Real-time observation of the expansion behavior of intercalated graphite flake

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Graphite is a layered mineral having large aspect ratio-like layered silicates. It consists of a huge number of graphene layers held together by weak van der Waals forces. Single crystal graphite has an elastic modulus of over 1 TPa, which is many times greater than nanoclay. Unlike clay, graphite is thermally and electrically conductive. Expandable graphite, which is composed of natural graphite flake intercalated with acid, can be expanded up to hundreds of times its initial volume at high temperature, resulting in separation of the graphene sheets at the nanoscopic level along the *c* axis of graphene layers [1–4]. The intercalated graphite flake material is often called a graphite intercalation compound (GIC) [5, 6].

The objective of this study is to observe the real-time thermal expansion behavior of intercalated (expandable) graphite flake (IG). Expandable graphite flakes (GrafGuard$^{\text{TM}}$ 160–50A) were supplied from UCAR Carbon Company (USA) after being proprietarily intercalated by a mixture of sulfuric acid and nitric acid. It is informed from the supplier that the contents of intercalant are about 22% by weight. The expansion volume per gram at 600 °C is about 250 mm^3 and the expanded graphite flakes have carbon contents of about 97%.

The real-time thermal behavior was successfully observed on a hot-plate at 300 °C using a high-speed digital camera (Coolpix 990, Nikon). A series of photos was obtained in a sub-second time scale for a single intercalated graphite flake. A Thermomechanical Analyzer (TMA 2940, TA Instrument) was also utilized to investigate the onset temperature, rate and ratio of thermal expansion. The measurements were performed on a quartz stage from ambient temperature to 500 °C at a heating rate of 2 °C/min while purging with a N_2 gas at 50 cc/min. A standard expansion mode was used. The microstructures of the graphite flakes before and after the expansion were observed using a scanning electron microscope (SEM, JSM-5900, Jeol).

Fig. 1 presents scanning electron micrographs showing a single IG particle. The average flake size of the IG, as representatively seen from the top of Fig. 1, is approximately 800–900 μm with a thickness of 80–100 μm. The aspect ratio is about 8–11. Each flake is built up with multiplatelets consisting of a number of very thin layers of submicrometer thickness, as shown at the bottom of Fig. 1. It is likely that the aspect ratio of single crystal graphite is in the range of 100–1000.

The photos in Fig. 2, which were taken with a high-speed digital camera, show the real-time expansion

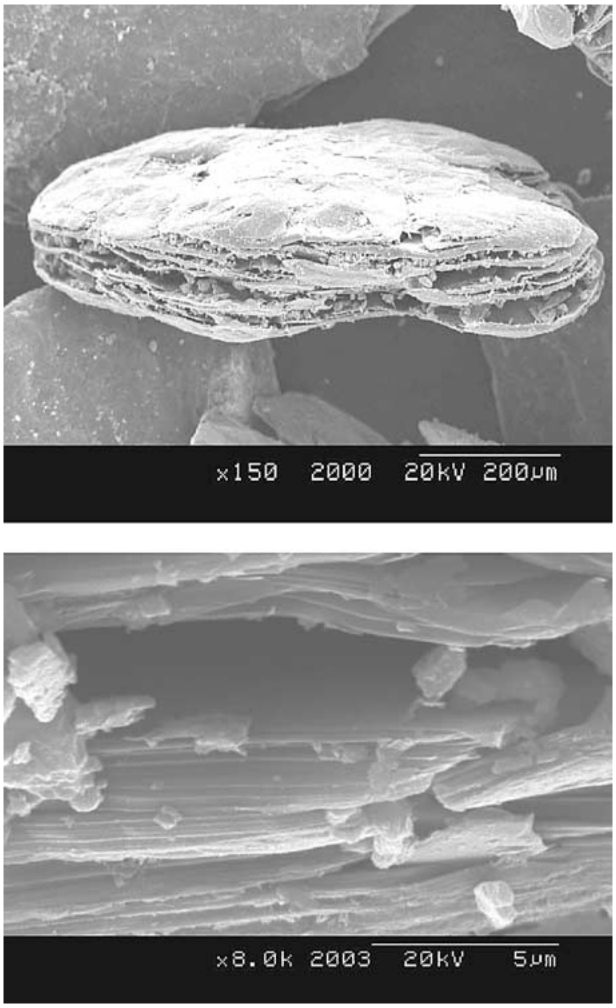

Figure 1 Scanning electron microphotographs of a single intercalated graphite flake observed at different magnifications: ×150 (top) and ×8000 (bottom).

