

# Thermogravimetric and Differential Scanning Calorimetric Behavior of Ball-Milled Nuclear Graphite

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## 1. Introduction

In a high temperature gas-cooled reactor, nuclear graphite has been widely used as fuel elements, moderator or reflector blocks, and core support structures owing to its excellent moderating power, mechanical properties and machinability. For the same reason, it will be used in a helium cooled ceramic reflector test blanket module for the ITER. Each sub-module has a seven-layer breeding zone, including three neutron multiplier layers packed with beryllium pebbles, three lithium ceramic pebbles packed tritium breeder layers, and a reflector layer packed with 1 mm diameter graphite pebbles to reduce the volume of beryllium. The abrasion of graphite structures owing to relative motion or thermal cycle during operation may produce graphite dust. It is expected that graphite dust will be more oxidative than bulk graphite, and thus the oxidation behavior of graphite dust must be examined to analyze the safety of the reactors during an air ingress accident. In this study, the thermal stability of ball-milled graphite powder was investigated using a simultaneous thermogravimeter-differential scanning calorimeter.

## 2. Experiments

A high purity, isotropic nuclear graphite, IG-110 from Toyo Tanso Co. Ltd. Japan was initially crushed with a jaw crusher (Fritsch, Pulverisette-1) and then grinded with a mortar grinder (Fritsch, Pulverisette-2). The grinded graphite powder was used as the starting materials. The ball milling was performed on a Fritsch planetary mill set at 400 rev./min for 10, 20, 30, 60, 300, 600, and 1200 min. With a ball-to-weight ratio of 20, 40 g of the graphite powder and hardened steel balls (8.0 mm in diameter) were sealed under an argon atmosphere in a hardened steel vial. The powders were taken out and put into bottles in a glove box filled with argon, and the loosely capped bottles were then kept in the atmosphere.

The particle size distribution was measured using a laser scattering particle size distribution analyzer (Horiba LA950) and the surface area was determined by multipoint nitrogen adsorption (Micromeritics, ASAP 2420). Raman spectroscopy was measured at room temperature using a Jobin-Yvon LabRam HR with a LN<sub>2</sub> cooled CCD multichannel detector in a

conventional backscattering geometry. The spectra were excited with the 514.5 nm line of an Ar-ion laser. Thermogravimetric and differential scanning calorimetric analyses were performed using a Setaram DTA, GA 92-18 at a heating rate of 10 °C/min for up to 900 °C.

## 3. Results and Discussion

The particle size distribution of the milled powders is shown in Fig. 1. The initial 10 min of milling led primarily to a size reduction by the fracturing of the larger particles. However, the particle size increased after milling for 30 min and then decreased up to 300 min. Once again the particle size increased slightly but remained nearly steady after 1000 min. The simultaneous breaking and agglomeration of particles during milling will lead to this behavior.

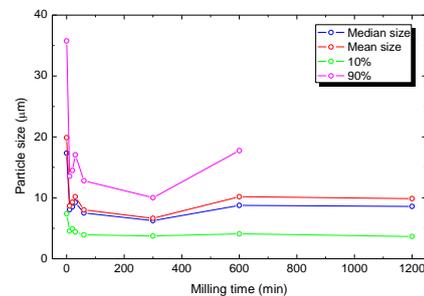


Fig. 1. Particle size of ball milled graphite.

Fig. 2 shows the changes in the measured BET surface area with the milling time. The specific surface area increased lineally up to 60 min (528 m<sup>2</sup>/g), but abruptly decreased after 300 min (332 m<sup>2</sup>/g), and then gradually decreased until 1200 min (267 m<sup>2</sup>/g).

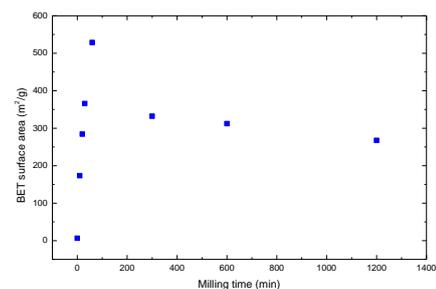


Fig. 2. BET surface area of ball milled graphite.

