

KINETICS OF CHLORINATION OF TANTALUM PENTOXIDE WITH CARBON TETRACHLORIDE

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Tantalum chloride is used as a feed material for the plasma reduction using hydrogen and in the chloride bath fused salt electrolysis routes to produce tantalum. Most of the tantalum, however, occurs in nature in the oxide form. The traditional chlorination process employs gaseous chlorine and carbon as reductant at high temperatures (1073-1273 K). Use of carbon tetrachloride as the chlorinating agent is expected to reduce the chlorination temperatures significantly resulting in lower energy consumption and cost of capital equipment for chlorination. The purpose of the present study was to explore the use of carbon tetrachloride as an alternative chlorinating agent for Ta₂O₅. The kinetics of chlorination of pure tantalum pentoxide powders with carbon tetrachloride in nitrogen atmosphere was investigated in the temperature range 733-853 K and p_{CCl₄} in the range 20-60 kPa. The kinetic results were found to conform to a diffusion controlled reaction model. Equilibrium conversions to chloride and the gas phase composition at different temperatures and partial pressures of CCl₄ were calculated using the free energy minimisation technique.

INTRODUCTION

Tantalum is used in capacitors, corrosion resistant components and in high temperature alloys as a carbide former, solid-solution strengthener and for imparting microstructural stability at elevated temperatures. It occurs in nature almost exclusively as oxide in association with niobium. Extraction of Ta involves preconcentration of the ores by wet gravity separation followed by dry magnetic or electrostatic methods. The concentrates are then either chlorinated directly or digested in hydrofluoric acid; Nb and Ta separated by solvent extraction and Ta precipitated as pure Ta₂O₅ or K₂TaF₇. Tantalum can then be extracted by i) carbon reduction of tantalum oxide in vacuum, ii) hydrogen reduction of tantalum chloride in plasma, iii) metallothermal reduction of K₂TaF₇ by sodium and iv) fused salt electrolysis of either oxide or chloride melts. The processing, properties and applications of Ta has been recently reviewed by Kock and Paschen[1] and Gupta[2].

A knowledge of the thermodynamics and kinetics of the chlorination of Ta and Nb is therefore necessary to optimise the process conditions to enable their selective separation and to achieve high yields. Chlorination of mixed oxides of Nb and Ta by carbon tetrachloride was first reported by Ruff and Thomas[3] who tried to separate Nb and Ta by this method. Similar experiments were repeated by Schafer et al[4]. Chlorination of mixed Nb and Ta concentrates with chlorine in the absence of any reducing agent at 1473 K has been patented by Cuvellez[5,6]. Chlorination of mixed oxides using gaseous chlorine at lower temperatures (813-873 K) in presence of graphite has been studied by Hussain and Jena[7]. Subsequently, Mehra and co-workers[8,9] carried out a detailed analysis on the kinetics of the chlorination of pure niobium and tantalum pentoxides in the temperature range 873-1023 K by chlorine in

the presence of graphite. They observed that the chlorination of Nb_2O_5 has a higher activation energy (184 kJ/mol) than Ta_2O_5 (130 kJ/mol). The rate of reaction was found to be proportional to the partial pressure of chlorine in case of Nb_2O_5 and the square root of the partial pressure of chlorine for Ta_2O_5 . In a subsequent work, Srinivasan and Jena[10] investigated the kinetics of chlorination of Nb_2O_5 and Ta_2O_5 by chlorine and carbon monoxide in the temperature range 798-1023 K. Activation energies for the chlorination of Nb_2O_5 and Ta_2O_5 in the presence of CO were determined to be 31.8 and 21.3 kJ/mol respectively indicating that the rate of chlorination with CO and Cl_2 is faster than with C and Cl_2 . They also found that the rates of chlorination of Nb_2O_5 and Ta_2O_5 vary linearly with p_{CO} and p_{Cl_2} in the range of partial pressures and temperature adopted in their study. It can therefore be expected that the use of carbon tetrachloride as a chlorinating cum reducing agent will accelerate the chlorination process enabling use of lower temperatures resulting in lower energy consumption and cost of capital equipment. Use of carbon tetrachloride for reduction chlorination has been reported earlier for TiO_2 (anatase, ilmenite) by Jena et al[11] in the range 523-673 K and by Lavacchia et al[12] in the range 893-973 K, and for ZrO_2 by Jena et al[13] in the range 700-750K. Kinetics of carbo-chlorination of refractory metal oxides including Nb_2O_5 and Ta_2O_5 have also been studied recently by Allain et al[14] in the temperature range 653-1273 K using the gas mixture consisting of $\text{Cl}_2+\text{CO}+\text{N}_2$. They found that for chlorination at lower temperatures (<923 K), the activation energies for the chlorination of Nb_2O_5 and Ta_2O_5 were 75 and 100 kJ/mol respectively. The activation energies reported by Allain et al are much higher than that reported by Srinivasan and Jena[10] for similar studies and further the activation energy for the chlorination of Ta_2O_5 was higher than that of Nb_2O_5 in contradiction to the earlier results of Jena et al[8-10]. No systematic study is reported in the literature on the kinetics of the chlorination of pure tantalum pentoxide. The purpose of the present work was to investigate the kinetics of chlorination of pure tantalum pentoxide using carbon tetrachloride in the presence of nitrogen.

