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Reactivity of Cu_3Si of different genesis towards copper(I) chloride

H. Souha[a,b], F. Bernard[a], E. Gaffet[c], B. Gillot[a,*]

[a]Laboratoire de Recherches sur la Réactivité des Solides, UMR 5613, Université de Bourgogne,
9, Avenue Alain Savary, BP 47870 F-21078 Dijon, Cedex, France
[b]Laboratoire de Chimie Physique, Faculté des Sciences Dhar El Mehraz, BP 1716 Fès, Morocco
[c]UPR A806 CNRS, Groupe 'Nanomatériaux', Université de Technologie de Belfort-Montbéliard,
F-90010 Belfort, Cedex, France

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Abstract

A comparative study of the reactivity between copper(I) chloride and three types of Cu_3Si obtained in a molten medium (Cu_3Si-Ref) and from mechanical activation following an annealing process (Cu_3Si-M2AP) or a self-propagating high-temperature synthesis (Cu_3Si-MASHS) was performed by thermogravimetry under vacuum using non-isothermal and isothermal methods of kinetic measurement. It was established that for the three Cu_3Si/CuCl systems, the acceleration and decay stages in the temperature range 145–215°C are very closely approximated by an equation of the Prout–Tompkins type where an autocatalytic process was proposed. The lower apparent activation energy obtained for the Cu_3Si-MASHS/CuCl system (63 $kJ\ mol^{-1}$ against 68 and 78 $kJ\ mol^{-1}$ for Cu_3Si-M2AP and Cu_3Si-Ref, respectively) has been attributed to a small grain size which induces nanoscale contacts between reactants and impedes CuCl to sublime. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Cu_3Si/CuCl system; Mechanically activated powders; Thermogravimetry; Nucleation-growth; Autocatalytic process

1. Introduction

Methylchlorosilanes, in particular, dimethyldichlorosilane, which are the starting materials for the production of a variety of silicones, are synthesized by a gas–solid reaction between CH_3Cl and excess silicon in the presence of the alloy Cu_3Si (the so-called η-phase) as catalyst [1–4]. In practice, a large quantity of silicon is initially reacted in the solid phase with a small quantity of CuCl (8–10%) to prepare the contact mass for the main reaction. The contact mass consists of silicon and catalytic quantities of the Cu_3Si phase and its selectivity is defined by the ratio CH_3SiCl_3/$(CH_3)_2SiCl_2$. Most researchers consider that the formation of Cu_3Si is accomplished by the reaction between Cu and CuCl to give finely divided Cu and gaseous $SiCl_4$, Cu then diffuses into the remaining Si matrix to form Cu_3Si [5].

We have previously established [6] that the reaction between Si and CuCl can form the Cu_3Si, Cu_5Si and Cu phases through successive reactions according to

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[*] Corresponding author. Tel.: +33-3-80-39-61-42; fax: +33-3-80-39-61-67.
E-mail address: bgillot@satie.u.bourgogne.fr (B. Gillot)

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the scheme:

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

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

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

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 above reactions are the overall reactions, and one of the elementary steps 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).

The formation of Cu_3Si and its reactivity with CuCl have already been studied by different methods such as those using solid–solid reactions, solid–gas reactions [7,8] or melting environment [9]. Nevertheless, due to the complexity of the reaction mechanism and the difficulty of obtaining a pure Cu_3Si, in this paper, we report a comparative study of the reactivities of three samples of Cu_3Si of which two are prepared by mechanical activation (MA) of Cu and Si powder mixture. This mechanical high-energy ball milling was used to activate an annealing process (AP) or a self-propagating high-temperature synthesis (SHS) reaction. The kinetics of these three Cu_3Si/CuCl reactions which results in a change in mass due to evolution of $SiCl_4$ gas following the global reaction

$$Cu_3Si + 4CuCl \rightarrow 7Cu + SiCl_4 \quad (4)$$

has been investigated by thermogravimetry under vacuum.

2. Reactants and analytical methods

Three different powder samples of Cu_3Si were used:

One prepared from Cu and Si in a molten medium at 880°C. This powder with a grain size close to 300 nm is referred to hereafter as Cu_3Si-Ref. The X-ray analysis reveals in addition to the Cu_3Si phase, the presence of a large proportion of copper (Fig. 1c).

