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The influence of various factors on the kinetics of the reaction between copper(I) chloride and germanium

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Abstract

The kinetics of the reaction between CuCl and Ge powders has been studied under vacuum by means of thermogravimetry in the range 226–274° C. The reactivity of the Ge/CuCl system is affected significantly by the mixing operation, the thickness of the GeO_2 film on the Ge particles and the proportion of Ge and CuCl in the mixture. It is established that the kinetics is governed by a nucleation-growth mechanism with an apparent activation energy of 75 ± 3 kJ mol^{-1} Cu_3Ge, Cu_5Ge and Cu were identified as reaction products and a successive reaction mechanism is proposed with Cu as the final phase.

INTRODUCTION

We reported recently [1,2] that the reaction between copper(I) chloride and silicon powders is influenced strongly by the presence of an oxidation layer on the silicon and by the grinding which increases significantly the rate of the reaction. We wondered whether such a strong influence could occur in other similar systems, such as the reaction between copper(I) chloride and germanium or titanium. It has been shown that in the reaction between CuCl and Si, the solid products of the reaction are Cu_3Si, Cu_5Si and Cu whereas Cu_3Si and Cu_5Si are intermediate compounds which react with CuCl to give Cu as final phase. Silicon are germanium have the same crystal structure and the phase diagram of the copper–silicon and copper–germanium systems are much alike [3]. In the low temperature range (< 500° C), two compounds exist: the γ- and ζ-phases or Cu_5Si and Cu_5Ge, respectively, for compositions below 19 at.% Ge and the η- and ϵ-phases or Cu_3Si and Cu_3Ge, respectively, for compositions at approximately 24 at.% Ge. The ζ-phase has a hexagonal close-packed (hcp) structure (A3-type) with

$a = 0.2596$ and $c = 0.4224$ nm and is regarded as a 3 : 2 electron compound based on the composition Cu_5Ge with 16.7 at.% Ge [4,5]. The ϵ-phases consist of a group of 3 compounds but the θ-phase which is evident at low temperatures has an orthorhombically distorted A3-type structure with $a = 0.2642$, $b = 0.4537$ and $c = 0.4221$ nm at 25 at.% Ge [6,7]. Both the Cu_3Ge and Cu_5Ge phases were reported to have a high initial reactivity and selectivity for direct synthesis of dimethyldichlorogermane [8].

To our knowledge the reaction between CuCl and germanium has not been reported previously. Thus, we have used thermogravimetry to study the kinetics of this reaction which is associated with a mass loss owing to evolution of the germanium tetrachloride which occurs during the reduction process according to the global equation

$$Ge + 4CuCl \rightarrow GeCl_4 + 4Cu \qquad (1)$$

Special attention was paid to the occurrence of intermediate compounds such as Cu_3Ge and Cu_5Ge, and the effects of a few more factors such as the mixing operation, the thickness of the GeO_2 film on the grains of Ge and the proportion of Ge and CuCl in the mixture.

EXPERIMENTAL

The total mass change due to evolution of $GeCl_4$ gas was measured as a function of time by means of a MacBain thermobalance with a sensitivity of 0.02 mg for various CuCl and Ge loadings. Ge (100 mesh, 99.999% pure, lot 78595, Alfa Products) and CuCl (99.999% pure, lot 400151, Alfa Products) powders were mixed intimately and ground in an agate mortar for different times for a mole ratio of Ge : CuCl greater than 0.25. Then 15 mg of the mixture was spread as a thin layer on the balance arm; the reactor was then evacuated, outgassed in vacuo (1 Pa) for 2 hours at room temperature, and then for one hour at 190 ° C before the sample was heated to the temperature of the experiment. The $GeCl_4(g)$ liberated during the reaction was condensed in a liquid-nitrogen trap and the mass loss was calculated for 100 mg of CuCl.

A comparative study was also carried out for powdered Ge samples, either etched in 40% HF solution to minimise the GeO_2 layer thickness or oxidized in air at 600 ° C for various reaction times to produce a GeO_2 growth which varies in thickness from 23 to 51 nm. The thickness of the GeO_2 layer was calculated from the mass gain after oxidation by assuming that all the Ge grains are spherically shaped with a mean radius of 4.50 μm. The thickness of the GeO_2 film which always covered the surface (native oxide with hexagonal form) was calculated from thermogravimetric data at 500 ° C for a complete reduction of the original GeO_2 by H_2 [9] according to the reaction

$$GeO_2 + 2H_2 \rightarrow Ge + 2H_2O \qquad (2)$$

The analysis gave a thickness of 5 nm. The experiments were also conducted by substituting Ge for GeO_2. The solid products of the reaction were identified by X-ray diffractometry.

