CHEMICAL KINETICS MODELISATION IN DC PLASMA JETS. APPLICATION TO THE REACTIONS OF $SiCl_4$ IN AN H_2 PLASMA REACTOR.

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ABSTRACT

A chemical kinetics modelisation of a conventional DC plasma reactor is proposed: As the gas mixture {plasma-reactants} is submitted to a certain 'temperature history' in the reactor, the different species react according to the assumed chemical chanels. The chemical composition is then computed versus time. An application of that model to the reduction of $SiCl_4$ in an H_2 plasma is discussed.

1. INTRODUCTION.

The developpement of Photovoltaic Energy is conditionned by the possibility to produce large quantity of Solar grade Silicon at reasonable price. As shown by AMOUROUX /1/, the plasma reduction of Silicon containing species can be a possible way to reach that goal. Following thermodynamic considerations, hydrogen reduction of Silicon tetrachloride appears to be the most promissing chemical system. The reduction of $SiCl_4$ in the high-temperature zone of the jet produces gaseous Silicon wich must be condensed without recombinations with free chloride. In the present paper, we intend to show that it is possible to obtain pure Silicon by quenching the high-temperature mixture. A special attention is paid to the consequences of the departure from chemical equilibrium in the quenching section of the reactor.

II. DESCRIPTION OF THE MODEL

II.1. Description of the reactor

Our model has been established to modelize the real situation skeched on figure 1.

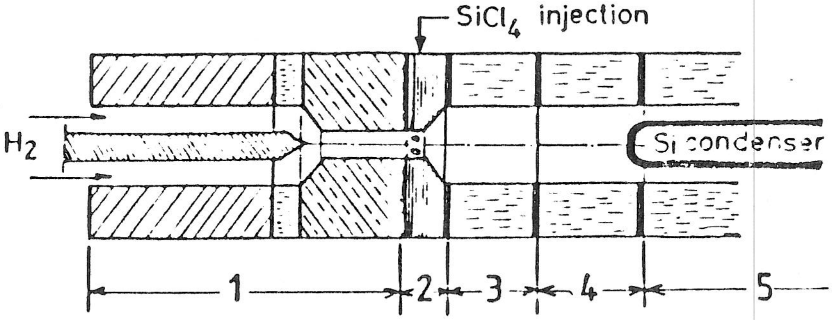

Figure 1_ DC torch and reactor_

The hydrogen plasma is produced by a conventional DC torch (1) wich is fixed to the reactor composed of four sections ; Gaseous $SiCl_4$ is injected radiali through holes in section (2) just after nozzle exit. The high temperature reactions proceed in section (3) and the mixture is "quenched" (or cooled) in section (4). If present, gaseous Silicon is condensed on the probe located at the proper axial position (5) after the quenching section.

The present model does not include the condensation of the vapeurs on the probe.

II.2. "Temperature history" of the gas mixture

Typical temperature and velocity charts of the plasma jet are shown on figures 2 and 3 / 2 /. When the reactants are fed through session (2) they are entrained by the plasma flow as sketched on figures 2 and 3. Here, we assume that the reactants are immediately heated to the temperature of the plasma and entrained at the same velocity following a straight trajectory parallel to the plasma flow. Thus, we are able to know what are the temperature and velocity at any point in the reactor. With these assumptions, the temperature of the mixture has been calculated and plotted versus time on figure 4. The different curves (R = 0mm, R = 0,5 m,...) represent "temperature histories" of mixtures following trajectories at different radius from the reactor axis ;

for example, the curve R = 0mm represents the "temperature history" on the jet axis, and the curve R = 3mm represents the "temperature history" at 3 mm from the jet axis. *It is to be noticed that the natural quenching rate of the flow is approximately the same for all the trajectories :* 610^{7} *K/s.* The reactants wich do not penetrate the jet core do not "see" temperature greater than 8 000° K, but reactants wich penetrate the jet core are only shortly submitted to high-température (510^{-5} s). Finaly we can notice that whatever is the degre of penetration into the plasma jet, all the reactions must proceed in less that *1 ms wich can be considered as the typical dwell time of the species in that kind of reactor.*

II.3. Chemical kinetics differential equations 6

The I chemical species $\mathcal{A}_i$ of the mixture react in J chemical reactions of rate constant k_j ($j = 1 \ldots J$).

