

Porous Matrixes for Immobilization of Radioactive Wastes.

B.G. Ershov, A.A. Minaev, M.M. Afonin, D.G. Kuznetsov
Institute of Physical Chemistry and Electrochemisrty, Russian Academy of Sciences,
31 Leninsky Prospect, Moscow 119991, Russia

ABSTRACT

The process was studied and the technology developed to obtain a highly porous coke based material with the solid dispersed filler (zirconium dioxide); properties and technological characteristics of the material were investigated. Technological process was developed for the fabrication of products out of the highly porous high melting compound (zirconium carbide). Technology for the fabrication of products out of the highly porous high melting compound bypassing the necessity of obtaining the dry radioactive feed powders and allows producing the material with a wide range of compositions and properties. In this paper we describe a technological process for the fabrication of materials, assuming the impregnation of a porous zirconium carbide form by the liquid highly concentrated solution of actinides followed by the decomposition of the obtained product during the thermal treatment to form stable oxides. We are investigating the properties of the final form as a possible target in a nuclear reactors to use neutrons to burn up the actinides.

INTRODUCTION

Long-lived actinides represent the most hazardous fraction of radioactive waste (RW). One of the safest method of high level radioactive waste (HLW) immobilization is their fixation in glass like, basalt like and ceramics matrices. Another possible method for immobilization the waste in future could be the nuclear burn-up under the irradiation by neutrons, either in a nuclear reactor or an accelerator (transmutation). In this case the immobilization blocks and the transmutation targets should be, first of all, suitable for the long-term safe storage for the period of about 10^3 years, i.e. they should be chemically and thermally stable and leach-resistant to the ground water. Secondly, those composites should necessarily meet the radiation stability requirements not just under the storage conditions but in the powerful neutron fields of the burn-up facilities as well. In other words, they should possess high nuclear inertness. Besides, to attain the high actinide burn-up factor, the chemical form of targets should provide the resistance to swelling of fuel particles and the possibility for the gaseous fission product evacuation. That could be easily performed using for the matrix carrier the highly porous materials based on high melting transition metal compounds.

Possible advantages of the technique for fabricating the composite materials by means of the capillary impregnation of porous targets are the following:

- significant reduction up to the complete elimination of the technological procedures associated with the powdered RW processing;
- application of the technology for the intermediate solutions from the spent nuclear fuel processing;
- increased RW loading of the targets;
- improved operational target characteristics (heat conductivity, compatibility, lower segregation under irradiation).

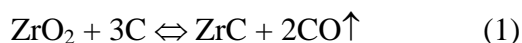
EXPERIMENTAL APPROACH, RESULTS AND DISCUSSION

Fabrication and Properties of Zirconia Carbide Targets

Fabrication of the compound is based on the carbothermal reduction of oxides. Coal pitch (CP) used for the carbon carrier simultaneously played the part of the technological binder, the carbon carrier, and, during the low temperature sintering stage, of the foaming agent. CP is a cheap, industrially implemented material with the high coke remainder (about 50% by mass). It has good solubility in technical solvents, e.g. trichloroethylene, that helps to maintain good contact of the reacting oxide and carbon carrier components and allow penetration of the CP solution in trichloroethylene into defects of the feed oxide particles during the mixing – grinding procedure.

To obtain products with less nitrogen and oxygen content the carbothermal reduction of oxides by carbon with simultaneous sintering of the pieces was conducted under vacuum. For the feed materials we used zirconia, high temperature coal pitch (CP), trichloroethylene and others. One of the important CP characteristics is the coke remainder yield, as it characterizes the fraction of carbon remaining in the materials after the thermal treatment. As the pitch softening temperature increases, the coke remainder yield grows, therefore, in our work we used the high temperature CP. Carbon remainder of the CP was determined after the high temperature sintering in vacuum at the temperature of 2400 °C for 1 hour. It amounted 46.5±0.05% by mass.

Blend calculation was performed according to the reaction:



Mixing – grinding of the feed component powders was conducted in trichloroethylene media. Mix was dried in the vacuum oven for 6 – 8 hours at 50°C. Dried blend was grated through the sieve with cell size of 0.315 – 0.4 mm.

