The kinetics and mechanism of the low temperature corrosion of titanium with copper(I) chloride. A comparison with silicon and an Si–Ti alloy

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Abstract

Kinetics analysis of the thermogravimetric curves obtained for the corrosion of titanium or $TiSi_2$ with copper(I) chloride($CuCl$) in the temperature range 240–290 °C revealed that the isothermal reaction is governed by a nucleation–growth mechanism with an apparent activation energy of 207 kJ mol^{-1} for the Ti/CuCl and 153 kJ mol^{-1} for the $TiSi_2$/CuCl system. In both cases X-ray diffraction analysis indicated the formation of only copper during the course of the reaction, in contrast to Me/CuCl systems (Me $\equiv$ Si, Ge) where $MeCu_x$ compounds are also identified as intermediate reaction products.

1. Introduction

The subject of this paper has already been considered in a number of other publications [1–3] which focused on a kinetics study of the reaction between silicon or germanium and copper(I) chloride(CuCl). It has been shown that for powdered samples the initiation temperature of the solid–solid reaction and the degree of conversion of silicon or germanium are affected by, among other factors, the purification methods for the metals and the purity of the CuCl. S-shaped kinetic curves indicate a process of nucleation and growth. We have established that the reaction between Me (Me $\equiv$ Si, Ge) and CuCl leads to Cu_3Me, Cu_5Me and copper through successive reactions according to the following scheme:

$$7Me + 12CuCl \longrightarrow 3MeCl_4 + 4Cu_3Me \tag{1}$$

$$9Cu_3Me + 8CuCl \longrightarrow 2MeCl_4 + 7Cu_5Me \tag{2}$$

$$Cu_5Me + 4CuCl \longrightarrow MeCl_4 + 9Cu \tag{3}$$

In this scheme copper is the final product of the reaction whereas Cu_3Me and Cu_5Me are intermediates which react with CuCl.

The phase diagram of the Cu–Ti system (Fig. 1) shows the existence in the low temperature range (below 500 °C) of the compounds $TiCu_4$, Ti_2Cu_3,
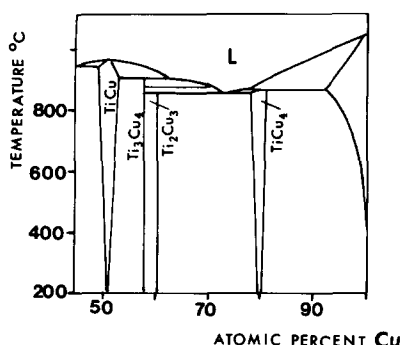
Fig. 1. Cu–Ti phase diagram in copper-rich alloy [4].

Ti₃Cu₄ and TiCu containing between 50 and 80 at.% Cu [4]. The difference in comparison with the phase diagrams of the Cu–Si and Cu–Ge systems is the presence of a minimum in the liquidus–solidus curve near the centre of the diagram. In the Cu–Si and Cu–Ge diagrams the minimum in the liquidus–solidus curve is found at approximately 75 at.% Cu with $MeCu_3$ and $MeCu_5$ confined to the first 27 at.% of solute [5]. Also, in the middle of the diagram there exists no equivalent in the Cu–Si system to the phases Ti_3Cu_4 and TiCu.

To our knowledge the reaction between CuCl and titanium has not been reported previously. Thus we have used thermogravimetry to study the kinetics of this reaction, which is associated with a mass loss due to the evolution of $TiCl_4$ which occurs during the reduction process according to the global equation

$$Ti + 4CuCl \longrightarrow TiCl_4 + 4Cu \qquad (4)$$

With titanium the formation of copper can still be recognized but the overall mechanism resulting from simultaneous and successive reactions is much less clear than with silicon or germanium. In addition, some relevant observations on the reaction of CuCl with the silicide $TiSi_2$ will also be reported.

