KINETICS OF CHLORINATION OF SILICON BY Cl_2 GAS

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ABSTRACT

Studies on the kinetics of chlorination of pure silicon power by gaseous chlorine have been carried out in a flow system. The effect of time, temperature (773-973 K), bed height (2.5 and 5 mm) and partial pressure of chlorine (0.50 to I.0 atm) on the chlorination of pure silicon powder (-4+14 mesh) has been studied. In all the cases, the chlorine flow rate of 1800 ml/min has been fixed as the optimum flow rate which has been established by conducting some preliminary experiments. The amount of Si chlorinated is found to increase with increase in temperature and, the activation energy of the process has been calculated to be 15 kJ/mole. The amount of silicon chlorinated is found to be proportional to the partial pressure of chlorine. Utilising these results a probable mechanism for the chlorination of silicon by gaseous chlorine, has been proposed.

INTRODUCTION

Chlorine is extensively used not only to open up various ores and minerals but also to produce many metal chlorides which are used as the starting material for producing the respective metals in pure form. Because of the difference in the kinetics of formation of many chlorides and their boiling points, the chlorination method is conveniently used for separating and recovering various constituents present in an alloy scrap. In this context, the studies on the kinetics of the chlorination of concerned elements are essential. Some time back, studies on the chlorination kinetics of germanium, silicon, iron, tungsten, molybdenum, columbium and tantalum were undertaken by Landsberg and Block (1965) in the low te1mperature range of 229 to 517 °C. Recently, some -studies on the chlorination of Cu, Ni, Fe and ferronickel have been reported in the literature (Strafford et.al., 1987, Svetsov et.al. 1988, Strafford et.al., 1989). Nelson and Eric (1989) have investigated the kinetics of chlorination of ferrochromium in the temperature range of 800 to 975 °C. They suggested a topochemical reaction model for the chlorination process.

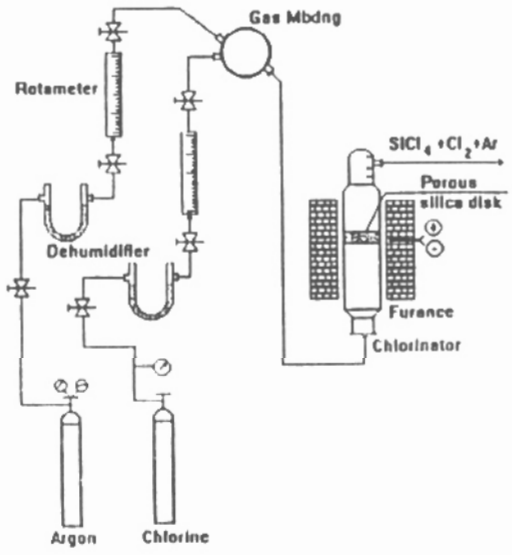
However, in view of the very limited literature available on the kinetics of chlorination of silicon, and as silicon is used extensively in production of various alloys and for other industrial purposes, the present studies on the gaseous chlorination of silicon particles have been undertaken in the temperature range of 773 to 973 K. to throw more light on the mechanism of the process.

EXPERIMENTAL

The studies on the chlorination of pure silicon particles (-4+14 mesh) by gaseous chlorine were carried out in a vertical bed silica chlorinator which was externally heated by an electric resistance furnace.

The silicon particles of known weight were placed on a porous quartz disk positioned in the central part of the reactor. Dry Cl_2 gas or its mixture with dry argon was passed through the bed of silicon particles, kept at a desired temperature.The product chlorides were collected in an ice cooled receiver and the unreacted Cl_2 was allowed to be absorbed in sodium hydroxide solution and water scrubbers. After chlorinating for the desired period, the weight of the remaining silicon particles was determined. A sketch of the chlorination unit is given in Figure I.

Figurel - Chlorination Setup.