Block molding was conducted by means of hydrostatic compacting. When molding blocks from the blends under study the compacting pressure was within the range of 2.5 – 50.0 MPa. One of the primary factors affecting the formation of the porous structure in the studied materials is the initial blank compacting pressure. As the compacting pressure grows, the volumetric blank weight increases. That could be explained by the thermoplastic nature of the CP which enables it to penetrate deeper in the cavities and pores of the ZrO₂ filler as the compacting pressure increases thus promoting more optimum packing of the oxide grains due to the facilitated movement thereof against one another and embedding into the cavities.

Sintering of the compacted blocks is one of the main technological processes governing both the porous material structure (open and gross porosity, permeability, specific surface, distribution of pores by radii, etc.) and its chemical, physicomachanical, and thermophysical properties. Study

of the sintering process pursued two goals, namely, fabrication of “coke – filler” porous material (coke – zirconium oxide) and fabrication of highly porous zirconium carbide.

The first stage of low temperature sintering (LTS) within the temperature range of 20 – 800 °C is the stage where the porous “coke – ZrO₂” material and the additional porosity in the blanks are formed. LTS process is accompanied by the conversion of the thermoplastic carbon CP carrier into the coke that cements the oxide particles and gives the solid mechanically strong body. LTS should provide maximum coke formation from the CP and fabrication of a homogeneous porous structure possessing neither external nor internal defects. Therefore, this phase is one of the most important in the formation of the structure and defines properties of the porous carbide materials. In Table 1 the studied LTS conditions are given. Blank holding time at 800°C was one hour. Residual vacuum in the furnace space during the sintering process was not lower than 0.133 Pa; blanks were cooled under vacuum with the furnace.

The second sintering stage within the temperature range of 800 - 1800°C is for conversion of a porous blank consisting of the zirconia and coke into the carbide one. The major fraction of the zirconium carbide is formed due to the reaction of ZrO₂ with carbon. At the second sintering stage removal of the carbon dioxide evolving as the reaction product does not cause of fracturing of the blanks as the latter have the open-ended channel pores formed at the previous sintering stage. The third stage of high temperature sintering (HTS) was conducted within the temperature range of 1800 – (2000 – 2550) °C. The second and the third stage (HTS) are combined into the one step procedure and performed in the power vacuum furnace with graphite heater. HTS conditions are the following: heating up to 800 °C for 1 hour, temperature raising rate within the range of 800 – 2550 °C – 50, 100 – 300 °C/hr; holding time at the predetermined temperature – 1 hr; residual pressure in the furnace space – 0.133 Pa; cooling down to 800 °C with the rate of 300 °C/hr and further with the furnace.

TABLE I. Low Temperature Sintering Conditions

Temperature raising rate °C/hr within the temperature range, °C		Time of heating, hrs
20 - 500	500 – 800	
5	10	251
10	120	63
20	50	30
50	100	31
100	300	6

In Table 2 the results of the dependence of shrinkage and porosity from the blank compacting pressure for the P-30 blend are given. Temperature raising rate during the LTS was 10/20, during the HTS – 100 °C/hr.

TABLE II. Influence of the Compacting Pressure on the Properties of the HTS Processed Blocks.

Compacting pressure, MPa	Sintering temperature at the HTS, °C	Linear shrinkage, %	Porosity, %	True density, 10 ³ kg/m ³
10	1900	18.0 ± 0.1	79.2 ± 0.4	6.57 ± 0.02
20	1900	18.0 ± 0.1	79.0 ± 0.4	6.58 ± 0.02
50	1900	17.9 ± 0.1	79.0 ± 0.4	6.55 ± 0.02
100	1900	18.0 ± 0.1	78.5 ± 0.4	6.57 ± 0.02
10	2100	20.5 ± 0.5	72.0 ± 0.4	6.61 ± 0.02
10	2400	27.0 ± 0.6	59.4 ± 0.4	6.64 ± 0.02

Note: 1. Values given in columns 3 through 5 are averaged for 5 – 7 readings.
 2. Density of ZrC is 6.66*10³ kg/m³.