Fig. 3 shows the changes in the Raman spectra with milling time. The Raman spectrum of the as-received sample shows an intense graphite peak at  $1580\text{ cm}^{-1}$  in addition to a very weak peak at  $1350\text{ cm}^{-1}$ , which suggests a finite crystal size. The milled powder exhibits a intense  $1350\text{ cm}^{-1}$  peak stronger than the  $1580\text{ cm}^{-1}$  peak. This results corresponds with a decrease in the graphite crystal size and an increase in the induced defects of the graphitic structure (activated surface).

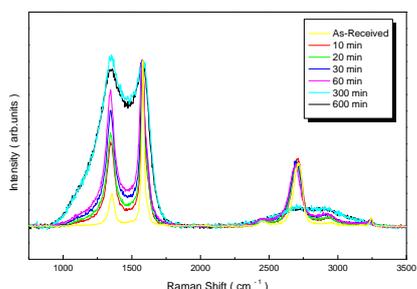


Fig. 3. Raman spectra of ball milled graphite.

In the as-received powder, the heat flow owing to an exothermic oxidation reaction began to increase linearly at  $726\text{ }^{\circ}\text{C}$ , while the weight decreased proportionally. In the milled powders, the reaction heat was detected at  $122\text{ }^{\circ}\text{C}$  with minimal weight loss, and the temperature where the bulk oxidation begins to occur decreased, i.e.,  $600\text{ }^{\circ}\text{C}$  for the 30 min powder, and  $400\text{ }^{\circ}\text{C}$  for the 600 min powder.

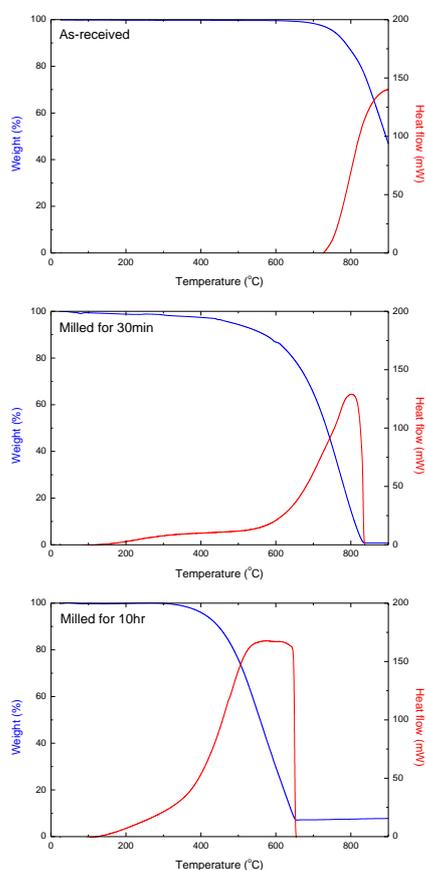


Fig. 4. TG-DSC behavior of ball milled graphite .

According to previous work [1], the abrupt decrease in the BET surface area of the 300 min powder is attributed to the chemisorption of oxygen on an activated surface after exposure to air. Accordingly, it is reasonable to assume that the weight loss and heat flow at low temperature is attributed to the presence of the absorbed  $\text{CO}_2$ . The increase in chemical reactivity after the ball milling is caused not only by increasing the specific surface area but also by the growing disorder at the atomic scale [2, 3]. Distortion and topological rearrangement of  $\text{sp}^2$  bonds in the sense of two-dimensional random networks plays an essential role in the enhancement of chemical reactivity of nano-sized carbon powder.

### 3. Conclusions

An examination was made to characterize the oxidation behavior of ball-milled nuclear graphite powder through a TG-DSC analysis. With the ball milling time, the BET surface area increased with the reduction of particle size, but decreased with the chemisorptions of  $\text{O}_2$  on the activated surface. The enhancement of the oxidation after the ball milling is attributed to both increases in the specific surface area and atomic scale defects in the graphite structure.

### ACKNOWLEDGEMENT

This study was supported by Nuclear Research & Development Program of the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIP).

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