

The evaluation of the pyrochemistry for the treatment of Gen IV nuclear fuels – Inert matrix chlorination studies in the gas phase or molten chloride salts

S. Bourg *, F. Péron, J. Lacquement

Commissariat à l'Energie Atomique, DEN/VRH/DRCP/SCPS/LPP, Bat 399, CEA Marcoule, BP 17171, 30207 Bagnols/Cèze cedex, France

Abstract

The structure of the fuels for the future Gen IV nuclear reactors will be totally different from those of PWR, especially for the GFR concept including a closed cycle. In these reactors, fissile materials (carbides or nitrides of actinides) should be surrounded by an inert matrix. In order to build a reprocessing process scheme, the behavior of the potential inert matrices (silicon carbide, titanium nitride, and zirconium carbide and nitride) was studied by hydro- and pyrometallurgy. This paper deals with the chlorination results at high temperature by pyrometallurgy. For the first time, the reactivity of the matrix towards chlorine gas was assessed in the gas phase. TiN, ZrN and ZrC are very reactive from 400 °C whereas it is necessary to be over 900 °C for SiC to be as fast. In molten chloride melts, the bubbling of chlorine gas is less efficient than in gas phase but it is possible to attack the matrices. Electrochemical methods were also used to dissolve the refractory materials, leading to promising results with TiN, ZrN and ZrC. The massive SiC samples used were not conductive enough to be studied and in this case specific SiC-coated carbon electrodes were used. The key point of these studies was to find a method to separate the matrix compounds from the fissile material in order to link the head to the core of the process (electrochemical separation or liquid–liquid reductive extraction in the case of a pyrochemical reprocessing).

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1. Introduction

The structure of the fuels for the future Gen IV nuclear reactors will be totally different of those of PWR, especially for the GFR concept including a closed cycle (i.e. the fuel will be treated to separate all the actinides together from the fission products and to recycle them to fabricate new fuel assemblies) [1]. In these reactors, fissile materials (carbides or

nitrides of actinides) should be embedded in an inert matrix.

In order to build a reprocessing process scheme, the feasibility of the dissolution either of the fissile material or of the inert matrix must be assessed by hydrometallurgical or pyrometallurgical methods, and then a core of process must be developed to separate all the actinides from the fission products.

In the present paper, which is dedicated to pyrochemistry, we present the results concerning the high temperature dissolution of some matrix candidates: silicon carbide (SiC), titanium nitride (TiN), and zirconium carbide (ZrC) and nitride (ZrN).

* Corresponding author.

E-mail address: stephane.bourg@cea.fr (S. Bourg).

This includes the study of the reactivity of the materials towards chlorine gas in gas phase and then chemical and electrochemical studies in molten chloride melts. The key point of these studies was to find a method to separate the matrix compounds from the fissile material in order to link the head of the process to a core of the process either by hydro- or pyrometallurgy, for example, the liquid–liquid reductive extraction in molten fluoride/liquid aluminum [2].

2. Experimental

All the experiments were carried out in quartz cells, heated in a well furnace under argon or reactive (HCl, Cl₂) atmosphere. At the exit of the cell, the reactive gases are trapped by bubbling into two washing flasks (NaOH, 5–6 M).

Matrix powders were commercial and used without any further treatment (SiC, ZrC, ZrN and TiN from Goodfellow; 90% 45 μm). Massive SiC and TiN samples were made by Boostec (natural sintering, extruded, 1 mm thickness plates). ZrN electrodes were made at CEA Saclay (3 mm diameter rods). SiC and ZrC POCO electrodes were made at CEA Grenoble by CVD technique (2 mm diameter rods).

2.1. Chlorination in gas phase

Typically 400–800 mg of studied compounds (powder or massive sample) were placed in a quartz crucible. The crucible was introduced into a quartz cell. Prior the heating, the cell was flushed with pure argon (5.6) for at least 1 h (flow rate 4 l/h) and then flushed with chlorine gas (N40, 99.99%, air liquid) (3 l/h). When the preheated cell was under chlorine atmosphere, it was introduced rapidly into the furnace. At the end of the chlorination period, the cell was removed from the furnace and flushed with argon. The chlorination yield was determined by weighing the samples before and after experiment. For carbide matrices, the quantity of produced carbon was determined by TG analysis under oxygen atmosphere at 400 °C.