$$(1) \quad \sum_{i=1}^{I} \nu_{ji} \mathcal{A}_i \xrightarrow{k_j} \sum_{i=1}^{I} \nu'_{ji} \mathcal{A}_i$$

During their dwell time in the reactor the I molar concentrations (mole/cc) of the considered species vary with time according to the differential kinetics equations

$$(2) \quad \frac{dy_i}{dt} = \omega_i - \left(\frac{y_i}{\rho} \sum_{i=1}^{I} \omega_i - \frac{y_i}{T} \frac{dT}{dt} \right)$$

where ρ is the mass density of the mixture (mole/cc) and w_i is the production and loss term of the i^{th} specie

$$(3) \quad \omega_i = \sum_{j=1}^{J} k_j . (\nu'_{ji} - \nu_{ji}) \prod_{\ell=1}^{I} y_\ell^{\nu_{j\ell}} .$$

In eq. (2) the temperature time dependent term is easely calculated using temperature history relations described in part 2.2.

The I coupled differential equations (2) are computer solved using a predictor-corrector algorithm developped by WINSLOW /3/. The vector solution gives the concentrations versus time along a particular trajectory. Concentrations versus axial position can be easely computed using temperature-time history relations.

II.4. The $SiCl_4$ - H_2 system. Chemical reaction rates data

Applied to the reduction of $SiCl_4$ in an H_2 plasma, our model can be run if the chemical reaction rates of all the reaction channels wich are supposed to be important are known. In the case of $SiCl_4$ - H_2 these data are scarce unless missing.

we have included the following species ;

H_2, H, Cl_2, Cl, HCl, $SiCl_4$, $SiCl_2$, Si (g).

The species react in 14 reactions listed in table 1. As it can be noticed the reduction reactions ot the type

$$SiCl_n + H \rightarrow SiCl_{n-1} + HCl$$

$$SiCl_n + H_2 \rightarrow SiCl_{n-1} + HCl + H$$

are missing and intermediate chlorides $SiCl_3$ and SiCl have not been considered. The modelisation is consequently incomplete and probably does not correctly modelise the situation at intermediate temperature (≈ 5 000 K) where these reactions would be efficient. However comparisons (cf part 3) with equilibrium calculations show that this lack is not sufficient to cancel the model.

III. DISCUSSION OF RESULTS ON $SiCl_4$ - H_2 SYSTEM

III.1. Comments on a typical chemical kinetics result

A typical result of that modelisation is plotted on figure 5. For that example the trajectory R = 3 mm as been considered the left vertical scale represents the molar fraction, the right vertical scale represents the mixture temperature, curves are plotted versus time. The results are discussed in three time intervals corresponding to the parts (3, 4 and 5 of figure 1).

- From time 10^{-5} s to time 10^{-4} s (high temparature section (1) $SiCl_4$ and H_2 are decomposed into $SiCl_2$, H and Cl. Up to time 310^{-5} s (7 000° K) HCl is formed from H and Cl, and decomposed from 310^{-5} s (7 000° K) to 10^{-4} s (8 000° K). As $SiCl_4$ and HCl are decomposed Si (g) is formed (33 % conversion at time 10^{-4}s).
- From time 10^{-4} s to time 10^{-3} s (quenching section (2)) the mixture is cooled at 610^7 K/s from 8 000° K down to 2 000° K. During that time interval HCl, H_2 and to a less extend Cl_2 are recombined, but up to time 310^{-4}s $SiCl_2$ continues to decompose into Si and Cl. The reason is that hydrogen catch more efficiently Cl than Si and $SiCl_2$ do. That means that hydrogen does not act as a reducer (HCl is not a high-temperature stable specie) but efficiently prevents the recombinaison of chlorine with Silicon.
- The maximum concentration of gaseous Silicon is obtained at the entrance of the condenser section (5). In this section $SiCl_2$ recombines slowly with Cl to forme $SiCl_4$, HCl is stable and prevents the recombinaison of chlorine with Silicon. On the trajectory R = 3 mm, wich is experimentaly reasonable, the maximum conversion of $SiCl_4$ into Si(g) is 61 %.