To ascertain whether the solid reaction products analysed are the same as in thermogravimetry, a parallel set of these experiments was conducted in a closed system where $GeCl_4(g)$ was allowed to remain in contact with the sample during the course of the reaction. After grinding in an agate mortar, the sample was placed in the glass reactor which was evacuated (10^{-3} Pa) at room temperature, and sealed and then heated at 340 °C for 3 days.

RESULTS AND DISCUSSION

Kinetic studies

The studies were made in order to determine the influence of the parameters causing changes in the rate of the reaction.

The effect of mixing and grinding operations

The effect of the mixing and dry grinding operations are shown in Fig. 1. Curves 2–6 show the variation in the total mass loss with time for a mixed sample (curve 2) and for a sample ground in an agate mortar for 1, 2, 5 and 10 min with a Ge : CuCl molar ratio of 1.10 (curves 3–6). Curve 1 shows the time dependence of the sublimation of copper chloride when it is placed alone in the scoop.

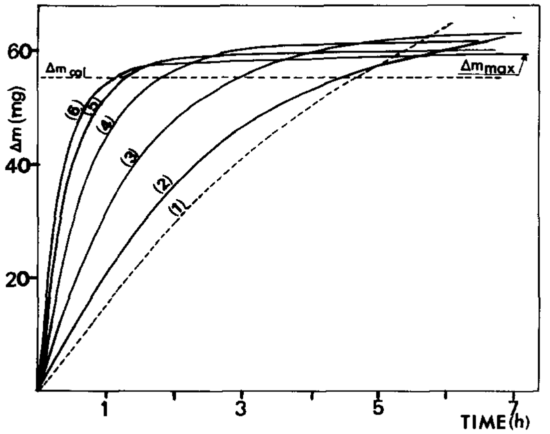

Fig. 1. Effect of the grinding duration on the reactivity of the Ge/CuCl system with a molar ratio of 1.10 at 240 °C: 1, sublimation of CuCl; 2, mixed sample; 3, sample ground for 1 min; 4, sample ground for 2 min; 5, sample ground for 5 min; 6, sample ground for 10 min.
]

The theoretical maximum mass loss (Δm_{cal}) of the system is calculated ($\Delta m = 54.2$ mg, broken line) for a complete reduction of CuCl by Ge according to the reaction

$$Ge + 4CuCl \rightarrow GeCl_4 + 4Cu \qquad (3)$$

It may be seen from Fig. 1 that the deviation between the experimental (Δm_{max}) and the theoretical maximum mass loss decreases with longer grinding times, which implies that the mass fraction of CuCl, which sublimes without reaction with Ge, decreases as the grinding time is increased. The reaction is enhanced by grinding the sample, the reactivity increasing with longer grinding times. This behaviour is believed to be due to the grinding which is effective in removing germanium dioxide (native oxide) from the germanium particles which results from Ge–O bond cleavage and generates clean crystallographic planes. The GeO_2 film, like a chemical barrier, plays a significant part in the initiation and progress of the reaction. Therefore, we studied the effects of a germanium oxide layer on the Ge/CuCl reaction where the oxide layer is increased deliberately by thermal oxidation of germanium or where the native oxide layer is thinned by chemical etching processes.

The effect of the thickness of the GeO_2 layer on the Ge particles

The effect of oxide layer thickness on kinetic behaviour was demonstrated directly by observing the loss in mass Δm with time (curves 1–5, Fig. 2) when mixtures of Ge and CuCl were heated under vacuum at 240 ° C. The reactivity of the Ge/CuCl system is enhanced as the thickness of the GeO_2 layer decreases whereas the experimental mass loss was greater than that calculated assuming the total comsumption of CuCl by Ge. The difference

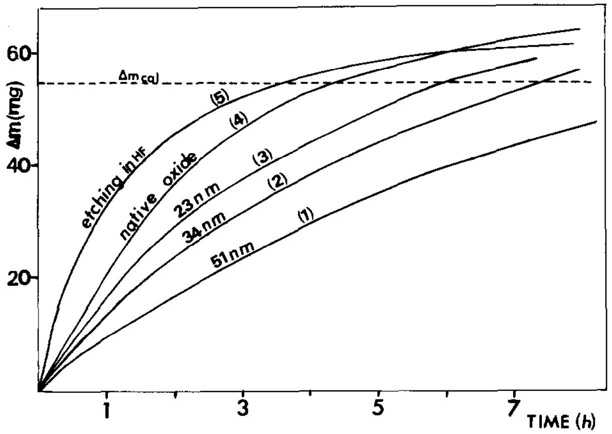

Fig. 2. Effect of the thickness of the GeO_2 layer on the reactivity of the Ge/CuCl system for a mixture heated for 10 min at 240 ° C.