2.2. Chlorination in molten salts

The LiCl–KCl eutectic is prepared with pure LiCl (Aldrich 99.99%) and KCl (Aldrich 99.99%), in quartz crucible. The mixture of powders is first heated at 350 °C for 4 h, then heated at 500 °C

and purified by bubbling pure HCl gas (N50, 99.999%, air liquid) for 1 h and then argon for 1 h. The eutectic is crushed into powders and store under argon atmosphere. The eutectic is then used without any further purification.

For an experiment, typically 400–800 mg of studied compounds are mixed with 20 g of LiCl–KCl eutectic powder, in a quartz crucible. The crucible is placed in the cell, under argon atmosphere. The cell is introduced in the furnace and then heated at 350 °C for 4 h and then, at the required temperature. The argon atmosphere is replaced by the chlorine gas and then the tube is plunged into the molten salt for bubbling during the required period. Then argon is bubbled into the salt and the furnace is stopped. At the end of the experiment, the solid salt is dissolved in water. The solid residue is filtered and dried, then weighted to determine the weight loss. For experiments on carbides, TGA under oxygen at 400 °C is used to determine the carbon fraction in the residue.

2.3. Electrochemical experiments

The LiCl–KCl is prepared as described above. Similarly, pure KCl is dehydrated by bubbling pure HCl gas (N50, 99.999%, air liquid) for 1 h at 800 °C. For a typical experiment, a quartz crucible, containing 20 g of salt, is placed in the quartz cell, then flushed with argon. The cell is heated at the required temperature and purification with HCl is done prior each experiment, just before the introduction of the electrodes. The reference electrode is a silver/silver chloride electrode (0.75 mol/kg) in LiCl–KCl, in a Pyrex tube. Working electrodes are made with a massive sample of the matrix compound to be studied, attached to a tungsten wire for electrical conduction. The counter electrode is a tungsten wire. The experiments are piloted by an Autolab potentiostat (GPES software).

3. Behaviour of inert matrices

3.1. Thermodynamical data

Energies of the chlorination reactions were calculated with HSC Outokompu software for all the matrices. It showed that on a thermodynamical point of view, the chlorination of TiN, ZrN, ZrC and SiC, at 500 °C, leads to the formation of the corresponding chloride compounds, gaseous at the temperature of the experiments (Table 1). For

Table 1
Energies and thermodynamical potentials of chlorination of SiC, ZrC, ZrN and TiN at 500 °C, HSC calculations

Equation	Energy (kJ)	E vs. Cl_2/Cl^- (V), MCl_4 (g)
$\text{SiC} + 2\text{Cl}_2(\text{g}) = \text{SiCl}_4 + \text{C}$	-494.6	-1.28
$\text{ZrC} + 2\text{Cl}_2(\text{g}) = \text{ZrCl}_4 + \text{C}$	-591.4	-1.53
$\text{TiN} + 2\text{Cl}_2(\text{g}) = \text{TiCl}_4 + 1/2\text{N}_2(\text{g})$	-405.7	-1.05
$\text{ZrN} + 2\text{Cl}_2(\text{g}) = \text{ZrCl}_4 + 1/2\text{N}_2(\text{g})$	-488.5	-1.26
$\text{Li}(\text{l}) + 1/2\text{Cl}_2(\text{g}) = \text{LiCl}$	-344.9	-3.57

the nitride compounds, the by-product is nitrogen. For the carbide ones, there is formation of solid carbon. The oxidation potentials were also calculated. The obtained values showed that, from a thermodynamical point of view, it is possible to dissolve anodically the four matrices in the LiCl–KCl eutectic, at 500 °C.

3.2. Chlorination in the gas phase

In the gas phase, TiN and ZrN and ZrC powders were easily attacked by chlorine gas from 400 °C whereas temperatures over 900 °C were needed to have a significant attack of SiC.

As predicted, there was no residue with nitrides TiN and ZrN. Typically, during the first 30 min under chlorine gas, it seems that there is no reaction

and then a white fog appears in the cell and condenses in the cold parts of the top of the cell as a coloured liquid with TiN and as a white powder with ZrN. After a total time of 2 h, the crucible was empty. The liquid TiCl_4 is very volatile and nothing remains in the cell at the end of the chlorination time. The white solid ZrCl_4 dissolves in water as ZrOCl_2 .

With SiC and ZrC, the reaction is slower and at least solid carbon is recovered at the end of the experiment. With SiC, a temperature of 900 °C is required to have an efficient chlorination. The maximum theoretical weight loss of 70% (if all the Si is volatilised under SiCl_4 form and all the carbon remains in the crucible) is obtained after 5 h under Cl_2 . For a shorter chlorination time, a mixture of SiC and C is recovered, and the carbon can be removed by pyrolysis under oxygen at 400 °C (Fig. 1).