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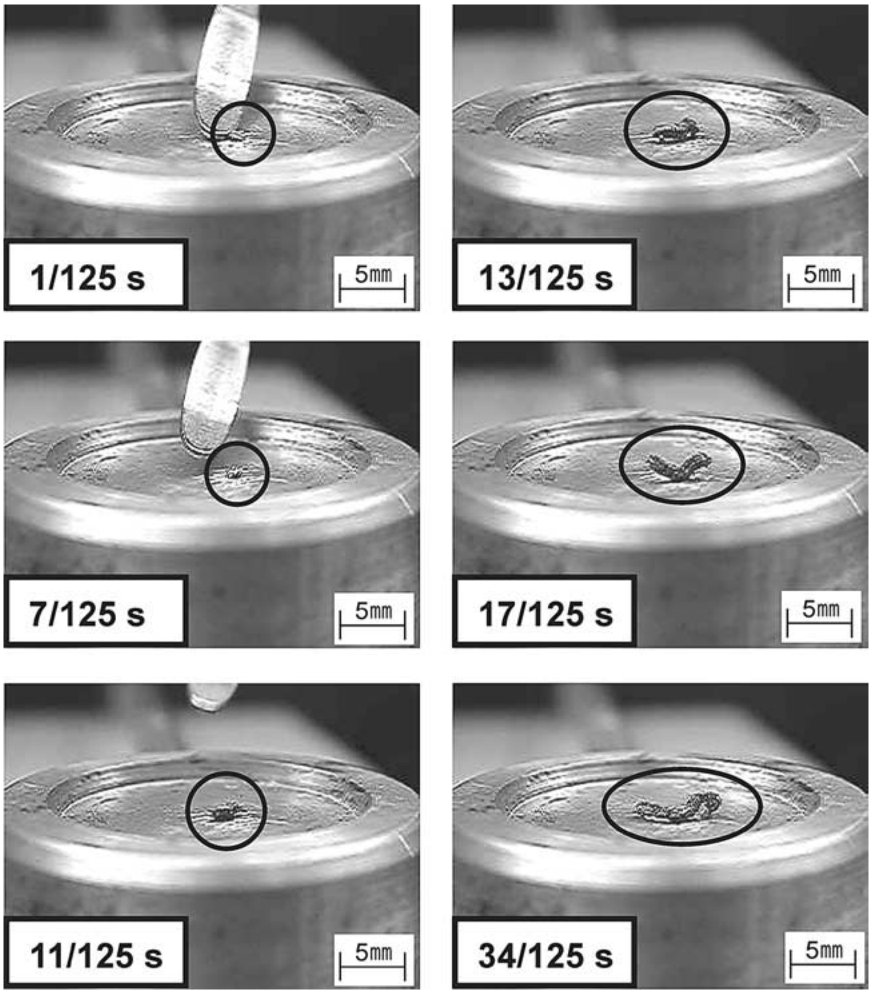

Figure 2 Serial views of the real-time expansion behavior of a single intercalated graphite flake occurring on a hot-plate at 300 °C.

behavior of a single IG particle occurring on a hot-plate set at 300 °C. As seen in Fig. 1, the thickness of a single IG particle is less than 0.1 mm before expansion (0 s). It was found that the expansion rapidly proceeds perpendicularly to the graphene layers and is completed within 0.3 s. The thickness of a single IG with multiple graphene sheets is dramatically increased up to 10 mm or longer after the expansion. As a result, it is expected that the expansion ratio is approximately 100 or greater.

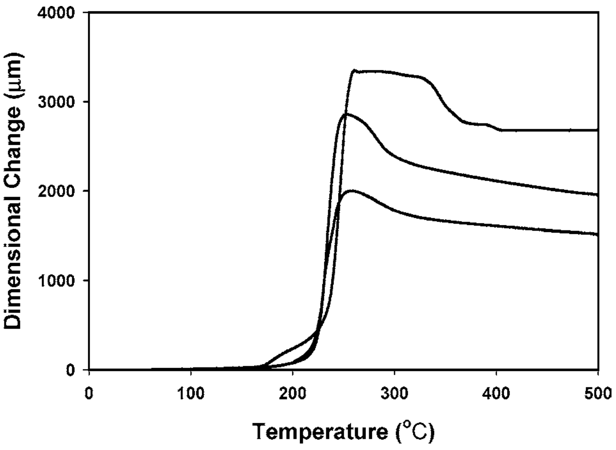

Figure 3 TMA thermograms monitored the expansion behavior of a single intercalated graphite flake as a function of temperature.

