

Zircaloy Cladding as Starting Precursor for Ceramic Waste-Forms – 15562

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ABSTRACT

Zircaloy cladding of spent fuel is regular waste-stream related to the process of reprocessing. It remains in the apparatus after spent fuel dissolution.

The most common technique of zircaloy cladding treatment is cementation and disposal in metallic containers. In view of the high cost of the cladding material (mainly zirconium), there have been a number of proposals for this material to be recovered and re-used. However, the residual contamination of the claddings following the dissolution of the fuel and the chemical stability of the zirconium militate against any proposal for a recycling process that might be economically reasonable. At the same time there is a lot of information available about synthesis of mineral-like materials based on zirconium for immobilization of long-lived radionuclides. The object of this work was to study experimentally electrochemical dissolution of fuel rod cladding for further obtaining starting precursor for the synthesis of ceramic-waste forms. The results of experiments on electrochemical dissolution of zirconium and zirconium alloy (fuel rod cladding) in nitric acid solutions are presented. The peak dissolution rate of specimens is shown to be observed in dilute nitric acid at elevated temperatures. The rate of dissolution rises with temperature, reaching ~40-70 mg/cm²·h at 90°C. The current yield at this point is 0.6-0.7 g/A·h. The results of analysis of the surface oxide film on specimens and residues formed during dissolution are also presented. An electrochemical dissolution of zircaloy claddings is the common technique for preparation of zirconium solutions to be used for ceramic waste form synthesis.

INTRODUCTION

The process of radioactive waste isolation must be accompanied with the conversion of waste into the stable final waste forms to reduce potential hazards associated with the temporary waste storage, transportation, and final disposal.

One of the waste types formed during reprocessing of irradiated nuclear fuel is fuel element claddings, which remain in the apparatus after spent fuel dissolution. The average volume of unconsolidated hulls and cladding wastes is about 0.3 m³ per 1 ton of uranium but it can vary in a broad range from 0.2 to 0.6 m³ depending on the type of fuel assembly. However the bulk density of hulls is approximately 1.8-2.5 t/m³, and this will depend on the actual waste densities. We have to note also besides fuel claddings zirconium admixture is typical for matrix of spent fuel quite essential quantities (4-5 kg Zr per 1 ton of fuel with a burn-up of 40-50 MW·day/kg uranium).

The most commonly-used method of isolating spent fuel claddings is to encapsulate them in concrete and place them in metal containers.

The problems associated with the zirconium wastes in Russia, is similar to all other countries which deal with reprocessing of spent fuel.

In view of the high cost of the cladding material (zirconium), there have been a number of proposals for this material to be recovered and re-used.

But the actual situation very often differs greatly from the picture established in the public conscience.

However, the residual contamination of the claddings following the dissolution of the fuel and the chemical stability of the zirconium militate against any proposal for a recycling process that might be economically justifiable. Use of reagents such as hydrofluoric acid is not really feasible on a commercial scale because of the problems in finding materials from which to build the dissolver unit and in dealing with the resulting wastes.

There is, however, information to be found in the literature on the synthesis of mineral-like materials based on zirconium [1-4]. The idea of using zirconium (from fuel and claddings) to synthesize ceramic waste forms for long-term storage or underground disposal is conceptually attractive.

The concept of using crystalline materials to immobilize high-level radioactive wastes (HLW) has been developed by numerous contributors however the majority of developments (for example, Synroc) were based on immobilization HLW without partitioning. Existing technologies in Russia allow reprocessing of spent fuel and separation of radionuclides of high-level wastes into fractions. Researches carried out at the V.G. Khlopin Radium Institute have demonstrated the possibility to immobilize actinide fraction of HLW in mono-phase or double-phase ceramics based on host-phase such as zircon, $(Zr,An)SiO_4$, and cubic zirconia, $(Zr,Y,An)O_2$ [4]. The aim of this work was to investigate the process of electrochemical dissolution (breakdown) of fuel rod claddings in nitric acid solutions. A successful outcome to this task would enable zirconium separated from claddings to be utilized at the stage of encapsulation of high-level waste through immobilization in a matrix based on zirconium dioxide, which features a high level of chemical stability. In this case the need to cleanse the zirconium of radionuclides would be eliminated. It should be emphasized that if this solution were to be adopted, the need for a unit to encapsulate the material in concrete and the disposal of this encapsulated waste would disappear also.