Two other Cu_3Si powder referred as Cu_3Si-M2AP and Cu_3Si-MASHS were prepared by mechanical high-energy ball milling. Pure elemental powders (3Cu+Si) were sealed into 45 ml stainless steel vials

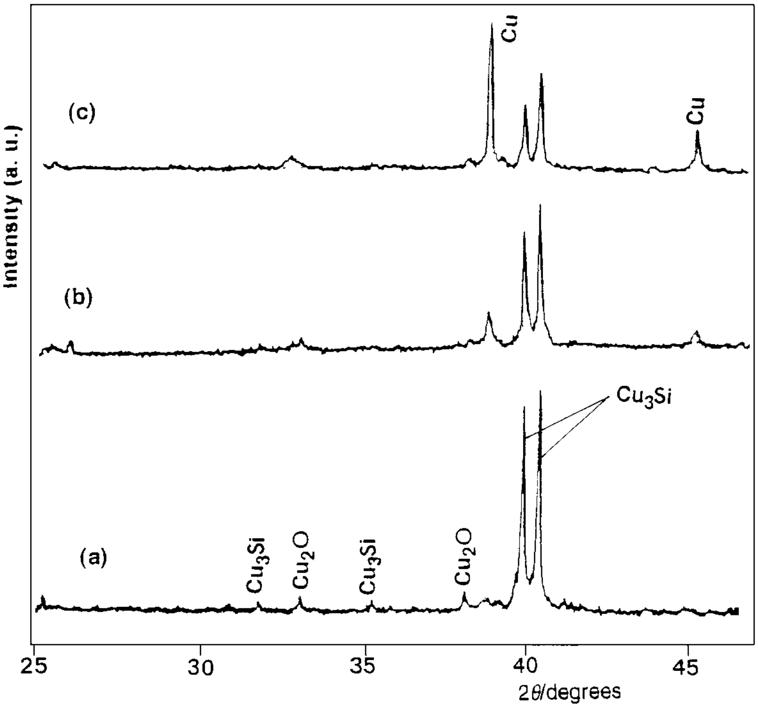

Fig. 1. X-ray diffraction patterns of Cu_3Si: (a) Cu_3Si-MASHS; (b) Cu_3Si-M2AP; (c) Cu_3Si-Ref.

with four stainless steel balls (15 mm in diameter, 14 g in weight) under enclosed air. The ball to powder mass ratio was 6/1. Mechanical activation was performed using a planetary ball mill, hereafter described as the G5 machine, which allows shock frequency and shock energy to be independently selected [10]. The vials were fixed onto a rotating disc (rotation speed Ω) and rotated in the opposite direction to the disc with a speed ω. The milling duration was equivalent to 2 h to avoid the formation of some intermetallic fractions, but to form a chemical gradient at a nanoscale. G5/350/50/2 h ball milling condition was selected to study the reactivity under extreme thermal conditions of an 3Cu+Si mechanically activated powders. In order to obtain the pure Cu_3Si compound, the mechanical activation was followed by a second step which consists of a high temperature annealing (500°C for 24 h) for Cu_3Si-MA2P and of a self-propagating low-temperature synthesis reaction (180°C for 10 s) for Cu_3Si-MASHS [11,12]. X-ray diffraction patterns of the solid products formed show that only the mechanical activation step added to the SHS process leads to the formation of Cu_3Si without copper formation (Fig. 1a). Small amounts of copper were observed in Cu_3Si prepared using the M2AP process (Fig. 1b). The grain size determined by XRD profile analysis and scanning electron microscopy were 150 and 80 nm, respectively.

Thermogravimetric analysis (TG) was used first to determine the main features of the reaction by investigating the mass loss from the Cu_3Si sample during reduction. The total mass change due to evolution of $SiCl_4$ was measured as a function of time by means of a Setaram B70 thermobalance with a sensitivity of 0.02 mg. Cu_3Si and CuCl (300 mesh, 99.999% pure, lot 400151, Alfa Products) powders were mixed intimately and manually ground at room temperature under an inert atmosphere in an agate mortar for 15 min in a reactant ratio Cu_3Si:CuCl=1.50:1.00 corresponding to an excess of Cu_3Si. 50 mg of the mixture was subsequently evacuated, outgassed in vacuo (1 Pa) for 1 h at room temperature and then for 1 h at 70°C before the sample was heated to the temperature of the experiment. The preheating at 70°C is useful to remove any moisture present and to shorten the time required for the mixture to reach the selected temperature. The $SiCl_4(g)$ liberated during the reaction was condensed in a liquid nitrogen trap and the mass loss was calculated per 100 mg of CuCl.