2. Experimental details

The total mass change due to evolution of $TiCl_4$ 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 titanium loadings. Titanium (100 mesh, 99.999% pure, lot 76595, Alfa Products) and CuCl (99.999% pure, lot 400151, Alfa Products) powders were mixed intimately and ground in an agate mortar for different times in a mole ratio Ti:CuCl > 1.5, corresponding to an excess of titanium. Then 25 mg of the mixture was spread as a thin layer on the balance arm; the reactor was subsequently evacuated, outgassed *in vacuo* (1 Pa) for 2 h at room temperature and then for 1 h at 180 °C before the sample was heated to the temperature of the experiment. The $TiCl_4(g)$

liberated during the reaction was condensed in a liquid nitrogen trap and the mass loss was calculated per 100 mg CuCl. A few runs were carried out with different dry-grinding times, since in the case of a solid–solid reaction it is necessary to mix the substances at the molecular level [6] in order to enhance their reactivity.

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 $TiCl_4(g)$ was allowed to remain in contact with the sample during the course of the reaction. After grinding in an agate mortar, the mixture was placed in a Pyrex glass capsule, sealed under vacuum and then heated at 310 °C for 2 days. The reaction between CuCl and $TiSi_2$ has also been investigated. For this purpose weighed amounts of titanium and silicon were induction melted in recrystallized alumina crucibles under an argon gas atmosphere. The alloy after quenching was subjected to metallographic and X-ray diffraction investigation.

X-ray diffraction patterns were recorded on an "INEL CPS 120" linear counter (curved position sensitive) equipped with monochromatized Cu Kα radiation and calibrated by a quartz standard. The resolution was 0.02° (2θ) at 2 deg min^{-1}.

3. Results and discussion

3.1. Effect of grinding operation

The effect of the dry-grinding operation is shown in Fig. 2. Curves (2)–(6) show the variation in total mass loss with time for a sample ground in an agate mortar for 2, 3, 5, 7 and 9 min respectively with a Ti:CuCl molar ratio of 6.80 and at a temperature of 248 °C. Curve (1) shows the time dependence of the sublimation of CuCl when it is placed alone in the scoop. The theoretical maximum mass loss Δm_{cal} of the system is calculated
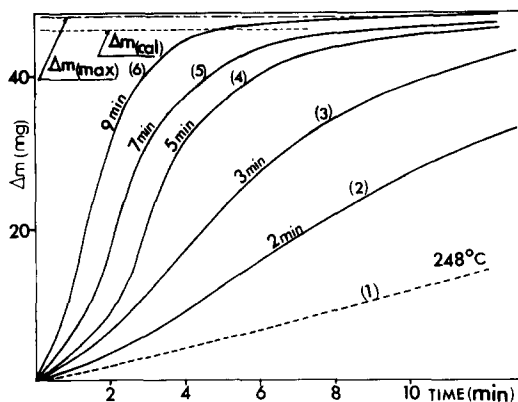

Fig. 2. Effect of grinding duration (curves (2)–(6)) on reactivity of Ti/CuCl system at 248 °C with Ti:CuCl = 6.80. Curve (1) shows time dependence of sublimation of CuCl.

($\Delta m = 47.2$ mg, broken line) for complete reduction of CuCl by titanium according to the reaction $Ti + 4CuCl \rightarrow TiCl_4 + 4Cu$.

It may be seen from Fig. 2 that the experimental maximum mass loss Δm_{max} was slightly greater than that calculated considering the total consumption of CuCl. The difference $\Delta m_{max} - \Delta m_{cal}$ is associated with the partial sublimation of CuCl, indicating that a fraction of CuCl in the gaseous state does not react. However, the difference $\Delta m_{max} - \Delta m_{cal}$ decreases with longer grinding times, which implies that the mass fraction of CuCl which sublimates without reaction with titanium decreases as the grinding time is increased. These observations enabled the study of this reaction by the isothermal mass loss method.