RESULTS OF EXPERIMENTS AND DISCUSSION

The installation used to study the process of electrochemical dissolution of zirconium was comprised of the following units: electric power source, thermostat, electrochemical cells with magnetic mixer and monitoring and measuring instruments. The surface area of the zirconium specimens (anodes) was 4 cm^2 , and the solution volume was 40 cm^3 . Prior to each experiment, the specimens underwent identical preparation (polishing and oxidation in a $K_2Cr_2O_7$ solution). In the first phase of the study, flat zirconium electrodes were used. At low voltages (5-25 V), the breakdown process was found not to occur. The reason for this negative result was the presence of a thick oxide film on the surface of the specimens, which at low potential values prevented sufficient current from being passed. The analysis results revealed that when the specimens were passivated, the oxide film thickness on flat electrodes is from 200 ± 10 to 800 ± 200 nm). When the voltage was raised to 180 V in the nitric acid solutions (1-8 mol/L), the rate of breakdown (K) became significant, and absolute values reached a magnitude of $70\text{ mg/cm}^2\cdot\text{h}$. The results obtained are shown in Table I.

In the next series of experiments, solutions of nitric acid and calcium nitrate were used as electrolytes (Table II). Peak breakdown rates were achieved using 1M calcium nitrate in 1M nitric acid as the electrolyte. When the nitric acid concentration was raised to 8 mol/L the breakdown rate was significantly lower than in 1M acid, and bore little relation to temperature.

TABLE I. Results of electrochemical dissolution of metallic zirconium specimens in nitric acid.

Experimental conditions		Current and voltage values		Rate of specimen breakdown K, mg/cm ² ·h
Acid concentration, mol/L	T, °C	U, V min/max	I, mA	
8.0	54±5	178/180	350-70	19.6
	51±2		50-14	0.17
	88±3	175/180	250-50	38.3
3.0	20±1		70-20	8.2
	86±2	175/180	450-200	48
	86±2		250-125	21.8
1.1	22±3	180/180	70-40	7.4
	25±4		50-20	6.8
	56±4	177/180	500-260	42.5
	70±3	173/180	155-75	49.5
	91±2	173/179	250-75	65.4

The reason for the increase in the zirconium breakdown rate should probably be seen as lying in the formation of calcium zirconate, the properties of which are different from those of zirconium oxide, (the density of zirconium oxide and calcium zirconate is 5.73 g/cm³ and 4.78 g/cm³ respectively). The increase in dissolution rate is brought about by a fragmentation of the surface oxide layer and this increases the effective surface and reduces the insulation due to the oxide film.

TABLE II. Experimental conditions and results of electrochemical dissolution of metallic zirconium specimens in nitric acid.

The composition of solution, mol/L		T, °C	Mixing	Voltage, U min/max	Zr concentration, g/L	Current yield, M _i , g/A·h
[HNO ₃]	[Ca(NO ₃) ₂]					
1.1		56±4	–	177/180	0.5	0.65
		50±2	+		0.2	0.70
3.1		56±4	–	175/180	0.7	0.73
		49±2	+		0.3	0.75
8.0		54±5	–	178/180	0.3	0.66
		51±2	+		0.05	0.04
8.0	1.0	65±16	+	140/145	0.4	0.54

X-ray phase analysis was used to determine the composition of the oxide film formed on the surface of the specimens, following electrochemical dissolution at different acidities. At the same time an analysis was made of the slurry left behind after dissolution of specimens in nitric acid. The results are given in Table III.