EXPERIMENTAL

Specpure Ta_2O_5 obtained from Atomic Energy Laboratory, Brazil, chemically pure CCl_4 and high purity dry N_2 gas were used in this study. The experimental apparatus used to conduct the chlorination experiments was identical to that used earlier by Jena and co-workers[13]. The set up consists of a transparent silica tube horizontally placed inside an electric resistance furnace. The temperature of the furnace was controlled to within $\pm 2^\circ\text{C}$. The nitrogen from the cylinder was bubbled at the desired rate monitored by a flowmeter through the liquid carbon tetrachloride, kept in a flask and connected to the chlorinator. The flask has three passages, one for the introduction of N_2 into the liquid CCl_4 , the second to pass the nitrogen gas into the chlorinator and the third for the inlet of the N_2+CCl_4 mixture into the chlorinator. The flask was heated by a water bath to the desired temperature maintained within $\pm 2^\circ\text{C}$ by a controller. The pressure inside the flask was measured by a manometer. The outgoing product gases were cooled in a condenser and liquid TaCl_5 was collected in a flask. The other off gases containing an excess of CCl_4 , Cl_2 , COCl_2 , CO, CO_2 and N_2 were bubbled through caustic soda solution and released through the exhaust. The experimental procedure usually followed was to preheat the reactor to the desired temperature, then introduce the pre-weighed charge held in an alumina boat into the reactor and continue heating till the temperature stabilizes at the desired value. The reactor was thoroughly flushed with pure dry N_2 prior to introducing the sample into the reactor to eliminate the presence of moisture and air in the reactor. When the experimental temperature, as measured by a chromel-alumel thermocouple placed inside the reactor and in contact with the alumina boat stabilised for 5

min, the mixture of $\text{CCl}_4 + \text{N}_2$ was introduced into the reactor for specified periods. At the end of the specified period, the sample was removed from the reactor in hot condition, cooled to room temperature and then weighed. The effects of chlorination time, temperature and partial pressure of carbon tetrachloride were studied. The latter was varied by changing the temperature of the bath while maintaining a constant flow of nitrogen. The partial pressure of CCl_4 was calculated from the change in volume of the liquid in the flask during a particular period of chlorination, the density of gaseous CCl_4 and the total quantity of nitrogen bubbled through the flask over the same period. Temperature was varied in the range 733-853 K and times up to 90 min were adopted. The chlorination behaviour as a function of time was studied at every 5 to 10 minute interval.

RESULTS AND DISCUSSION

The effect of particle size of Ta_2O_5 powders on its chlorination behaviour in the range 43 to 208 μm ($T=833\text{ K}$, $p_{\text{CCl}_4}=60\text{ kPa}$ and $\text{time}=75\text{ min}$) is shown in Fig. 1. It is seen that within the limits of experimental uncertainty, the % conversions to TaCl_5 is independent of particle size or surface area. The variation of percent conversion to TaCl_5 with time as a function of temperature in the range 733-853 K is shown in Fig. 2 at $p_{\text{CCl}_4}=60\text{ kPa}$.