3.2. Effect of temperature

The kinetic curves $\Delta m = f(t)$ at temperatures ranging from 237 to 263 °C are shown in Fig. 3. For reaction times below about 15 min the curves are the typical S-shape characteristic of the nuclear–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. 4) 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 [7]. 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 titanium (Ti:CuCl
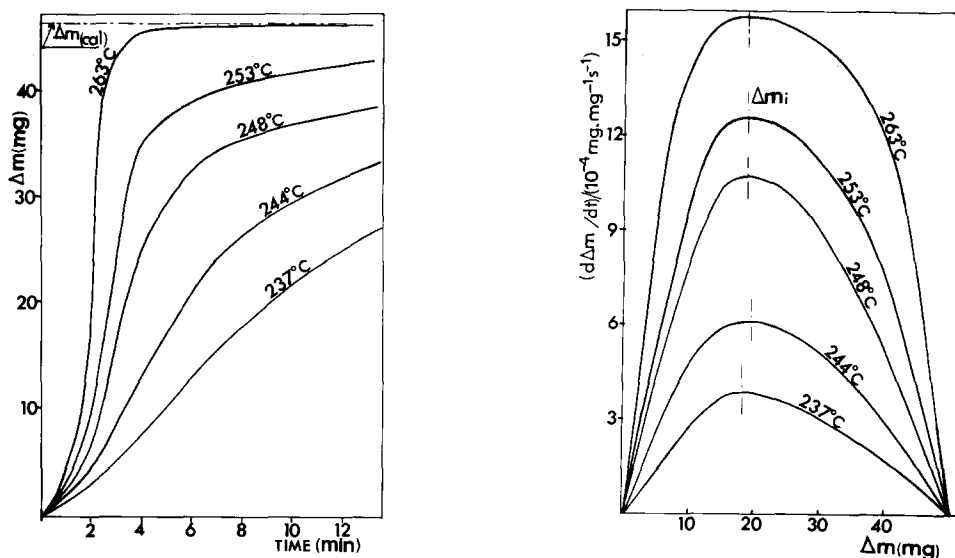

Fig. 3. Mass loss Δm vs. time as a function of temperature for Ti/CuCl system.

Fig. 4. Rate $d(\Delta m)/dt$ vs. Δm for Ti/CuCl system.

molar ratio of 6.80) and a long grinding time (5 min.). It is evident from Fig. 4 that α_i can be considered as constant in the range 237–263 °C.

The isotherms were best fitted with the equation

$$\ln\left(\frac{\alpha}{1-\alpha/2\alpha_i}\right) = kt + C^{te} \tag{5}$$

for $0.15 < \alpha < 0.75$, where α is the fractional mass change at time t defined by $\alpha = \Delta m_t \Delta m_{max}$ and k is the rate constant. This equation is the integrated form of the Prout–Tompkins equation [8]. The rate for the process can thus be written as

$$\frac{d\alpha}{dt} = k\alpha\left(1 - \frac{\alpha}{2\alpha_i}\right) \tag{6}$$

The apparent activation energy E calculated by plotting $\ln k$ against $1/T$ at different constant values of α is 207 kJ mol^{-1}, with a standard deviation of 5 kJ mol^{-1} (least-squares method). If we compare the activation energy obtained for the reaction between titanium and CuCl with that for the reaction between silicon and CuCl (207 and 125 kJ mol^{-1} [1] respectively), we can see that the reaction rate for the Ti/CuCl system is much slower.

3.3. Solid products of the reaction

Based on a consideration of the X-ray diffraction data, the phase obtained during the course of the reaction between titanium and CuCl can be identified as only copper (Fig. 5, curve (a)), in contrast to the Si/CuCl and Ge/CuCl systems where phases of the type MeCu$_x$ were also identified as reaction products. A parallel set of experiments was conducted in a closed system for different molar ratios Ti:CuCl = 0.25, 0.50, 1 and 1.25, corresponding to almost selective formation of copper, Cu$_4$Ti, Cu$_4$Ti$_3$ and TiCu according to the equations
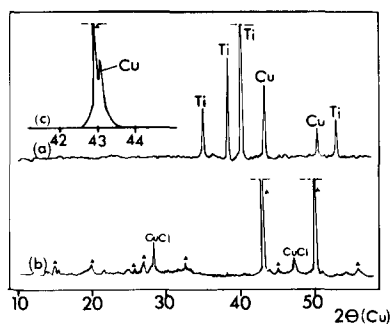