TABLE III. Results of analysis of the composition of the oxide film on the surface of zirconium electrodes and composition of the slurry formed during dissolution.

Acid concentration, mol/L	T, °C	Oxide film composition, %			Slurry composition, %		
		ZrO ₂ tetrag.	ZrO ₂ monoclin	Zr met.	ZrO ₂ tetrag	ZrO ₂ monoclin	Zr met.
1	20	15	30	55	90	–	10
3	20				80	–	20
3	90	30	70	–	–	–	–
8	90	30	70	–	80	20	–

When calcium was present in the solution, the X-ray patterns showed lines relating to cubic forms of zirconium dioxide, calcium zirconate and also compounds such as CaO, Ca(OH)₂ and CaCO₃. The peak yield of cubic zirconium dioxide was observed in a Ca(NO₃)₂ solution without nitric acid.

The results obtained are of interest because the formation of the cubic modification of zirconium dioxide under the conditions described is unexpected. We can only assume, with considerable reservations, that the appearance of these forms is linked to the electrochemical process that is occurring at the sample surface. When the acid concentration is raised to 8 mol/L no zirconate phase is formed, and the results obtained are no different to the data for nitric acid without calcium nitrate.

It should be stressed that in many experiments we were unable to keep the current and voltage parameters constant and a considerable scatter was seen in the data obtained for parallel experiments. Disruption to the course of the process was caused by the particular features of electrochemical dissolution of zirconium. Strictly speaking, the process we are looking at should be called electrochemical destruction (breakdown), not dissolution.

The high degree of chemical stability of zirconium is caused by the formation of an oxide film on the surface. Attempts to remove the protective oxide film provide no perceptible benefit, precisely because of the high level of activity of the metal, which gives rise to new oxide layers, and it is consequently quite difficult to evaluate the contribution made by the electrochemical dissolution process itself. A certain amount of information may be obtained if we calculate the rate of dissolution from the loss of mass of the specimen over a unit of time, related to the current magnitude; in other words, if we evaluate the current yield (M_i) for different experiment conditions.

It should be emphasized that in this case the current yield magnitude is largely formal, but it does nevertheless enable the required parameters and the productivity of the process to be evaluated. In the light of the results obtained, the mechanism of electrochemical dissolution (breakdown) of zirconium in nitric acid may be presented as follows.

Penetration of the oxide film leads to electrochemical oxidation of the surface with simultaneous formation of a new oxide layer. (The surface oxide layer plays the role of a sort of capacitor, and when it is broken down, there are sharp increases in voltage and current. The dissolution process does not, therefore, take place at low potential values at which the oxide layer cannot be broken down). Mass loss in the specimen is essentially caused by surface destruction and the formation of quite large fragments of slurry, containing metal particles as well as zirconium hydroxide.

When the oxide film has been penetrated, there is partial dissolution of fragments of the

specimen surface, and in this case the zirconium concentration is 0.1-0.9 g/L. In neutral electrolytes, breakdown of the specimen is linked to formation of calcium zirconate, as confirmed by the slurry analysis results.

Experiments with specimens of VVER reactor fuel rod claddings and PWR cladding (Zircaloy-4) were performed on the same rig using an equivalent methodology. The specimens used were not subjected to any treatment prior to commencement of the experiment. A stabilizing device was included in the electrical circuitry of the rig which enabled a significant smoothing out of the current-voltage relationship. The current magnitude was kept constant (100 mA), and the total charge in any given experiment was 0.2 A·h. In the experiments with alternating current, the same cladding material was used as the second electrode. (In calculating the rate, the loss of mass in the two specimens and their area was correspondingly added). The results of the experiments are shown in Tables IV and V.

TABLE IV. Results of experiments with electrochemical dissolution of fuel VVER fuel rods claddings using direct current.

