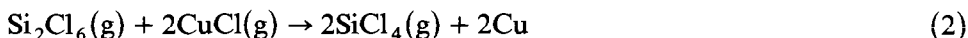
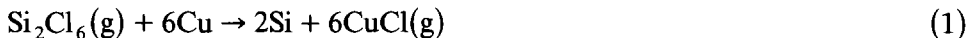


Fig. 8. X-ray diffraction patterns of the $\text{Cu}_3\text{Si}/\text{CuCl}$ system at 288°C showing the presence of CuCl and Si for a reaction time of 2 h. η , Cu_3Si ; γ , Cu_5Si .

the Si/CuCl reaction, Si_2Cl_6 is supposed to react above 280°C with Cu and CuCl to give Si and SiCl_4 according to the following reactions



According to this hypothesis, we are tempted to suggest that the mass gain corresponds to the reaction of $\text{Si}_2\text{Cl}_6(\text{g})$ with CuCl [eqn. (2)] and that the mass loss that follows results from the reaction between $\text{Si}_2\text{Cl}_6(\text{g})$ and Cu [eqn. (1)]. This mechanism is also supported by the X-ray analysis, where the additional peaks (indicated by an arrow) observed on Fig. 8 (curve b) for the $\text{Cu}_3\text{Si}/\text{CuCl}$ reaction can be attributed to Si and CuCl according to eqn. (1).

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