Fig. 5. X-ray diffraction patterns obtained for reaction between CuCl and titanium (a) in open system (thermogravimetry) with Ti:CuCl = 6.80 and (b, c) in closed system with Ti:CuCl = 1; ▲, diffraction peak of Cu$_4$Ti$_3$.
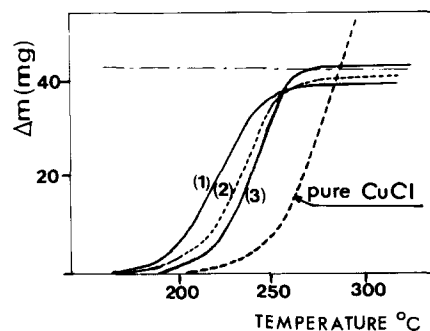
Fig. 6. Comparative thermogravimetric curves $\Delta m = f(T)$ in vacuum for (1) mixture of silicon and CuCl, (2) mixture of Si$_2$Ti and CuCl, (3) mixture of titanium and CuCl and (4) pure CuCl.

$$Ti + 4CuCl \longrightarrow TiCl_4 + 4Cu \tag{7}$$

$$2Ti + 4CuCl \longrightarrow TiCl_4 + Cu_4Ti \tag{8}$$

$$4Ti + 4CuCl \longrightarrow TiCl_4 + Cu_4Ti_3 \tag{9}$$

$$5Ti + 4CuCl \longrightarrow TiCl_4 + 4TiCu \tag{10}$$

X-ray diffraction analysis indicated the presence of only copper for the reactant ratio of 0.25 according to eqn. (7). For reactions (8)–(10) other phases were detected but between 50 and 80 at.% Cu there occurs a cascade of reactions which obscure the existence of several intermetallic compounds and there is some ambiguity about the proper identification of one line, that at about $2\theta = 43.20°$. Moreover, metallic titanium is highly reactive, so a reaction between titanium and the slight trace of oxygen impurities present in the closed system can be expected to form titanium oxides. A large number of titanium oxides and suboxides exhibit strong diffraction peaks in the X-ray diffraction region investigated [9]. The diffraction peaks can, however, be allocated for reactions (8) and (9) to Cu_4Ti_3 (Fig. 5, curve (b)) of tetragonal structure [10, 11], with $a = 0.312$ nm and $c = 1.996$ nm. On the other hand, the titanium peak has disappeared, indicating that titanium and CuCl react at temperatures less than 300 °C, which also supports the spontaneity of the reaction as written in eqn. (5). It should be stressed that the ideal match of observed and theoretical d values for Cu–Ti alloy cannot be expected owing to the crystallite size effect, non-stoichiometry and disorder.

For a reaction carried out in thermogravimetry (open system) with titanium excess or in a closed system with a reactant ratio of 0.25 the strong peak of copper is located at $2\theta = 43.20°$. The reaction between titanium and CuCl with a molar ratio above 0.25 is dominated by a pronounced feature between $2\theta = 43°$ and 43.20°. The diffraction peak consists of at least two distinct components (Fig. 5, curve (c)). The peak at the higher Bragg angle is rather narrow and can be assigned to the Cu(111) reflection shifted by $2\theta = 0.04°$ with respect to pure copper. The second component at lower diffraction angle is attributable to the (107) reflection of Cu_4Ti_3. The intensity of this diffraction peak increases with both the molar ratio Ti:CuCl and the reaction time.

3.4. Reaction between CuCl and Si₂Ti

Since one expects reactions effected by thermogravimetry to produce only copper between titanium and CuCl and Cu–Si compounds between silicon and CuCl, there is a natural desire to investigate the reaction of CuCl with an Si–Ti alloy. Some heating curves under vacuum ($3°C\ min^{-1}$ heating rate) are shown in Fig. 6 for the Si/CuCl, Si₂Ti/CuCl and Ti/CuCl systems. Under identical applied conditions CuCl begins to react with titanium at about 188 °C (curve (3)) whereas a lower initiation temperature (165 °C) is observed for the Si₂Ti/CuCl (curve (2)) and Si/CuCl (curve (3)) systems. As a result of the experiments performed, it was established that the place

of Si_2Ti, as judged from the reaction initiation temperature, should be between silicon and titanium. X-ray investigations of the $Si_2Ti/CuCl$ system during the course of the reaction indicate only the formation of copper, e.g.