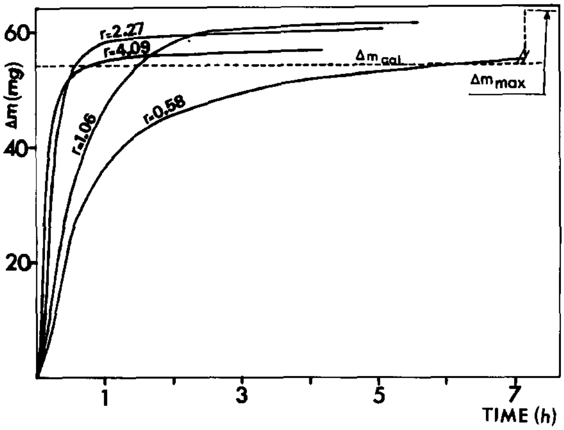

Fig. 3. Effect of the molar ratio of Ge to CuCl on the reactivity of the Ge/CuCl system for a grinding time of 5 min at 260 ° C.

was associated with the partial sublimation of CuCl which increased with the thickness of the oxide layer.

The proportion of Ge and CuCl in the mixture

The molar ratio of Ge to CuCl was varied from 0.58 to 4.10 for a grinding time of 5 minutes. Figure 3 shows that the reactivity of the system at 260 ° C increases with higher mass percentages of Ge, because of the increase in the reactive area of Ge. Moreover, in this case, the mass fraction of sublimated CuCl which does not react with Ge increases with a decrease in the molar ratio.

The effect of temperature

The kinetic curves $\Delta m = f(t)$ at temperatures ranging from 226 to 274 ° C are shown in Fig. 4. For reaction times below about 15 minutes, the curves are the typical S-shape characteristic of the nucleation growth mechanism of the phases formed at the active sites in the crystal, i.e. the rate increased initially, reached a maximum and then decreased. The $d(\Delta m)/dt = f(\Delta m)$ curves (Fig. 5) allow us to determine the maximum rate located at $\alpha_i = \Delta m_i / \Delta m_{\max}$ where Δm_i corresponds to the Δm value at which the rate $d(\Delta m)/dt$ is maximum. The kinetic data were considered only where α_i shows no change with temperature, because a change in α_i indicates a shift in the controlling mechanism of the reaction [10]. In order to prevent the CuCl sublimation which affects the kinetic behaviour [1] and changes the α_i value, we enhanced the reactivity by using a high percentage of Ge (molar ratio of 4.10) and a long grinding time (10 minutes). It is evident from Fig. 5 that α_i can be considered as constant in the range 226–274 ° C.

The isotherms were best fitted with the equation $\ln \alpha/(1-\alpha) = kt$ for $0.15 < \alpha > 0.75$ where α is the fractional mass change at time t defined by

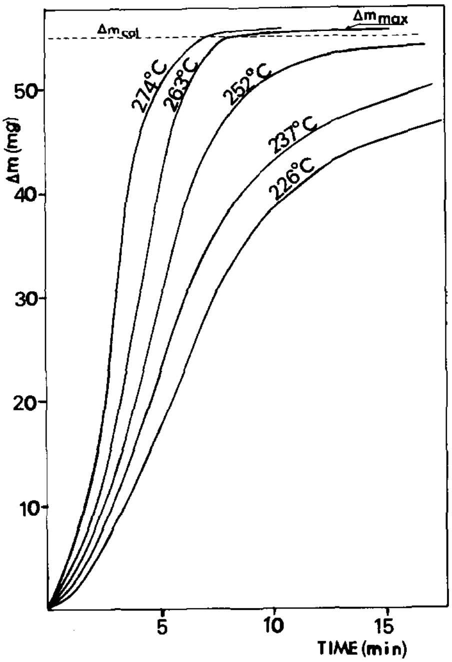

Fig. 4. Mass loss Δm against time as a function of temperature.

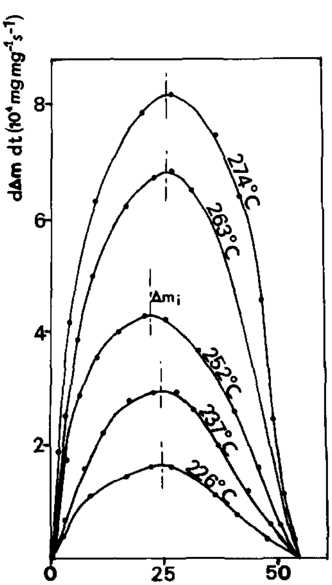

Fig. 5. Rate $d(\Delta m)/dt$ as a function of Δm.

