



HTR Fuel Waste Management: TRISO separation and acid-graphite intercalation compounds preparation

Fabrice Guittonneau, Abdesselam Abdelouas*, Bernd Grambow

SUBATECH, UMR 6457, IN2P3/CNRS-Ecole des Mines de Nantes/Université de Nantes, 4 Rue Alfred Kastler, 44307 Nantes Cedex 3, France

ARTICLE INFO

Article history:

Received 4 May 2010

Accepted 14 September 2010

ABSTRACT

Considering the need to reduce waste production and greenhouse emissions and still keeping high energy efficiency, various 4th generation nuclear energy systems have been proposed. As far as graphite-moderated reactors are concerned (future high temperature fast or thermal reactors), one of the key issues is the large volumes of irradiated graphite encountered. With the objective to reduce volume of waste in the HTR concept, it is very important to be able to separate the fuel from low level activity graphite representing a large volume. The separated TRISO particles can then be reprocessed for waste separation or disposed off in geological repository. In addition, preparation of acid-GICs from the separated graphite may constitute a way to recycle this waste.

We used HTR-type compact fuel with ZrO_2 TRISO particles to test two separation methods: low ($H_2SO_4 + H_2O_2$) and high ($H_2SO_4 + HNO_3$) temperature acid treatments. In both cases the TRISO separation was complete but some TRISO layers oxidized at high temperature. At low temperature, the desegregation of graphite grains is facilitated by intercalation of sulfuric acid between the graphene layers. The acid-GIC obtained consists of pure phases of high quality suggesting their potential industrial recycling.

© 2010 Published by Elsevier B.V.

1. Introduction

With the increase of energy demand and the international wish to preserve the environment, nuclear energy may help to achieve these goals. One of the main objectives of nuclear industry is to reduce the waste volumes (waste fuel + decommissioning products). Operation of graphite-moderated reactors such as French UNGG (uranium natural graphite gaz), English AGR (advanced gas reactor) and Russian RBMK (high power channel-type reactor) produced large quantities of contaminated graphite that need to be recycled or disposed off in deep geological formations. Thereby, in June 2006, a French law (No. 2006-739) requests to provide a selection of a disposal facility for the irradiated graphite from the UNGG reactors for 2013.

Future reactors technologies including HTR (high temperature reactor) will use graphite blocks for reflector and fuel. Compacts from block-type and pebbles from PBMR (pebble bed modular reactor) will need reprocessing to separate the highly radioactive TRISO particles from the low level irradiated graphite. Some previous studies summarized in [1] dealt with graphite management such as furnace incineration, fluidized bed incineration, laser incineration, encapsulation into matrices (cement, bitumen, polymers, glass...), but economical and environmental criterions are not

really satisfied, allowing to treat even a small fraction of the about 250,000 tonnes of irradiated graphite which has been accumulated worldwide. A few studies on TRISO separation from graphite have been conducted [2,3] and showed some weaknesses like high cost, coating failure, partial separation, complexity... The separated TRISO could be vitrified and disposed off in deep geological formation as suggested by Abdelouas et al. [4]. However, heat load must be taken into consideration to determine whether TRISO separation provides volume reduction advantages for geological disposal. Reprocessing of the irradiated TRISO could also be considered for U and Pu recovery and waste separation.

We present in this paper a fast method with potential economical advantages, which allows a total desegregation of graphite blocks, still preserving the integrity of TRISO particles. The method consists of intercalating compounds into graphite layers to cause grain separation.

Since graphite intercalation compounds (GICs) were discovered by Schffäutl by intercalation of potassium, a great number of GICs were synthesized with intercalates such as alkali, earth alkali, transition metal chlorides, acids, halogens, etc., in gas–solid or liquid–solid phase. A good summary of synthesis types can be found in the book of Enoki et al. [5]. These authors give a definition of the stage number n which “is defined as the structure in which intercalates are accommodated regularly in every n th graphitic gallery”. We studied in this paper the desegregation of graphite via the intercalation of H_2SO_4 . In acid treatment, graphite is partially oxidized. Acids play the role of electron acceptor from graphite π -bonds.

* Corresponding author. Tel.: +33 251858462; fax: +33 251858452.

E-mail address: abdesselam.abdelouas@subatech.in2p3.fr (A. Abdelouas).

Reactions with acids are possible by oxidant-assisted (HNO_3 , CrO_3 , KMnO_4 , HClO_4 , H_2O_2 ...) intercalation or by electrochemical intercalation. Usually, high stage intercalation via oxidant-assisted intercalation is harder to obtain than via electrochemical process. Many studies worked on sulfuric acid intercalation [6–12] and sulfur-free acid intercalation [13–18]. Acid-GICs are often used as intermediate products before starting the exfoliation process, during which, above a critical temperature, a large thermal expansion by as much as a factor of 300 occurs, leading to products with high surface areas (up to $85 \text{ m}^2/\text{g}$). The exfoliation occurs when the gas pressure exceeds the internal stress parallel to the c -axis. The exfoliated graphite (EG) often has the shape of the famous “worm structure”, depending of the raw material properties and the GIC preparation. Compressed-EGs (CEGs) are industrially manufactured by Toyo Tanso notably, for the fabrication of flexible graphite sheets, gaskets, furnace insulators... [19] or simply non-compressed EG for oil sorption [20–26]. An excellent review on CEGs can be found in the publication of Celzard et al. [27]. CEGs are of great interest because nuclear graphite can be transformed in CEG for “second life” applications. However, the recycling of the graphite could be limited due to the remaining radioactivity of the treated material.