Dependence for the porosity increment ($P_{T_{max}} - P_{800}^{\circ C}$) for the HTS processed blocks against the compacting pressure is given in Fig. 1. Sintering temperature, °C for the curves was as follows: 1 – 1900; 2 – 2100; 3 – 2400.

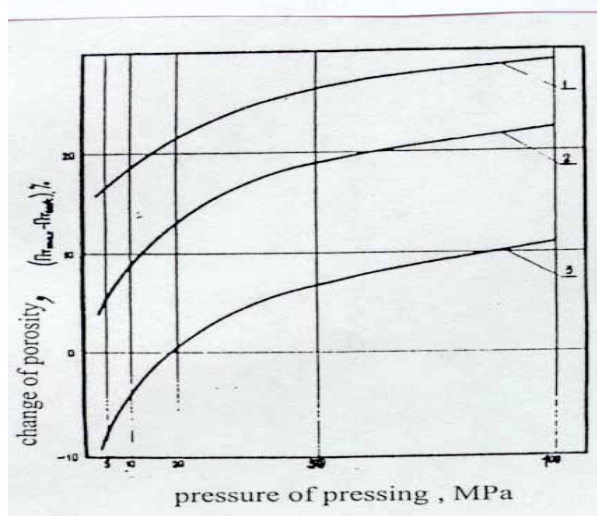


Fig. 1. Effect of the compacting pressure on the change in the blank porosity increment after the HTS. Sintering temperature, °C – 1 – 1900; 2 – 2100; 3 – 2400.

Analyzing the results obtained, one can suggest that as the compacting pressure increases, on the LTS processed blocks the thickness of membranes between pores increases as well. This suggestion is proved by the decrease in porosity and gas permeability with the shrinkage and the membrane density of the material (true density) being stable.

True density of the blanks after the HTS is somewhat less than the experimental density for ZrC, probably, due to the presence of the closed pores within the membrane that is proved by the difference between the gross and open porosity and by metallography. As the sintering temperature is raised from 1900 to 2400 °C, the density of membranes increases. It occurs due to the merger of small pores (100 – 1000Å radius) into the open ones (0.1 – 2 μm radius) that causes the membrane material to be more dense thus increasing the true density. In the course of

the carbothermal reduction of zirconia by carbon (coke) the additional number of pores is formed (see Fig. 1 (1)), and the following blank sintering causes the decrease in porosity (see Fig. 1(2, 3)).

Influence of the CP content in the initial blocks on the porosity, gross carbon and free carbon content was studied with the rods molded from the blanks of different composition and passed through the LTS and HTS. Results are shown in Fig. 2. Blank molding pressure was 10 MPa, temperature-raising rate for the LTS was 20/50 °C/hr, for the HTS – 300 °C/hr, and holding time at 1900 °C was 1 hour. From the data of Fig. 2 one can see that the maximum porosity is observed for the blank mould from the blends calculated to obtain the stoichiometric zirconium carbide. Decrease in the blank porosity according to the decrease in the CP content is explained by the decrease in quantity of the pore-forming agent, which part is played by the CP.

Fig. 3 presents the differential curves describing the distribution of pore volumes by the equivalent radii in blanks sintered at different temperature. Sintering temperature was as follows: 1 – 1900; 2 – 2100; 3 – 2400. Temperature raising rate during the LTS was 5/10 °C/hr, during the HTS – 300 °C/hr, the blend used – P30, blank compacting pressure – 10 MPa.