X-ray diffraction patterns were recorded on an ‘INEL CPS 120’ linear counter (curved position sensitive) equipped with monochromatized Cu K_α radiation and calibrated by a quartz standard. The resolution was 0.02° (2θ) at 2 deg min^{-1}. The morphological analysis was carried out with a scanning electron microscopy (SEM ‘Cambridge’ 250 MK2).

3. Results

3.1. Non-isothermal reduction

Fig. 2 shows the thermogravimetric curves $\Delta m = f(T)$ at a heating rate of 3°C min^{-1} for the sublimation of CuCl, when it is placed alone in the scoop (curve 1) or mixed with an inert oxide such as Al_2O_3 (curve 2). In the absence of an inert oxide, the sublimation temperature of CuCl is lowered by ca. 40°C. As a result, the temperature at which CuCl begins to react with Cu_3Si can serve as a criterion for the reactivity of the mixture. For comparison, curves 3, 4 and 5 give the variation of mass loss with temperature for Cu_3Si-Ref, Cu_3Si-M2AP and Cu_3Si-MASHS, respectively. The theoretical maximum mass loss of the system is calculated (Δm_{cal}=42.8 mg, dashed line) for the complete reduction of CuCl by Cu_3Si according to reaction (4). It can be seen from Fig. 2 that the difference between the experimental (Δm_{exp}) and the theoretical maximum mass loss (Δm_{cal}) decreases as the grain size of Cu_3Si is diminished, that is, when the reactive surface is larger. This implies that the mass fraction of CuCl which sublimes without reaction decreases as the grain size is decreased.

We can also postulate, that because the vaporization of CuCl starts at about 160°C, the mass loss from the mixture below this temperature is only due to a solid–solid reaction between CuCl and Cu_3Si. Above this temperature, we have also to consider that the solid–gas reaction prevails.

3.2. Isothermal reduction

The isothermal TG curves $\Delta m = f(t)$ for the reaction between CuCl and the three types of Cu_3Si are shown in Figs. 3–5 (curves (a)). These curves have an

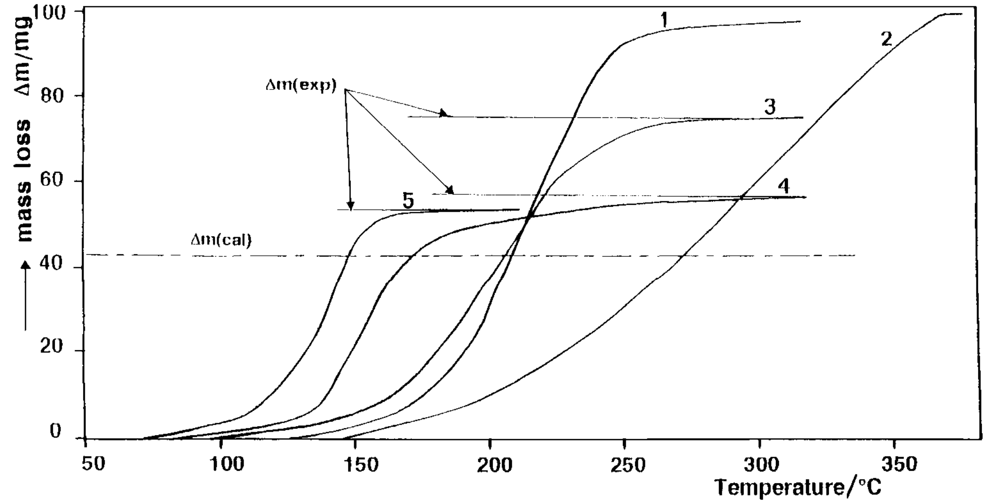

Fig. 2. Curves $\Delta m = f(T)$ obtained in vacuum for the reaction between Cu_3Si and CuCl powders: (1) CuCl alone in the scoop; (2) CuCl mixed with an inert oxide; (3) Cu_3Si-Ref; (4) Cu_3Si-M2AP; (5) Cu_3Si-MASHS.