$\alpha = \Delta m_t/\Delta m_{\max}$, and k is the rate constant. This equation is the integrated form of the Prout–Tompkins equation [11]. The apparent activation energy E, calculated by plotting ln k against $1/T$ at different constant values of α, is 75 kJ mol^{-1}, standard deviation 3 kJ mol^{-1} (least-squares method). If we compare the activation energy obtained for the reaction between Ge and CuCl with that for the reaction between Si and CuCl (75 and 125 kJ mol^{-1} [12]), respectively, one can see that the reaction rate for the Si/CuCl system is much slower. As postulated by Becht et al. [12] for the solid state reaction between copper and silicon, a barrier is present on the silicon which is nearly impenetrable by CuCl and results in an incubation time at low temperature [1]. The reactions of silicon are determined by the presence of an oxidation layer. The stability of the oxidation layer on germanium is much lower [13]. Some evidence for this statement has been found in the literature, namely the oxidation of copper–germanium and of copper–silicon alloys [13,14].

Solid products of the reaction

In the course of this study it became necessary to identify the phases formed during the reaction between Ge and CuCl by X-ray diffractometry. For this purpose, experiments were conducted in a closed system for three molar ratios of Ge to CuCl: 0.25, 0.45 and 0.58 corresponding to an almost selective formation of Cu, Cu_5Ge and Cu_3Ge according to the equations

$$\mathrm{Ge} + 4\mathrm{CuCl} \rightarrow \mathrm{GeCl_4} + 4\mathrm{Cu} \tag{4}$$

$$(9/5)\mathrm{Ge} + 4\mathrm{CuCl} \rightarrow \mathrm{GeCl_4} + (4/5)\mathrm{Cu_5Ge} \tag{5}$$

$$(7/3)\mathrm{Ge} + 4\mathrm{CuCl} \rightarrow \mathrm{GeCl_4} + (4/3)\mathrm{Cu_3Ge} \tag{6}$$

After 3 days of reaction at 340 °C, X-ray diffraction analysis indicated the presence of Cu only for the reactant ratio of 0.25 according to eqn. [4]. For reactions (5) and (6), Cu_5Ge (Fig. 6) and Cu_3Ge (Fig. 7) were detected and the d values were found to be very close to those reported in the literature

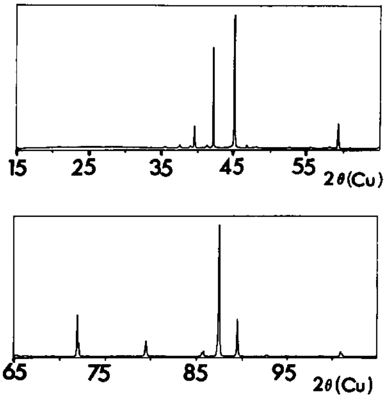

Fig. 6. X-ray diffraction patterns of Cu_5Ge (molar ratio of 0.45).

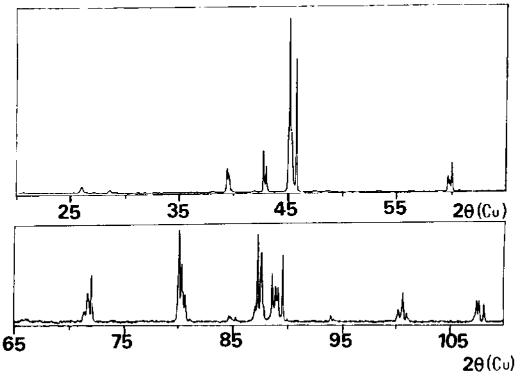

Fig. 7. X-ray diffraction patterns of Cu_3Ge (molar ratio of 0.58).

for Cu_5Ge and Cu_3Ge alloy systems [5,15] prepared by reaction between copper and germanium with 12 and 24 at.% Ge, respectively. Concerning the Cu_3Ge phase, the homogeneity region is much wider, and at 27.5 at.% Ge, the structure changes becoming hcp with $a = 0.420$ nm and $c/a = 1.20$. In addition, for reaction times of less than 3 days, CuCl reacts with Ge to give a mixture of Cu_3Ge, Cu_5Ge and Cu suggesting that these reactions are successive.