Experimental conditions					K, mg/cm ² ·h	M _i , g/A·h
The composition of solution	T, °C	Mixing	U _{init} , V	U _{fin} , V		
Direct current – 100 mA. PWR fuel rod claddings						
Ca(NO ₃) ₂ – 1.0M HNO ₃ – 1.0M	26±1	–	135	14	5.2	0.13
	26±1	+	150	150	13.0	0.31
Ca(NO ₃) ₂ – 1.0M	86±2	–	5(60)	5	31.6	0.75
	90±2	+	5	405	33.3	0.79
	28±2	–	145	135	15.7	0.37
	28±2	+	145	145	12.8	0.31
	87±3	–	5.5	5.5	34.6	0.83
Direct current – 100 mA. VVER fuel rod claddings						
Ca(NO ₃) ₂ – 1.0M HNO ₃ – 1.0M	23±2	–	140	146	13.3	0.31
	22±2	+	136	140	12.9	0.30
	86±2	–	80	82	27.8	0.64
	87±1	+	110(20)	5	33.5	0.77
Ca(NO ₃) ₂ – 1.0M	25±2	–	140	130	10.1	0.23
	25±1	+	150(130)	155	5.7	0.13
	88±1	+	140	108	27.3	0.63

Just as in the experiments with flat electrodes, the breakdown rate values obtained had a strong dependence on temperature. With a rise from room temperature to 90°C, the dissolution rate rose by roughly 3 times, reaching values of ~30 mg/cm²·h. It is interesting to note that the voltage values in the experiments with tubular electrodes (i.e. sections of fuel pin cladding) were lower than those for the flat specimens. The dissolution rate results obtained for claddings from PWR and from VVER fuel rods differed very little. The only difference was a certain diminution in voltage values for the PWR specimens.

In all the experiments with alternating current, the rate of breakdown was lower than with direct current electrolysis using otherwise equivalent conditions (solution composition, temperature).

TABLE V. Results of electrochemical dissolution experiments.

Experimental conditions				K, mg/cm ² ·h	M _i , g/A·h
The composition of solution	T, °C	U _{init} , V	U _{fin} , V		
HNO ₃ -0.1M	86	30	42	8.7	0.40
	87	70	46	7.9	0.36
HNO ₃ -1.0M	22	105	107	12.3	0.56
	22	115	125	12.1	0.55
HNO ₃ -3.0M	22	113	115	11.5	0.53
	22	100	100	11.5	0.53
Ca(NO ₃) ₂ -1.0M	22	84	105	13.1	0.60
HNO ₃ -1.0M	22	105	110	15.5	0.71
HNO ₃ -0.5M	83	5.6 (59)	7.2	32.9	0.79
NaF-0.1M	84	5.4 (180)	5.2	26.4	0.63

During the experiments with alternating current, instances were recorded where two electrodes (tube specimens of identical size) behaved differently. A clear asymmetry in their mass variation was observed. The specimens also differed in their external appearance. One specimen retained its initial coloring, while the other became covered with a thick white oxide film coat. We were unable to establish any pattern in the asymmetry of properties of specimens in relation to temperature or solution composition.

The only explanation for the phenomenon identified may be a difference in the state of the specimen surface at the beginning of the experiment. Non-identical conditions for the passage of current through the oxide film probably led to an enhancement of the differences in the structure of the oxide layer on one of the specimens. In this case a current rectification effect may occur, with the dissolution process taking place on one specimen only, while the other is not broken down i.e. minor differences in starting properties are enhanced through a feedback route controlled by the electrical properties of the oxide layer.

These considerations provide further proof of the complexity of the process as a whole and the presence of a number of conditions that are difficult to control and serve, in the final analysis, to bring about a considerable scatter in the results, as was observed throughout the work.

An increase in the current yield magnitude may be attained by the addition of fluoride ions to the solution (Table V). When this is done, finely-disperse residues are seen to form, which could not be separated out from the solution even using a centrifuge. The rate of dissolution was comparable with the levels obtained in calcium nitrate solutions. The specimen mass loss in this case is probably governed by the electrochemical process as such, rather than by the reaction with fluoride ions. (Control experiments without current applied to the specimens showed that the dissolution rate in a 1M HNO₃ – 0.1M NaF solution did not exceed 0.03-0.05 mg/cm²·h i.e. 0.1-0.2% of the electrochemical rate shown for 1M HNO₃ – 0.1M NaF in Table V).