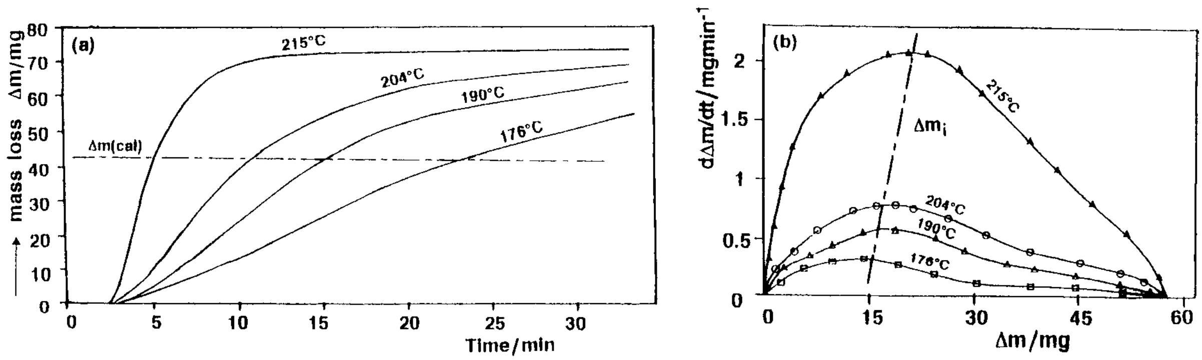

Fig. 3. Cu_3Si-Ref/CuCl: (a) mass loss Δm vs. time and (b) rate $\Delta m/dt$ vs. Δm.

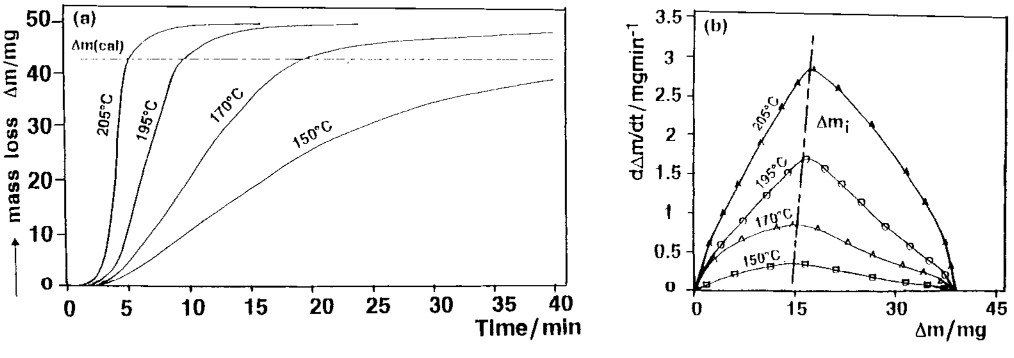

Fig. 4. Cu_3Si-M2AP/CuCl: (a) mass loss Δm vs. time and (b) rate $\Delta m/dt$ vs. Δm.

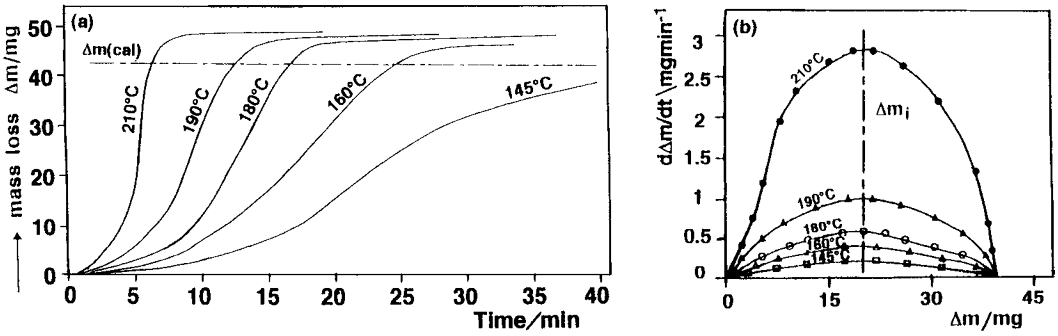

Fig. 5. Cu_3Si-MASHS/CuCl: (a) mass loss Δm vs. time and (b) rate $\Delta m/dt$ vs. Δm.

S-shape, indicating a nucleation growth mechanism, that is, the rate initially increases, reaches a maximum and then decreases. The corresponding rate curves $d(\Delta m/dt)=f(\Delta m)$ (Figs. 3–5, curves (b)) allow us to determine the maximum rate $\alpha_i=\Delta m_i/\Delta m_{exp}$ for each Cu_3Si, where Δm_i corresponds to the Δm value at which the rate is maximum. As already observed from the $\Delta m=f(T)$ curves, the mass loss for Cu_3Si-MASHS best approaches the calculated value. It is also evident from Fig. 5b that Δm_i (α_i=0.48) can be considered as constant in the range 145–210°C.