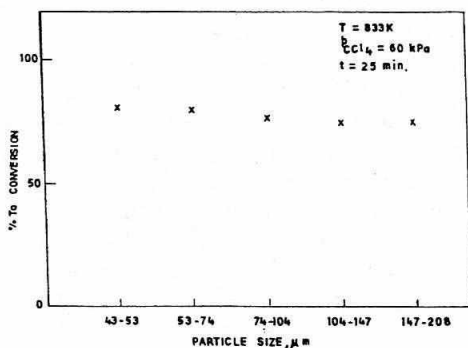


Fig.1 Effect of particle size on chlorination of Ta_2O_5

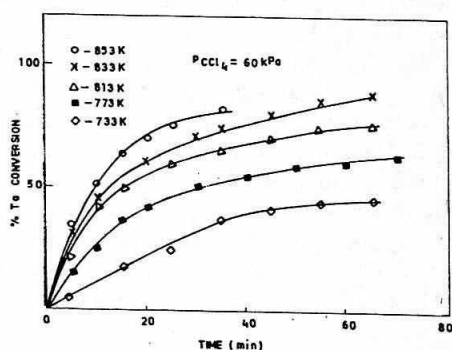


Fig.2 Effect of Temperature on chlorination of Ta_2O_5

The plots appear to show a parabolic behaviour. It was observed that an increase in temperature causes an increase in percentage of tantalum recovered as chloride. The extent of chlorination increased with time up to 70 minutes, after which, near steady state conditions were achieved. Nearly 90% of the tantalum pentoxide was converted to chloride in 35 minutes at 853 K and $p_{\text{CCl}_4}=60\text{ kPa}$. The effect of partial pressures of carbon tetrachloride on the conversions of Ta_2O_5 to TaCl_5 is shown in Fig. 3 at 833 K. Within the range of measurements ($p_{\text{CCl}_4}=20\text{--}60\text{ kPa}$), the amount reacted increases with rise in p_{CCl_4} .

The various kinetic models reported in the literature were examined to assess the reaction mechanism in the chlorination of pure Ta_2O_5 by gaseous carbon tetrachloride. The absence of surface area dependence of the chlorination of tantalum pentoxide indicates that the overall process is diffusion controlled. The results were found to fit best to Jander's equation:

$$(1 - (1 - X)^{1/3})^2 = kt$$

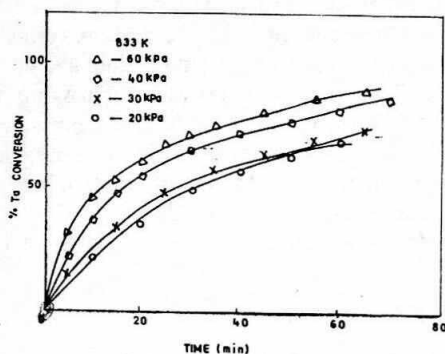


Fig. 3. Effect of p_{CCl_4} on chlorination of Ta_2O_5

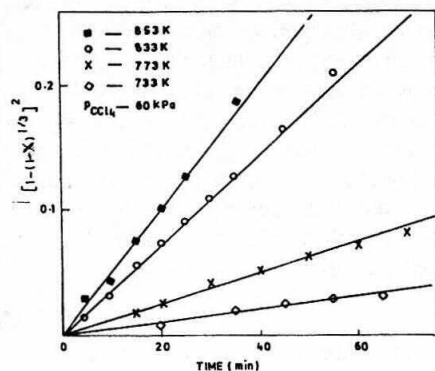


Fig. 4. Plot of $(1-(1-X)^{1/3})^2$ against time at different temperatures

which is valid for a diffusion controlled gas-solid reaction where the particles are spherical. The term X is the fraction reacted, t is the time and k is the kinetic rate constant. A plot of the function $(1-(1-X)^{1/3})^2$ as a function of time of reaction is shown in Fig 4 for all temperatures of study. The linear relationship of this function with time suggests that the chlorination of pure Ta_2O_5 is a diffusion controlled reaction in the range 733-853K. This plot was used to calculate the kinetic rate constant k for different T and the Arrhenius plot is constructed in Fig. 5. The activation energy for the chlorination of pure Ta_2O_5 by CCl_4 computed from this plot was found to be 24 kJ/mol. The value of activation energy obtained in this study for the chlorination of Ta_2O_5 using CCl_4 in the presence of N_2 is closer to that obtained with use of Cl_2 as chlorinating agent in the presence of $\text{CO}+\text{N}_2$ (32 kJ/mol)[10] than that obtained with gaseous Cl_2 in the presence of graphite (130 kJ/mol)[9]. This would imply that the CCl_4 would decompose to Cl_2 and C at the temperatures of the experiment and react with Ta_2O_5 .

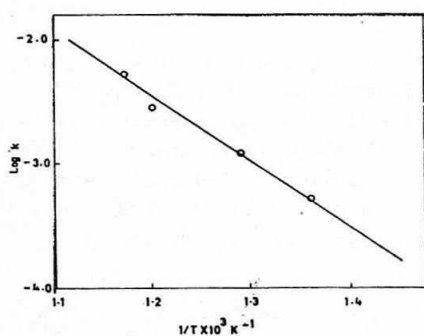


Fig. 5. Arrhenius plot for chlorination of Ta_2O_5

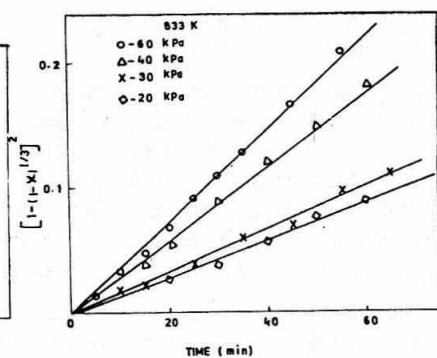


Fig. 6. Plot of $(1-(1-X)^{1/3})^2$ against time at different p_{CCl_4}

Further, it can be inferred from the lower activation energies that the carbon obtained from the decomposition of CCl_4 is far more reactive than elemental graphite or some CO