III.2. Comparisons with equilibrium calculations

It is worth comparing the chemical kinetics results with those obtained with chemical equilibrium calculations / 1,2 /. The complex chemical equilibrium diagrams commonly represent the molar fraction of the species versus temperature. Using the time-temperature history it is possible, with a variable change, to plot the equilibrium versus time. Such a diagram has been plotted on figure 6 for R = 3 mm. It represents the composition that would be obtained with chemical kinetics if all the reactions could proceed at the same rate during very short times (< 10^{-3}s).

At low temperature ($T<5\ 000°$ K), as the reactants are fed in the reactor, equilibrium considerations overestimate the decomposition of $SiCl_4$ and H_2. Above 5 000° K the chemical equilibrium is approximately realized for H_2, Cl_2, HCl, Cl, H (equivalent molar fraction on figure 5 and 6), but the decomposition reactions of $SiCl_4$ are far from equilibrium because $SiCl_2$ has a very long lifetime. In the cooling section of the reactor, at temperature lower than 5 000° K ($t > 310^{-4}$ s), the mixture departs again from equilibrium for all the species. If chemical equilibrium is considered the Si condenser must be placed in the reactor in the cooling section at approximately 7 cm from injection $SiCl_4$, in the case of chemical kinetics it must be placed at 13 cm from injection section. These results are significantly different and show that chemical kinetics must be investigated.

IV - CONCLUSION

Chemical equilibrium investigations of the performances of plasma reactor are not sufficient to modelize the real situations. In the case of $SiCl_4 + H_2$, it has been shown that the long life time of $SiCl_2$, the slow recombinaison of the molecules, and the retention of chloride by hydrogen on HCl give the possibility to convert 60 % of the fed $SiCl_4$ into gaseous Silicon wich must be condensed on a probe a the proper temperature.

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TABLE 1 Reaction rates $k = BT^{x} \exp(-E/RT)$

(d : direct. r : reverse. E (kcal/mole)

Reaction		B	x	E	Ref.
$SiCl_4 \underset{r}{\overset{d}{\rightleftharpoons}} SiCl_2 + Cl$	(d)	5E8	0	+ 88	4
	(r)	5.64E-50	2	- 83.240	-
$SiCl_2 \underset{r}{\overset{d}{\rightleftharpoons}} Si\ (g) + 2\ Cl$	(d)	5E7	0	126	4
	(r)	3.23E-49	2	- 84.330	-
$Cl2 + M \rightleftharpoons 2Cl + M$	(d)	7.58E-19	-3.1	57.1	5
	(r)	3.57E-9	-2.1	- 4.535	5
$H + HCl \rightleftharpoons Cl + H2$	(d)	1.36E-12	0.68	4.7	5
	(r)	2.236E-12	0.68	5.668	5
$HCl + M \rightleftharpoons H + CL + M$	(d)	8.18E-19	-3	102.170	5
	(r)	8.027E-9	-2	6.081	5
$Cl + HCl \rightleftharpoons Cl_2 + H$	(d)	2.99E-10	0	49	5
	(r)	5.344E-10	0	1.874	5
$H_2 + M \rightleftharpoons 2\ H + M$	(d)	1.22E19	-2.5	103.2	5
	(r)	0.776E-7	-2	0	5

Theses rates are expressed in s^{-1} or cm^3 $molec^{-1}$ s^{-1} or cm^6 $molec.^{-1}$ s^{-1}

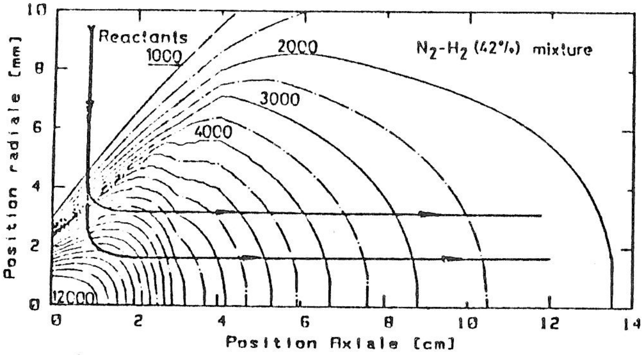

Figure 2 _ Temperature contours.