2. Materials and methods

Raw materials are ‘compacts’ manufactured by AREVA NP from natural graphite. Their manufacture is explained in reference [28]. To summarize it, graphite powder is mixed with a phenolic resin and then TRISO particles are added. Green compact is formed by a double piston and thermal treatment is made under vacuum at 1800°C . Compacts’ length is about 47.8 mm and the mean diameter about 12.4 mm (Fig. 1). We can notice here that phenolic resin does not graphitize during thermal treatment and forms an amorphous carbon, which has poor mechanical properties and reacts more easily than “real” graphite. XRD analysis of the graphite’s compact gave lattice parameters as follow: $a = 2.4645 \text{ \AA}$ and $c = 6.7171 \text{ \AA}$. These parameters are little larger than for usual graphite. Crystallite size calculations via the method of Scherrer showed $L_a = (412 \pm 18) \text{ \AA}$ and $L_c = (360 \pm 51) \text{ \AA}$, but this method is very sensitive to defects into crystals, e.g. dislocation, vacancy, etc. These distances correspond to the sizes of ‘perfect crystals’. SEM (scanning electron microscope) and TEM (transmission electron microscope) observations indicated very much larger crystals, up to micrometer scale in the direction of a .

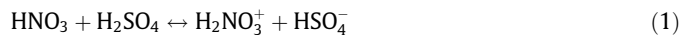
The compacts contain fuel spheres, the TRISO particles. For our experiments, for radiation protection purposes the TRISO particles kernels were made of ZrO_2 instead of UO_2 . They consist of $530 \mu\text{m}$ diameter kernels surrounded by four protective layers insuring chemical and mechanical integrities. These four layers are from the center to the outside porous pyrolytic carbon (buffer of $90 \mu\text{m}$ thickness), dense inner pyrolytic carbon (iPyC of $40 \mu\text{m}$), silicon carbide (SiC of $35 \mu\text{m}$) and a final outer pyrolytic carbon (oPyC

of $40 \mu\text{m}$). Fabrication, scheme and physical properties of fuel particles are described in [3,29–34]. The pyrolytic carbon is very pure graphite analog and reacts very slowly. Each compact containing 20% volume packing fraction comprises about 3000 TRISO particles.

Two types of experiences were conducted: high pressure/high temperature microwave treatments (MW) and room temperature chemical treatments under air atmosphere (RT).

2.1. Preparation of GICs via microwave

For MW treatments, an Anton Paar Multiwave 3000 mineralization device was used to separate graphite from the TRISO particles. Because of the limited capacity of this device, compacts (containing 10% packing fraction, PF) were cut in disks or half-disks of about 3 mm height. Samples were placed into the Teflon vessels with 10 mL of a mixture of sulfuric acid (95%) and nitric acid (69%). The reaction between these two acids is well known and creates the nitronium ion which is very oxidant:



Four vessels were simultaneously in operation. All sample masses and volumes and reagent acids are mentioned in Table 1 together with treatments results. Electric power, temperature, pressure and plateau were fixed in all experiments at 1400 W (constant rate at 140 W/min), 200°C , 55 bar (limited at 0.5 bar/s) and 15 min, respectively. After cooling into the microwave oven, the resulting samples of intercalated graphite + TRISO particles were rinsed in ultra-pure water. Samples were centrifuged to separate the particles. GICs are dried into an air oven at 85°C .

Solids (GICs) have been characterized by nitrogen adsorption at 77 K using the BET equation to estimate the specific surface area. The device employed was a Micromeritics ASAP 2010. X-ray diffraction analyses were conducted in a Siemens D5000 diffractometer using a Cu anode at $\lambda = 1.5406 \text{ \AA}$, $V = 40 \text{ kV}$ and $I = 30 \text{ mA}$. Infrared measurements (Shimadzu FTIR device) were recorded from 400 cm^{-1} to 4000 cm^{-1} (resolution 4 cm^{-1} , 50 scans) and from 400 cm^{-1} to 1400 cm^{-1} (resolution 1 cm^{-1} , 50 scans), using KBr pellets of about 300 mg.

A part of each sample has been kept to proceed with the exfoliation process. These samples were placed into an alumina crucible and were rapidly heated at 1000°C during 1 min in air. The intercalated sulfuric acid decomposed into SO_2 , O_2 and H_2O . The exfoliated graphite (EG) did not have enough time to burn in CO_x : EG are known to be resistant versus heat and oxidation. The mass loss was monitored and BET measurement allows observing the increase of the surface during the transformation of GIC into EG.

Optical observations were conducted with a binocular microscope Leica MZ16 coupled with the software Leica Application Suite for the image capture. SEM characterizations were conducted with a JEOL 5800LV and image capture was made with the

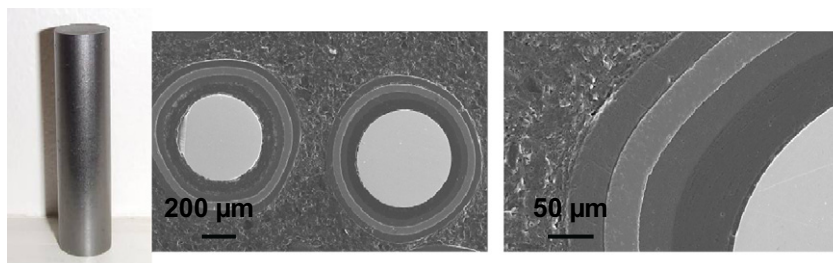


Fig. 1. Graphite compact (left) in which TRISO particles (center, right) are embedding.

Download English Version:

<https://daneshyari.com/en/article/1567243>

Download Persian Version:

<https://daneshyari.com/article/1567243>

[Daneshyari.com](https://daneshyari.com)