$$Si_2Ti + 12CuCl \longrightarrow 2SiCl_4 + TiCl_4 + 12Cu \tag{11}$$
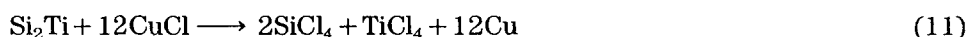
The kinetic curves of this reaction, $\Delta m = f(t)$ (Fig. 7), at temperatures ranging from 240 to 292 °C have an S-shape, indicating a typical nucleation and growth mechanism. The apparent activation energies E calculated by plotting ln k against $1/T$ at different constant values of α are listed in Table 1. The lowest value of activation energy found for the Si/CuCl system (125 kJ mol^{-1}) is thought to be caused by the presence of copper silicides (Cu_3Si, Cu_5Si) during the course of the reaction, which favour the formation of metallic copper. The absence of these intermediates in the reaction with titanium or Si_2Ti was observed to increase the activation energy. This is attributed to possible diffusional resistance due to the large quantity of copper formed, which covers the grain surface and acts as a barrier to further contact between reactants. Concerning the S-shaped kinetic curves, it has been postulated [12] that eqn. (5) is also valid for autocatalytic processes, especially for reactions involving *in situ* formation of metallic copper [13]. In view of the results obtained by X-ray diffraction for the Ti/CuCl and $Si_2Ti/$CuCl systems, an autocatalytic process rather than a branched chain nucleation mechanism, *i.e.* the Prout–Tompkins model, can also be considered. This problem will be discussed in more detail in a separate paper.
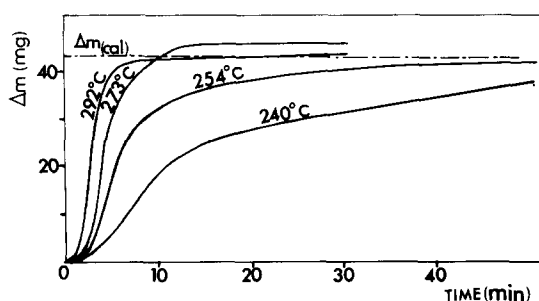

Fig. 7. Mass loss Δm *vs.* time as a function of temperature for $Si_2Ti/CuCl$ system.

TABLE 1

Values of α_i and apparent activation energies

System	α_i	E (kJ mol^{-1})
Si/CuCl	0.33	125
$Si_2Ti/CuCl$	0.41	153
Ti/CuCl	0.40	207

218

4. Conclusions

The solid state reactions between CuCl and titanium or Si_2Ti present the following features.

(1) From investigations by thermogravimetry in an open system the reaction between CuCl and excess titanium starts at 185 °C and proceeds to a nucleation–growth mechanism in the temperature range 240–267 °C with an apparent activation energy of 207 kJ mol^{-1}. The reactivity is the greatest for ground samples with a high Ti:CuCl mole ratio and treated under the highest vacuum.

(2) The reaction gives only copper according to the equation $Ti + 4CuCl \rightarrow TiCl_4 + 4Cu$.

(3) In a closed system and for Ti:CuCl = 0.50–1 the reaction leads from 310 °C to almost selective formation of Cu_4Ti_3 according to the equation $4Ti + 4CuCl \rightarrow TiCl_4 + Cu_4Ti_3$. Under the same conditions the end product is only copper if the reactant ratio is lowered to 0.25.

(4) For the reaction of Si_2Ti with CuCl the results of the kinetic runs, when plotted as mass change *vs.* time, showed a typical S-shape, indicating also a nucleation–growth mechanism. Again in this case only copper was detected during the course of the reaction.

(5) These results contrast with those obtained for the reaction between CuCl and silicon, where the final copper phase results from simultaneous and successive reactions.

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