Solutions obtained after electrochemical destruction are used for synthesis of ceramic waste forms. Partial dissolution of claddings or the presence of precipitates is not an obstacle for successful synthesis.

The examples of single-phase ceramic based on cubic zirconia and zircon been synthesized at V.G. Khlopin Radium Institute are given in Fig.1 and Fig.2.

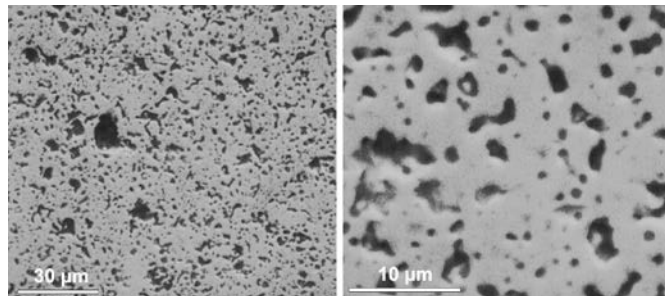


Fig.1. SEM-BSE images of single-phase ceramic based on cubic zirconia ($\text{Zr}_{0.72}\text{Gd}_{0.22}\text{Pu}_{0.06}\text{O}_{1.89}$). Sample was synthesized using co-precipitated precursor, which was cold-pressed and sintered in air at 1500°C for 3 hours. Content of ^{239}Pu – 10.3 wt.%. Black dots are pores.

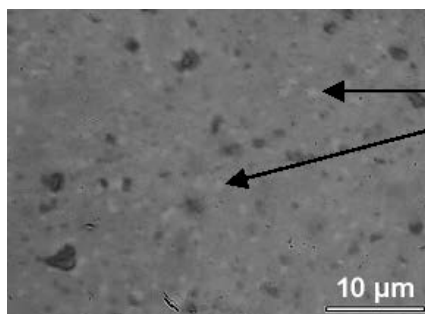


Fig.2. Reflected light optical microscope image of double-phase ceramic based on: zircon ($\text{Zr}_{0.955}\text{Pu}_{0.045}\text{SiO}_4$) – matrix and tetragonal zirconia ($\text{Zr}_{0.964}\text{Pu}_{0.036}\text{O}_2$) – light inclusions marked by arrays. Bulk content of ^{238}Pu – 4.7 wt.%, other isotopes of Pu – 1.1 wt.%. Sample was synthesized using sol-gel precursor, which was cold-pressed and sintered in air at 1500°C for 3 hours. Black dots are pores.

CONCLUSIONS

The results obtained allow us to conclude that Electrochemical Dissolution process has high efficiency for preparation of initial solution to be used for making precursor of ceramic waste form. The mechanism of the electrochemical breakdown process is fairly complex and the results obtained are not well understood so far in detail. Further research is needed. The main obstacle to direct anode dissolution is the formation of thick oxide film layers on the zirconium surface. This makes it necessary to apply quite high potentials (over 100 V) and gives rise to regimen instability (sudden jumps in current, sparking).

The process of electrochemical dissolution (destruction) of zirconium claddings may nevertheless be carried out in nitric acid, preferably in dilute solutions and in the presence of calcium nitrates. The rate of dissolution rises with temperature, reaching $\sim 40\text{-}70 \text{ mg/cm}^2 \cdot \text{h}$ at 90°C . The current yield under these conditions is $0.6\text{-}0.7 \text{ g/A} \cdot \text{h}$.

On the whole number of reasons the economic assessment in this technique is very hard to accomplish, but it requires very thorough and weighted approach anyway.

It should be emphasized that if zirconium is adopted for making ceramic waste forms, the need to encapsulate waste in concrete and further disposal of huge volume of concrete drums will disappear.

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