In this way, the effect of time and temperature of chlorination, partial pressure of Cl_2 and the bed height on the extent of chlorination of silicon particles was studied. As the possible product chlorides such as $SiCl_2$, $SiCl_3$ and $SiCl_4$ are highly volatile at the temperatures studied, the weight loss measurement was found to be suitable to follow up the kinetics of the chorination of Si.

RESULTS AND DISCUSSION

In this study, the overall reaction of the silicon particles (-4+14 mesh) by Cl_2 gas is assumed to be.

$$Si\ (s) + 2\ Cl_2\ (g) = SiCl_4\ (g\ \ldots\ldots\ldots\ldots\ (1)$$

The effect of various experimental variables on the rate of chlorination has been discussed in the following pages.

1. The effect of the flow rate of Cl2 on the chlorination of the Si particles (-4+14 mesh) at 973 K at different periods, has been studied. The extent of chlorination of the Si particles for a definite period has been found to be nearly independent of the flow rate of Cl_2 at and above 1800 ml/min. In view of this, the rest of the experiments have been carried out at this flow rate of Cl_2.

2. The effect of the temperature (773-973 K) on the chlorination of silicon particles having a bed height of 5 mm, has been studied using Cl2 at 1 atm. In all cases, the amount of silicon particles chlorinated is found to be nonlinear with the period of chlorination. The following possible rate equations for different reaction models have been examined.

Topochemical reaction control,

$$1-(1-\alpha)^{\frac{1}{3}} = kt \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Diffusion Control,

$$\left[1-(1-\alpha)^{\frac{1}{3}}\right]^2 = kt \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Diffusion Control,

$$1-\frac{2}{3}\alpha-(1-\alpha)^{\frac{2}{3}} = kt \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

where α is the fraction of silicon chlorinated in time t and k is the rate constant. The chlorination results have been found to fit well with the topo chemical reaction model as given in equation (2) and summarised in Figure II. In all cases, the linear correlation coefficient (L.C.C.) values are found to be better than 0.99. It is observed that with the increase in temperature, the rate of chlorination increases, but it is very small. The activation energy (E) for the chlorination process has been calculated by applying the Arrhenius equation. The logarithm of the rate constant values k (atm.min -1) obtained from Figure II have been plotted against the reciprocal of the temperature T (K) as shown in FigureIII. The L.C.C. is 0.995. The value of E is found to be l5 kJ/mole.

Figure II - 1-(1-α)1/3vs. t for chlorination of Si at diferent temperatures using pCl_2 = 1 atm.

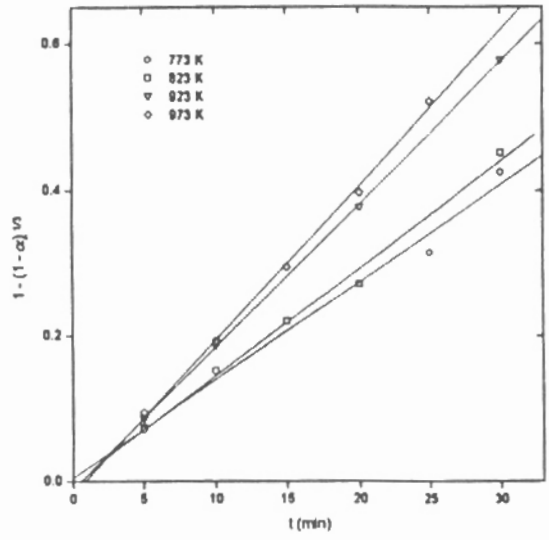
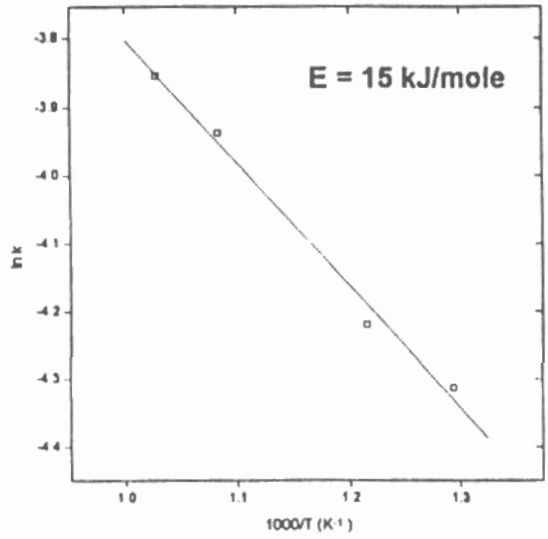


Figure III - ln K vs. 1/T for bed height of 5 mm.