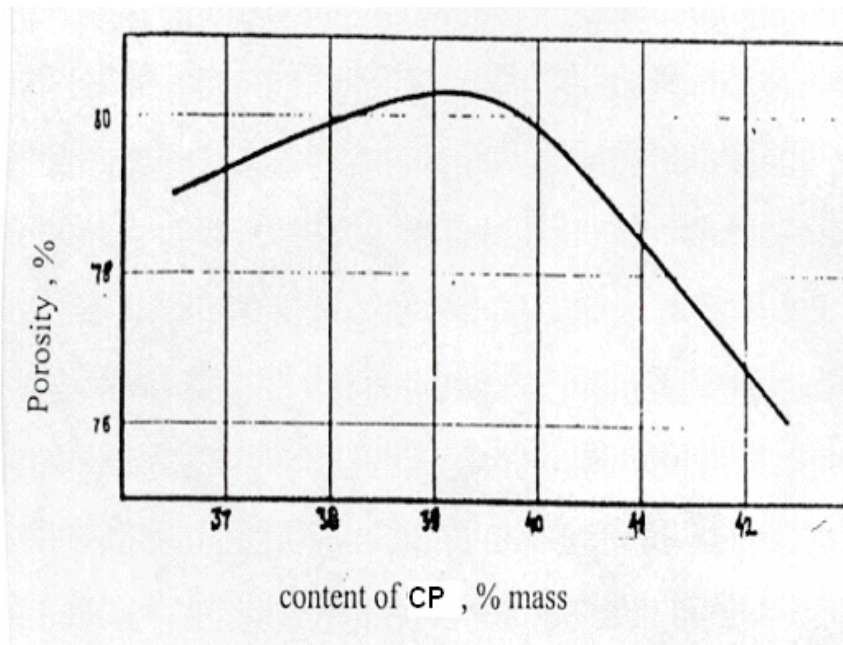


Fig. 2. Effect of the CP content in the feed blend on the blank porosity. Blank compacting pressure – 10 MPa, temperature raising rate during the LTS – 20/50 °C/hr, during the HTS – 300°C/hr, holding time at 1900°C – 1 hour.

Analysis of data given in Fig. 3 and in Table 2 shows that as a result of the sintering temperature increase the small pores coagulate (the mode is moved towards the increased equivalent pore radii) and the radii of bigger pores tend to decrease. At the same time the inherent shrinkage of blanks and the membrane material of the porous carbide frame becomes denser (see Table 2).

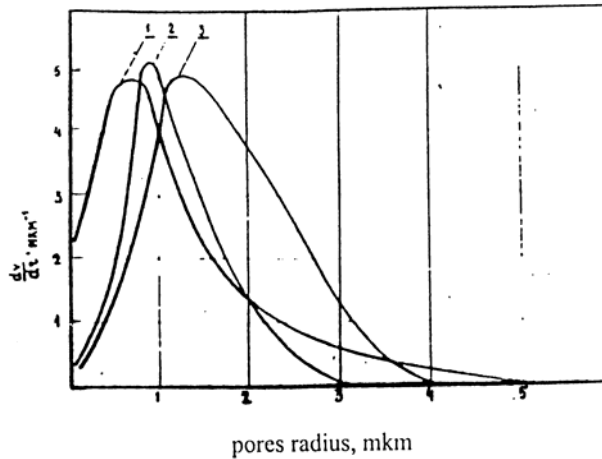


Fig. 3. Differential curves for the distribution of pore volume by the equivalent radii. Sintering temperature, °C – 1 – 1900; 2 – 2100; 3 – 2400. Temperature raising rate during the LTS – 5/10°C/hr, during the HTS – 300°C/hr, blank compacting pressure – 10 MPa, P-30 blend.

Fig. 4 presents the curves for dependence of the compression strength on the porosity value during the porous zirconium carbide compacting. Temperature raising rate during the LTS was 5/10 °C/hr. Experimental data obtained with the samples sintered at the temperature of 1900 – 2550 °C are described by the equation of the $\sigma_x = \sigma_0 \cdot e^{-BP}$ type, where the “B” constant calculated by means of the least square value technique appeared to be equal to 5.78 ± 0.07 . Compression strength of zirconium carbide with the porosity close to zero value (σ_0) was assumed to be equal to 1700 MPa.

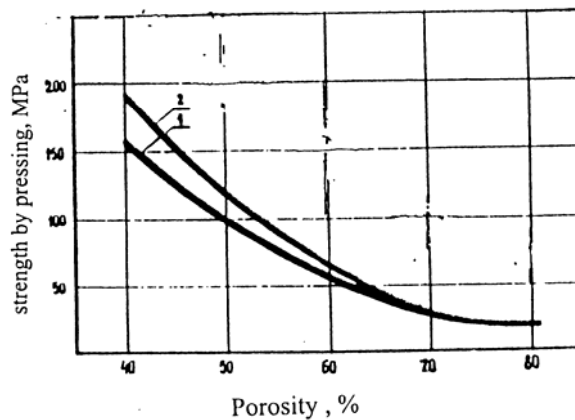


Fig. 4. Dependence of the compression strength on porosity. 1 – experimental data (temperature raising rate during the LTS – 5/10°C/hr) 2 – calculated results ($\sigma_x = \sigma_0 \cdot e^{-5.78P}$).