The chlorination of a ZrC powder is much easier and is possible even at 250 °C, but very slowly (Fig. 2(a)). At 550 °C, 4 h are necessary for a full chlorination of a 850 mg powder sample (Fig. 2(b)).

3.3. Dissolution in molten salts

In molten chloride, the bubbling of chlorine is efficient for the four materials in powder form but less than in gas phase, mainly owing to the low solubility of chlorine in molten salts (LiCl–KCl at

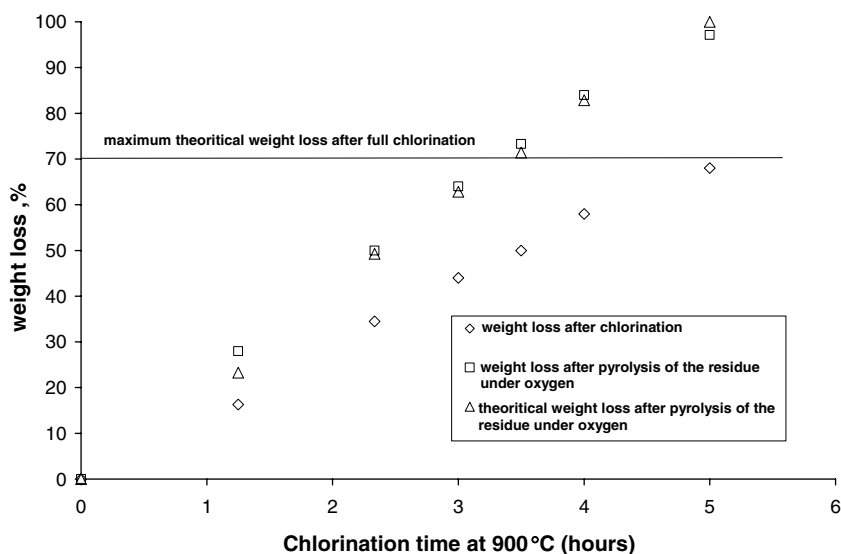


Fig. 1. Weight loss of a 400 mg SiC powder sample as a function of the chlorination time at 900 °C. The residue is then pyrolysed under oxygen at 400 °C.

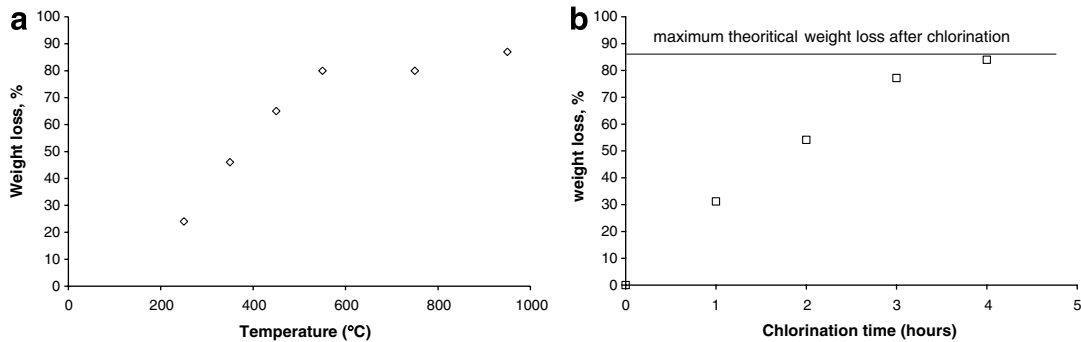


Fig. 2. Weight loss of a 850 mg ZrC powder sample (a) as a function of the temperature for a 4 h chlorination time and (b) as a function of the chlorination time at 550 °C.

500 °C for TiN, ZrN and ZrC, KCl at 900 °C for SiC). It is assumed then both dissolved chlorine and chlorine gas bubbles react with the solid. With the carbides, residual solid carbon remains in the melt whereas the volatile tetrachloride is eliminated. In these cases, it is very difficult to remove the residual carbon by bubbling oxygen in the molten salt.

Much more interesting is the electrochemical behaviour of the materials. First, an electrochemical study was performed both on TiN (Fig. 3) and ZrN (Fig. 4) massive samples as working electrode. These materials are conductors and it was clearly established that it was possible to oxidise them, as expected at 0.8 V vs. ref. and 0.6 V vs. ref. respectively. Ti(III)/Ti(II) and Ti(II)/Ti(0) couples on one hand [3] and Zr(IV)/Zr(II) and Zr(II)/Zr(0) couples on the other hand [4] were identified in solution.