3. The effect of the partial pressure of chlorine pCl_2 on the chlorination of silicon particles having a bed height of 5 mm, has been studied. The values of the fraction of

silicon particles chlorinated at different periods for pCl_2 of 0.5, 0.67 and 1.0 atm. are obtained. These values have also been found to fit well with the topo chemical reaction model as given in equation (2). The results have been plotted in Figure IV. The L.C.C. value is around 0.99. The rate constant values (k) obtained from Figure IV have been plotted against the corresponding pCl2 values as shown in Figure V. It is found that the rate of reaction is proportional to the partial pressure of chlorine, (L.C.C. value is 0.999).

$$k = k' pCl_2 \quad \text{.....(5)}$$

Where k' is another constant.

Figure IV - 1-(1-a)1/3 vs. t for chlorination of Si at 973 K for different pCl_2.

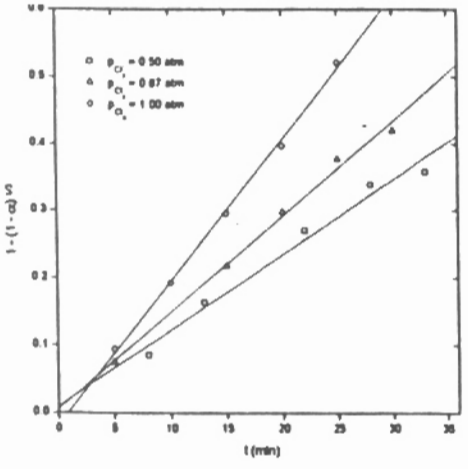


Figure V - k vs. pCl_2 at 973 K.

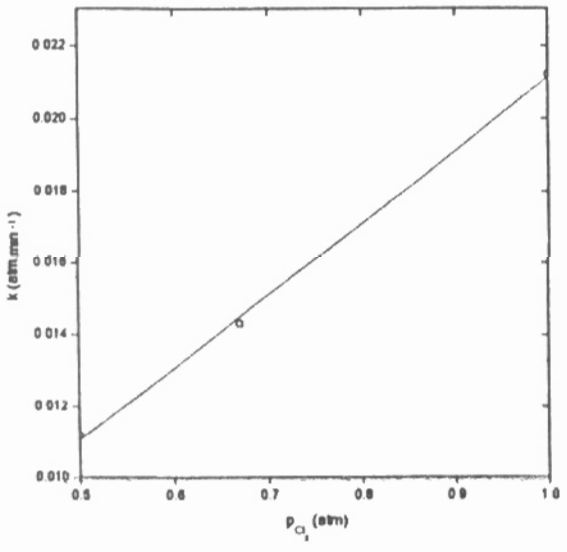


Figure VI - 1-(1-a)1/3 vs. t at different temperatures using pCl_2 = 1 atm and bed height = 2.5 mm.