It is worth mentioning that for the Cu_3Si-Ref/CuCl system where the mass fraction of CuCl which sublimes without reaction with CuCl is the highest, and thereby, affects the kinetic behavior, Δm_i strongly changes with temperature (Fig. 3b).

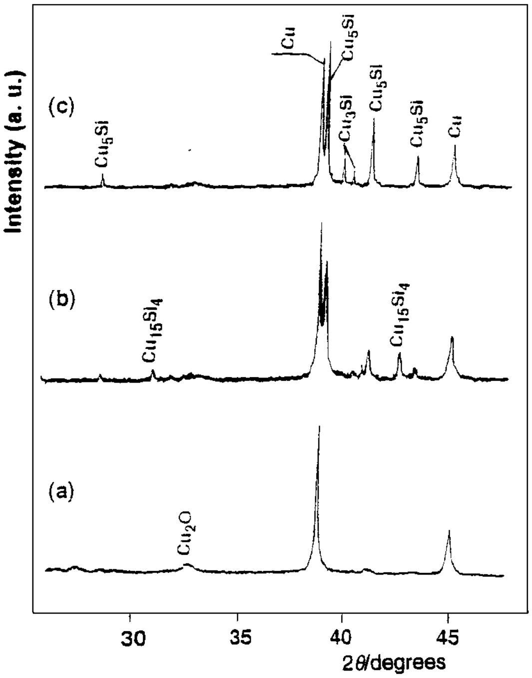

Fig. 6. X-ray diffraction patterns obtained after the reaction between CuCl and: (a) Cu_3Si-MASHS at 180°C; (b) Cu_3Si-M2AP at 190°C; (c) Cu_3Si-Ref at 230°C.

3.3. Solid products of the reaction

X-ray diffraction analyses for the Cu_3Si-MASHS/CuCl system during the course of reaction indicates only the formation of copper (Fig. 6a) which confirms the reduction of CuCl by Cu_3Si in a single step according to reaction (4). In the case of Cu_3Si-Ref and Cu_3Si-M2AP, the reaction with CuCl leads to $Cu_{15}Si_4$, Cu_5Si and Cu (Fig. 6, curves (b) and (c)) through successive reactions as follows:

$$31Cu_3Si + 12CuCl \rightarrow 7Cu_{15}Si_4 + 3SiCl_4 \tag{5}$$

$$9Cu_{15}Si_4 + 20CuCl \rightarrow 31Cu_5Si + 5SiCl_4 \tag{6}$$

$$Cu_3Si + 4CuCl \rightarrow 9Cu + SiCl_4 \tag{7}$$

4. Discussion and conclusion

From the studies just presented, it is clear that for the three types of Cu_3Si, the isothermal curves of fraction reduced versus time were typically sigmoïd. However, in the light of the above results, it appears from Fig. 5b that α_i can be only considered as constant with a value close of 0.50 for Cu_3Si-MASHS/CuCl system. Moreover, for this system, the isothermal curves $\alpha = f(t)$ can be superimposed for $0.10 < \alpha < 0.85$, when α is the fractional mass change at time t defined by $\alpha = \Delta m_t / \Delta m_{\text{exp}}$. By the use of scaling factors, an activation energy of 63 ± 3 kJ mol^{-1} was obtained. The affine character of the curves indicates that the states traversed by the system during the reaction are dependent on intensive variables such as temperature and pressure [13] (in our case, pressure of 1 Pa). The rate equation for the process can be written in terms of separated variables as:

$$v = \frac{\mathrm{d}\alpha}{\mathrm{d}t} = k_T k_p \, \mathrm{e}^{-E/kT} f(\alpha) \tag{8}$$

where $f(\alpha)$ usually represents the kinetic rate expression. At constant temperature and pressure, the shape of the curves is determined only by $f(\alpha)$. We find a very good linear representation of the sigmoid curves (Fig. 7) if $f(\alpha)$ is an equation of type:

$$f(\alpha) = \log\left(\frac{\alpha}{1 - (\alpha/2\alpha_i)}\right) = k_1 t + C \tag{9}$$

which is the integrated form of the Prout–Tompkins equation [14]. The rate for the process can be thus written as:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k_1 \alpha \left(1 - \frac{\alpha}{2\alpha_i}\right)$$