Then electro-dissolutions were carried out successfully, showing a fast dissolution/desegregation

of the anodes, probably owing to a specific attack at the grain boundaries. A charge of 400 °C for TiN and 300 °C for ZrN lead to a total desegregation of the immersed part of the anode, whereas a charge of 2500 °C was necessary to fully oxidise them. Cyclic voltammetry studies performed during the electrolysis showed that the quantity of titanium and zirconium species in solution increased progressively. With titanium, the dark blue colour of the bath confirmed also the presence of Ti(III) species in solution (see Figs. 5 and 6).

In order to perform an electrochemical study of SiC, the first tests were performed on massive anode plates (alpha SiC) but they were not conductive enough. We then use POCO rods coated with a SiC layer by CVD as anode. The very thin SiC layer (15 µm) was sufficiently conductive for a voltammetric study. It was possible to dissolve electrochemically the SiC layer by coulometry at 0.7 V vs. ref. After coulometry, the oxidation potential

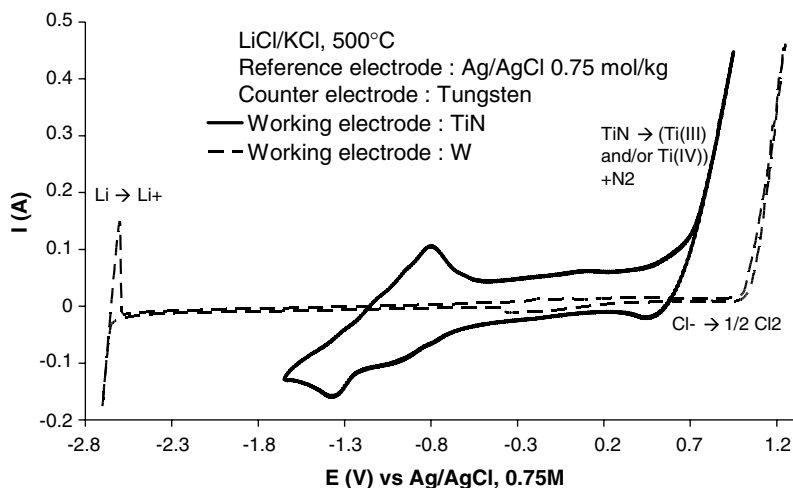


Fig. 3. Electrochemical study on a TiN working electrode (0.1 V/s).

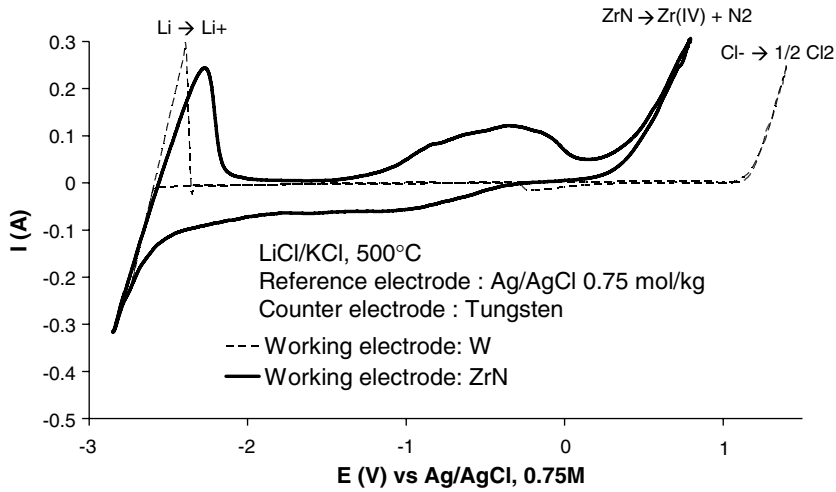


Fig. 4. Electrochemical study on a ZrN working electrode (0.1 V/s).