From the data shown in Fig. 4 one can see that the increase of sintering temperature leads to the increase of the material strength.

Summary of Properties of the Porous Zirconia Carbide Targets

Porous zirconium carbide was used as an example to show that the proper control of the technological parameters allows fabricating the material with the following properties:

Porosity, % by volume -	59 – 82;
True density, 10^3 kg/m^3 -	6.55 – 6.64;
Compression strength, MPa -	20 – 100;
Pores with 0.3 to 2 μm radii, %	94.

We also collected data on the specific surface area, gas permeability, and electrical resistivity of the samples. For these properties the ranges were:

Specific surface area, $10^{-3} \text{ m}^2/\text{kg}$ -	0.5 – 2.3;
Gas permeability, 10^3 m L/m^2 -	4.8 – 16;
Specific electric resistance, $10^{-4} \text{ Ohm}\cdot\text{m}$ -	0.04 – 22.

Studies with Impregnating Concentrated Solutions of Uranium in the Matrix

The next phase of work was to develop the technology for preparation of highly concentrated RW solutions (HCS RW) with the predetermined properties, such as metal concentration, viscosity, etc. that would provide, as a result of the thermal treatment at a temperature not higher than 1200°C , the solid oxide residues with the predetermined oxygen factor. Process of the HCS uranium preparation as the HCS RW simulator was considered in our work in detail. For feed components we used uranium dioxide, nitric acid, ammonium acetate, and distilled water. Sequence of the technological procedures comprises sampling of the uranium dioxide weight, digestion in nitric acid, addition of water and evaporation up to the temperature of the complete distillation, introducing the ammonium acetate solution, and mixing. Concentration of uranium in the liquid phase in equilibrium with the solid phase: at 20°C – 680g/L; at 50°C – 1100g/L. HCS is a heavy fluid with the odor of nitric acid, from yellow to dark brown color, which mixes with water at any ratio. Samples for study were prepared by the capillary impregnation of porous zirconium carbide targets of the predetermined composition by the HCS uranium followed by the thermal treatment thereof at 600°C in the flow of argon. Further the targets were subjected to the thermal treatment in vacuum at the temperature of $1000 - 1500^\circ\text{C}$ for 0.2 – 0.3 hours. Obtained results of the studies witness the fact that it is impossible to obtain the uranium dioxide under 1200°C from the HCS according to the discussed technology. To obtain the stoichiometric oxide, if necessary, it is reasonable either to introduce a carbon- containing reducing additive into the HCS or to impregnate the carbon containing carbide blank target. To prepare the HCS uranium in the presence of the reducing additives we used the carboxymethylcellulose (CMC). Solutions were prepared by adding CMC into the HCS uranium up to the predetermined ratio of carbon/uranium. Impregnated samples were subjected to the thermal treatment at the temperature of 400°C in the flow of argon followed by the vacuum thermal treatment at the temperature of 1000°C . Obtained results witness the fact that at the carbon content of 1.5 – 2.5 moles per 1 mole of uranium the resulting oxygen factor is close to the stoichiometric uranium dioxide.

The “impregnation – thermal treatment” procedure can be performed as many times as necessary. Thickness of the thermolysis product layer per one procedure ranges from 0.1 to several microns depending upon the uranium concentration of the HCS.

CONCLUSION

The process was studied and the technology developed to obtain a highly porous coke based material with the solid dispersed filler (zirconium dioxide); properties and technological characteristics of the material were investigated. Technological process was developed for the fabrication of products from the highly porous high melting compound (zirconium carbide).

Technology for the fabrication of products from the highly porous high melting compound eliminating the stage of obtaining the dry radioactive feed powder allows producing the material within the wide range of compositions and properties.