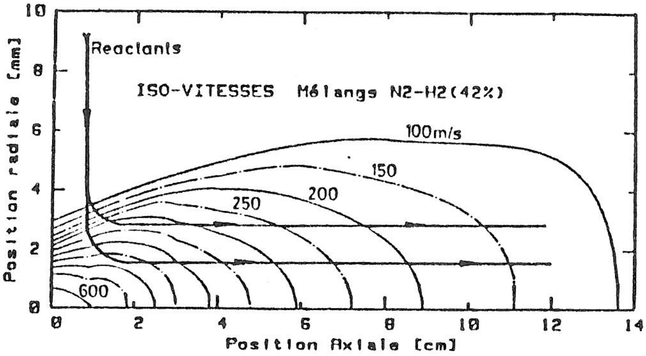

Figure 3_ Velocity contours.

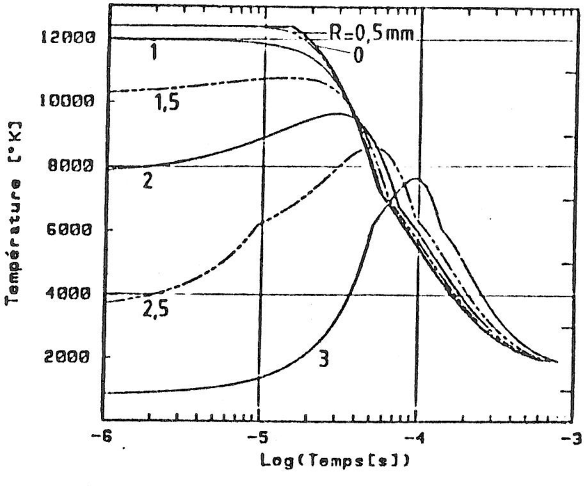

Figure 4 Temperature-time histories

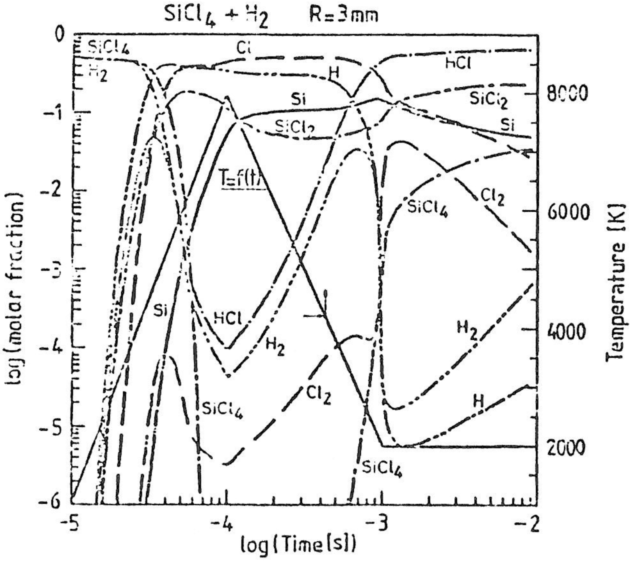

Figure 5 _ Results of the kinetics model.

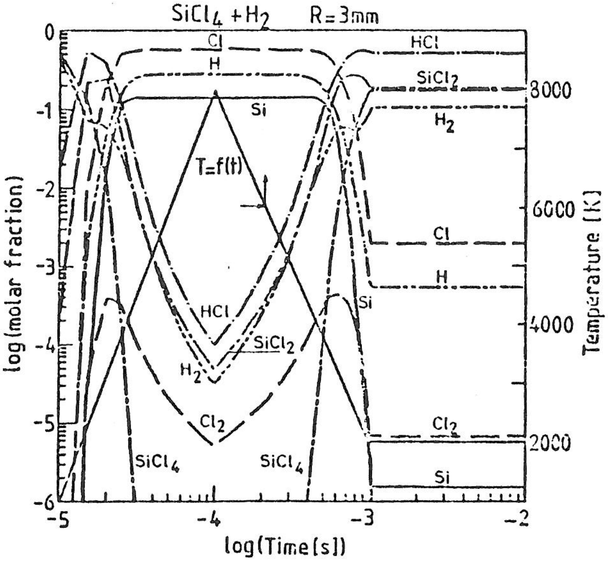

Figure 6 _ Results of the equilibrium model.