forms which reacts with Ta_2O_5 . Jena et al[13] have also proposed that the CCl_4 decomposes to Cl_2 and C before chlorination. The variation of the function $(1-(1-X)^{1/3})^2$ with p_{CCl_4} is shown in Fig. 6. It is evident that this function is directly proportional to p_{CCl_4} implying a first order dependence of the rate constant (k) on p_{CCl_4} .

To determine the equilibrium condensed and gas phase composition at the temperatures and partial pressures of CCl_4 used in the experiments, free energy minimisation calculations were carried out using the SOLGASMIX programme[15]. All phases in the Ta-O-Cl-C-N system reported in the literature and whose thermodynamic data is available were included in the analysis. For simplicity, a single step minimisation was done. Thermodynamic data were taken from JANAF thermochemical tables[16]. Species whose data were not available in JANAF, were taken from the recent compilation of Kubaschewski et al[17]. The results obtained for a typical case at 853 K is given in Table I. It was seen that for all the temperatures and partial pressures of N_2 and CCl_4 adopted in this study, no tantalum carbides or nitrides form. However, substantial amounts of solid carbon is left behind. The equilibrium gas consists mostly of Cl_2 , N_2 , $TaCl_5$, CO, CO_2 , $COCl_2$ and some unreacted CCl_4 . The other species of tantalum chlorides and oxychlorides are found to be negligible. Jena et al[10,11] and Allain et al[14] propose that considerable amounts of $COCl_2$ forms during the chlorination reaction in presence of C or CO which dissociate at temperatures above 873 K. The free energy minimisation calculations substantiates their observation.

Table I. Equilibrium Condensed and Gas Phase Compositions at 853 K.

Specie	Moles Input	Moles Output	Partial Pressure, atm	Specie	Mole Input	Moles Output	Partial Pressure, atm
Invariant Condensed Phases				Gas Phase			
C	0.0	0.5026		CO_2	0.0	8.34e-4	5.93e-4
Ta	0.0	0.0		$COCl$	0.0	9.76e-8	6.93e-8
Ta_2O_5	0.00226	0.0		$TaCl_5$	0.0	4.53e-3	3.21e-3
TaC	0.0	0.0		CO	0.0	7.74e-3	5.5e-3
Ta_2C	0.0	0.0		CCl_2	0.0	4.0e-14	2.82e-14
TaN	0.0	0.0		Cl_2O	0.0	8.0e-23	5.67e-23
Ta_2N	0.0	0.0		CCl	0.0	1.0e-25	7.18e-26
$TaCl_5$	0.0	0.0		ClO_2	0.0	1.2e-37	8.31e-38
$TaCl_4$	0.0	0.0		TaCl	0.0	3.3e-50	2.3e-50
$TaCl_3$	0.0	0.0		$TaCl_2$	0.0	2.2e-34	1.59e-34
$TaOCl_3$	0.0	0.0		$TaCl_3$	0.0	3.8e-22	2.72e-22
Gas Phase				$TaCl_4$	0.0	8.0e-11	5.72e-11
N_2	0.3470	0.3470	0.2465	O_2	0.0	4.9e-28	3.46e-28
Cl_2	0.0	1.0130	0.7195	TaO	0.0	1.1e-60	8.08e-61
CCl_4	0.546	0.0329	0.0234	TaO_2	0.0	1.3e-53	9.03e-54
$COCl_2$	0.0	1.9e-3	1.35e-3	$TaOCl_3$	0.0		

CONCLUSIONS

Carbon tetrachloride was found to be a very efficient chlorinating agent for tantalum pentoxide even at low temperatures (733-853 K). Particle size appears to have negligible effect on the chlorination of Ta_2O_5 . The amount of tantalum chlorinated was found to increase with temperature in the range 733-853 K. Nearly 90% of the tantalum oxide could be

converted to its chloride at 853 K in 35 minutes at a carbon tetrachloride pressure of 60 kPa. The kinetic results were found to conform to a diffusion controlled reaction model proposed by Jander. From the Arrhenius plot, the activation energy of the process was estimated to be 24 kJ/mol. The reaction rate constant was also found to be directly proportional to the partial pressure of carbon tetrachloride in the range 20-60 kPa.

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