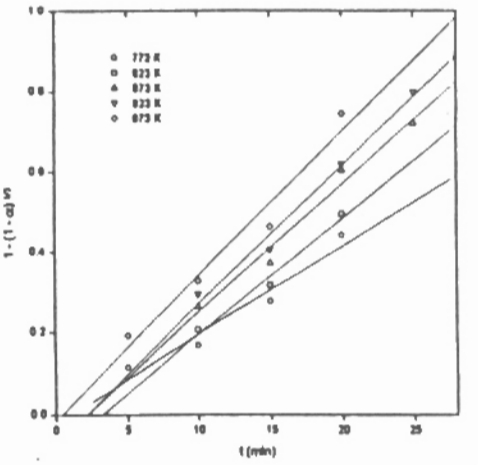
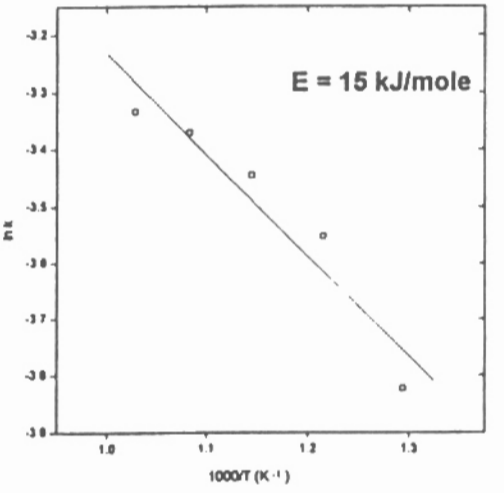


Figure VII - ln k vs 1/T for bed height of 2.5 mm.



4. In order to find out the effect of the bed height on the *extent of chlorination, experiments have been performed in* a similar way by using silicon particles of same size (4+14 mesh) with a bed height of 2.5 mm. in the same temperature range (773-973 K). The results have been also found to fit well with the topo chemical reaction model. The results are summarized in Figure VI. The L.C.C. values vary from 0.975 to 0.993. The logarithm of the k values obtained for each temperature have been plotted against 1/T (K-1), as shown in Figure VII. The L.C.C. value is 0.956. The activation energy value is found to be 15kJ/mole. This value is exactly the same as that obtained for the bed height of 5 mm. However, in this case, the fraction of the silicon reacted has been found to be higher than that obtained for 5 mm. bed height. For example, at

773 K, the k values are $1.32x10^{-2}$ and $2.78x10^{-2}$ $atm.min^{-1}$ for bed heights of 5 and 2.5 mm. respectively. The appreciable variation in the rate of chlorination with the bed height might be due to the partial fluidisation of the silicon bed with decrease in bed height and hence constant exposer of the fresh surface of the particles.

MECHANISM OF THE PROCESS

The chlorination of the silicon particles in the temperature range of 773-973 K is found to fit well to the topo chemical reaction model. However, the activation energy of the process is very small (15 kJ/mole). The rate of chlorination is found to be directly proportional to the partial pressure of Cl_2. Based on these results, the mechanism for the chlorination of the silicon particles is suggested to be as follows:

$$Si(s) + Cl_2(g) \xrightarrow{slow} SiCl_2(g) \quad \text{.....(6)}$$

$$SiCl2(g) + Cl_2(g) \xrightarrow{fast} SiCl_4(g) \quad \text{.....(7)}$$

The chemical reaction of one molecule of chlorine gas with silicon forming $SiCl_2$ gas is considered to be the rate controlling step. The reaction of gaseous $SiCl_2$ with another molecule of Cl_2 to form the more stable $SiCl_4$ is likely to be quite fast. Similar mechanism has also been suggested by Landsberg et al., 1965, in their studies on the chlorination of silicon in the lower temperature range (375-517 °C). However, in order to have more insight to the chlorination of silicon in a vertical bed chlorinator detail studies particularly on the effect of particle size, bed height and extent of fluidisation are necessary.

CONCLUSIONS

1. The chlorination of the silicon particles by gaseous chlorine in the temperature range of 773 to 973 K is a very fast reaction. For example, the chlorination of Si at 973 K attains completion within a period of 30 minutes by using the Si particles in the size range of -4+14 mesh.

2. The chlorination of Si increases appreciably with decrease in bed height. This is attributed to the likely partial fluidisation of the particles by the chlorine gas.

3. The chlorination of the Si particles fits to the topo chemical reaction model. The rate is found to be directly proportional to pCl_2 with a low activation energy of 15 kJ/mole.

4. The chemical reaction of one molecule of Cl_2 on the surface of Si to form $SiCl_2$ is suggested to be the rate controlling step.

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