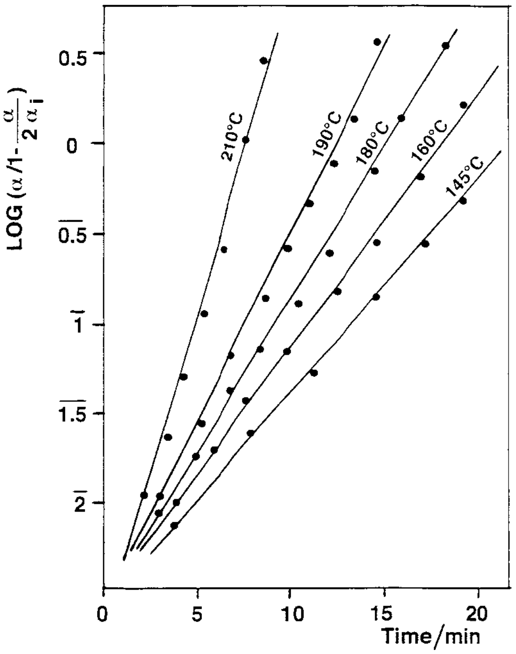

Fig. 7. Conversion as a function of time plotted in terms of Eq. (9).

From the temperature dependence of k_1, an apparent activation energy of 61 ± 3 kJ mol^{-1} is deduced. This value is very close to that calculated from the affinity ratio.

X-ray diffraction results and morphological information which show that finely divided copper is one of the reaction products predicted that we must consider an autocatalytic process rather than a branched chain nucleation mechanism, that is the Prout–Tompkins model. Reactions involving in situ formation of metallic copper are known to be autocatalytic in nature [15]. Thus, reduction of CuO and NiO by H_2 as well as by formaldehyde are both autocatalytic reactions [16].

For the Cu_3Si-Ref and Cu_3Si-M2AP/CuCl systems, the Δm_i (or α_i) value was found to decrease with decreasing temperature. This decrease is particularly noticeable for Cu_3Si/CuCl system (Fig. 3b) where the mass fraction of CuCl which sublimes is very important. The presence of some intermediate Cu-Si compounds, even after complete reaction, presumably also reflects the loss CuCl by sublimation.

A change in α_i with temperature indicates a shift in the controlling mechanism from one to another in a series of successive elementary steps [17]. The present reaction being a consecutive step in the series of reactions (5), (6) and (7), such a shift in controlling mechanism is possible. For these two types of Cu_3Si, the maximum rate take place, depending of the temperature, at values of $0.30 < \alpha_i < 0.40$ for Cu_3Si-Ref and $0.39 < \alpha_i < 0.44$ for Cu_3Si-M2AP. When the maximum rate occurs at a value different from $\alpha_i = 0.50$, it is necessary to integrate Prout and Tompkins original equation with different boundary conditions.

When this is done, Eq. (11) results [18]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{k_1}{2\alpha_i}(1 - 2\alpha_i + \alpha)(1 - \alpha) \tag{11}$$

Eq. (11) is valid for a maximum rate occurring at values of $0 < \alpha < 0.50$. It is obvious that the equations have no physical reality above $\alpha > 0.50$ because $\mathrm{d}\alpha/\mathrm{d}t$ values become negative for the onset of the reaction.

Integration of Eq. (11) gives

$$\log \frac{1-2\alpha_i+\alpha}{1-\alpha} = \frac{1-\alpha_i}{\alpha_i}(k_1 t + C) \tag{12}$$

For example, substituting α_i=0.35, which is a good average of α_i for Cu_3Si-Ref (an average value of α_i was used rather than individual values because of the flatness of the d Δm_i/dt versus Δm curves near each maximum), and rearranging gives:

$$\log \frac{0.3+\alpha}{1-\alpha} = (k_1' t + C) \tag{13}$$

In plotting the kinetic data according to Eq. (13), it was noticed that for α>0.77 for Cu_3Si-Ref and α>0.82 for Cu_3Si-M2AP, the data points deviate significantly from the linear part of the extrapolated model plot. Arrhenius plots within the restricted ranges of $0.25 \leq \alpha \leq 0.77$ and of $0.20 \leq \alpha \leq 0.82$ gave an apparent activation energy of 78±5 kJ mol^{-1} for Cu_3Si-Ref and 68±3 kJ mol^{-1} for Cu_3Si-M2AP.

In conclusion, this study clearly shows that the MASHS process leads to the production of a pure Cu_3Si compound with a low grain size which allows the reduction of CuCl in a single step where the kinetics is governed by a nucleation-growth mechanism and the maximum rate is observed at 50% reduction. Thereby, this reactant is more reactive than either Cu_3Si-Ref and Cu_3Si-M2AP where the particle size is more important and a uniform mixing of the powders could be achieved, probably yielding intermediate intermetallic compounds.

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