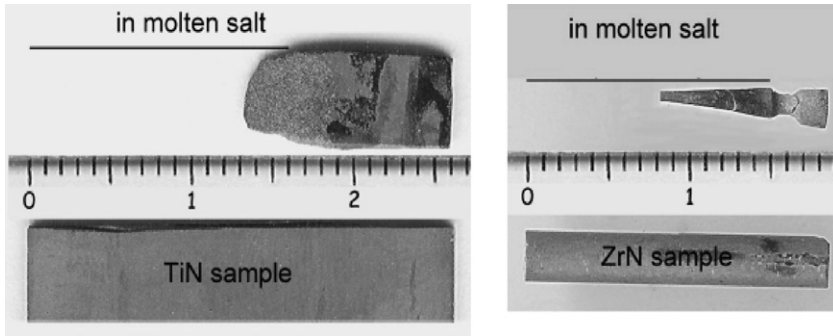


Fig. 5. TiN and ZrN anodes before and after electrodisolution tests.

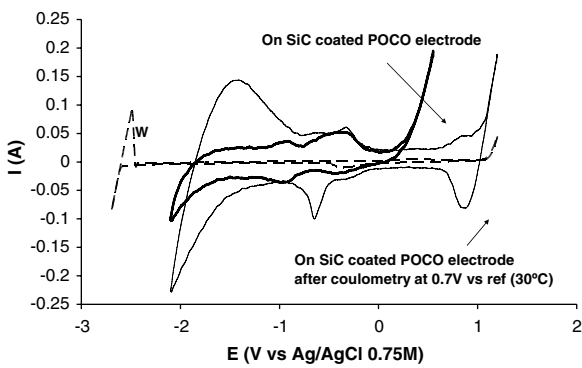


Fig. 6. Cyclic voltammograms in LiCl–KCl at 500 °C on SiC POCO WE before and after coulometry (0.1 V/s).

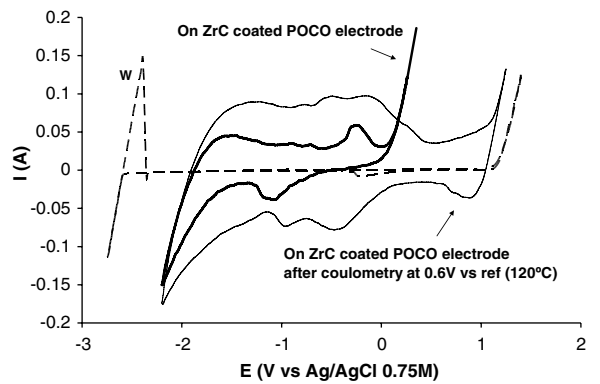


Fig. 7. Cyclic voltammograms in LiCl–KCl at 500 °C on ZrC POCO WE before and after coulometry (0.1 V/s).

of the anode was that of chloride ions (1.1 V vs. ref) and no more that of SiC (0.5 V vs. ref).

The same study was carried out on ZrC POCO electrode, with similar results (Fig. 7). The oxida-

tion potential of the ZrC-coated POCO anode was around 0.3 V and after the coulometry at 0.6 V, the oxidation potential was around 1 V.

4. Conclusions

Whatever the studied refractory matrix SiC, ZrC, TiN or ZrN, either a chemical or an electrochemical method was able to attack the material. The chemical attack with chlorine gas, directly on the solid seems to be the most efficient way to dissolve the material, at 500 °C for TiN, ZrN and ZrC and at 900 °C for SiC. With the nitride materials, no residue was recovered whereas solid carbon remains in the crucible with the carbide ones. If needed, an anodic dissolution is also possible on massive TiN and ZrN samples, and on thin SiC and ZrC layers at 500 °C.

Therefore, different scenarios can be developed to separate the fuel from the matrix in a head-end step of a reprocessing scheme: to volatilise the matrix and keep the fuel compounds as a solid (either oxide, carbide or chloride); to volatilise the fuel and keep the matrix as a solid; to dissolve the matrix in molten salt and not the fuel or dissolve the fuel and not the matrix and separate them by filtration; to dissolve both the matrix and the fuel and then find a chemical way to separate them.

Among the studied matrices, SiC is the most resistant one towards chemical attacks, with temperatures over 900 °C. In a dispersed GFR fuel concept, if SiC is used as a matrix, and if it is chemically possible to reach the fissile material, a selective dissolution of actinide compounds has to be investigated at a temperature under 600 °C, since SiC is quite inert at these temperatures. TiN, ZrN and ZrC exhibit low resistance towards chlorine and

are rapidly attacked from 500 °C. With them, it should be possible to volatilise the matrix and keep the fuel as a solid. Electrochemical methods can also be used, with some technological developments, with the risk to have then all the compounds in solution and then find a method to separate them.

With respect to a pyrochemical process, progress has been made at numerous levels, giving useful information to enable coherent scenarios to be proposed. In the future, the work will be focussed on the transition steps, allowing the coupling of each process part.

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