Based on consideration of the X-ray diffraction data, the phases obtained during thermogravimetry after the reaction between Ge and CuCl can be confirmed as Cu, Cu_5Ge and Cu_3Ge (Figs. 8–10). It should be emphasised that the thickness of the oxide layer has a great influence on the amount and proportion of phases formed. In comparison with the Ge treated in HF (Fig. 8), commercial Ge (Fig. 9) and Ge covered with an oxide layer of 23 nm (Fig. 10) show a decrease in the intensity of the peaks, indicating that the reaction is inhibited by the oxide layer. Moreover, Cu and Cu_5Si are formed preferentially in the presence of thick oxide layers.

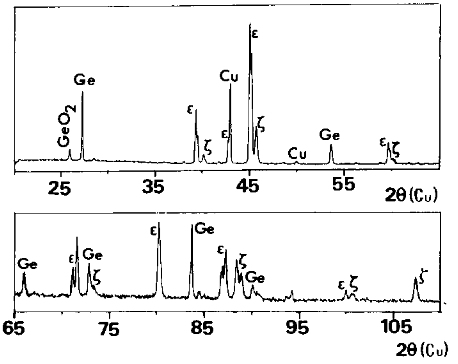

Fig. 8. X-ray diffraction patterns obtained for the reaction between CuCl and Ge after etching of Ge in HF.

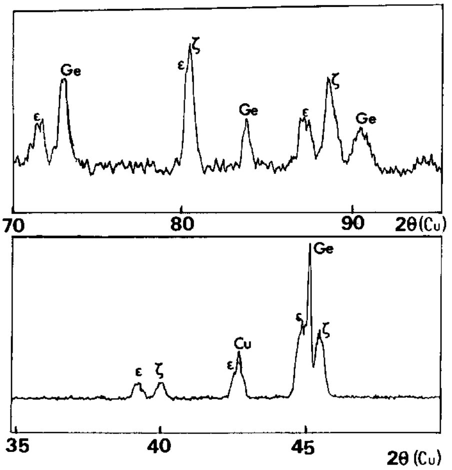

Fig. 9. X-ray diffraction patterns obtained for the reaction between CuCl and Ge covered with an oxide layer of about 5 nm (native oxide).

The formation of copper as the final phase may be explained if simultaneous and successive reactions are taken into account

$$7Ge + 12CuCl \rightarrow 3GeCl_4 + 4Cu_3Ge \tag{7}$$

$$9Cu_3Ge + 8CuCl \rightarrow 2GeCl_4 + 7Cu_5Ge \tag{8}$$

$$Cu_5Ge + 4CuCl \rightarrow GeCl_4 + 9Cu \tag{9}$$

It is apparent from the X-ray diffraction data that the intermediate Cu_3Ge compound was consumed preferentially by CuCl when the reactivity of the mixture decreased, i.e. for thick oxide layers and when the grinding time was decreased.

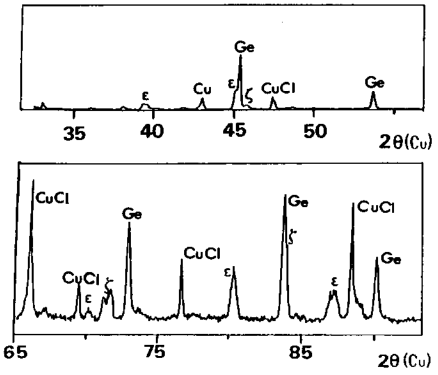

Fig. 10. X-ray diffraction patterns obtained for the reaction between CuCl and Ge covered with an oxide layer of 23 nm.

CONCLUSIONS

The reaction of Ge with CuCl was first carried out at constant temperature by means of thermogravimetry to study the variation of the mass loss with time. The reaction is affected by the time of mixing and grinding, by the thickness of the GeO_2 layer and by the proportion of Ge and CuCl in the mixture. The reactivity is greatest for ground samples with a high molar ratio of Ge to CuCl. The kinetic curves are sigmoidal and the data show a good fit with the Prout and Tompkins equation with an apparent energy of 75 ± 3 kJ mol^{-1}.

Copper is considered to be formed through successive reactions according to the following scheme: $Ge + CuCl(g) \rightarrow Cu_3Ge \rightarrow Cu_5Ge \rightarrow Cu$. In such a scheme, Cu is the final product of the reaction whereas Cu_3Ge and Cu_5Ge are intermediates which react with CuCl. Gaseous CuCl may play a significant part in the initiation of the reaction [1]. Therefore, because of the relative instability of the oxidation layer on germanium, its reaction with CuCl is much less hindered by a reaction barrier than for the reaction between CuCl and Si, the Si being covered with a SiO_2 layer which is nearly impenetrable by CuCl.

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