Fig. 3 shows the thermal expansion behavior of a single IG particle as a function of temperature studied by TMA. A single IG particle was used for each measurement. Each curve, which was obtained from a three times repeated experiment, respectively, indicates the comparable expansion pattern of individual particles. The result gives useful information on the onset temperature, rate, and ratio of thermal expansion for the IG used in this work. The onset temperature of expansion is about 160–170 °C. The expansion takes place rapidly in the range of 220–240 °C. The expansion ratio calculated from the TMA measurement is approximately 20–35, which is much less than expected from the result in Fig. 2. The following three reasons explain this. First, the flake is substantially loaded by a minimum normal force of 0.005 N due to the TMA probe itself in the opposite direction to the expansion during the measurement. Second, the expansion proceeds in a twisting and bending form, not in a straightforward direction, as seen in Fig. 3. Therefore the expansion is significantly suppressed under the probe during the measurement. Third, the TMA instrument normally cannot successfully monitor such extremely rapid expansion, measuring just the partial range of the expansion, not the full range.

Fig. 4 shows the microstructure of the expanded graphite flake observed at magnifications in the

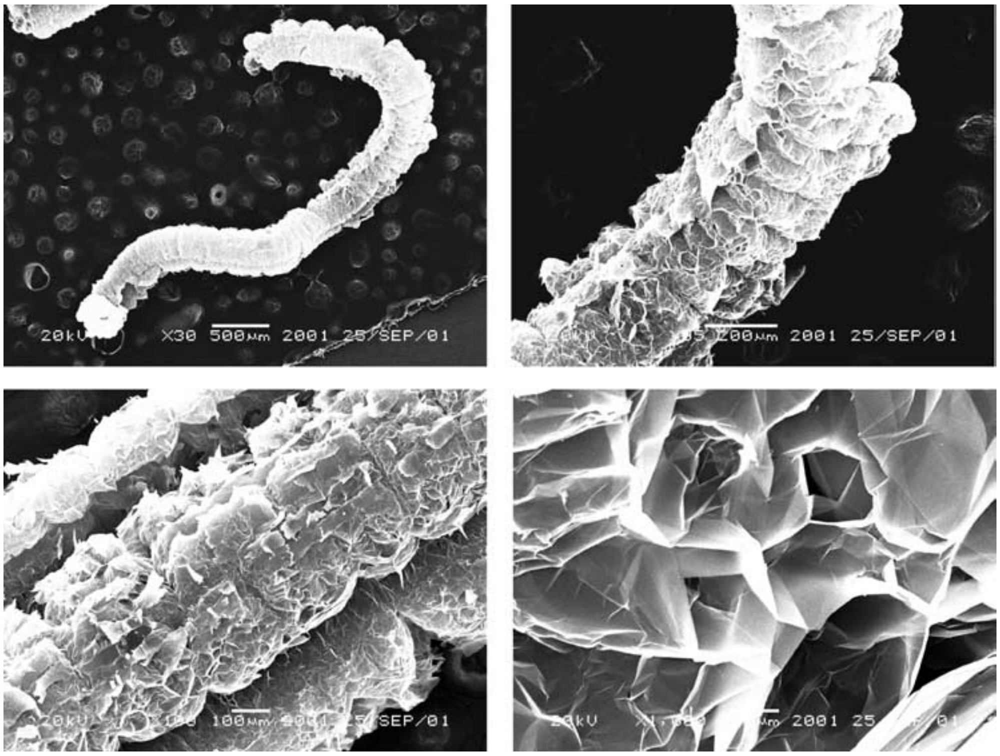

Figure 4 Scanning electron microphotographs of an expanded graphite flake observed at different magnifications from ×30 (top left) to ×1000 (bottom right).

×30–×1000 range after the heat-treatment of a single IG particle at 600 °C. The IG has expanded along with *c* axis of the graphene sheets. The multiple platelets in the IG can be very rapidly expanded and exfoliated up to a few hundred times their initial volume as a result of the vaporization of the intercalant between the graphene sheets during the heat-treatment at 300 °C or higher and also a result of the thermal shock of the lamellar structure in the crystalline graphene sheets [1]. The extent of expansion may depend on the heat-treatment temperature, processing method, the amount of intercalant, and the stage index of intercalant [4, 5, 7]. After expansion, the flake exhibits a worm-like or an accordion-like shape composed of multiple nanoscaled platelet layers held together at their edges. The graphene layers theoretically separate by 3.354 Å. The distance does not change significantly unless, ideally, every single graphene layer is intercalated and fully exfoliated during heat-treatment. Even after the expansion or exfoliation process, completely expanded graphene layers are hard to find. It is also observed that there are a large number of pores between the thin nanoplatelets.

Much attention has been paid to new polymer materials with high performance and/or functionality for the purpose of improving the polymer properties and extending their applications. Nanocomposite is one of the most promising materials. As layered reinforcements with large aspect ratio, like clay and graphite flake, are exfoliated and dispersed in a polymer matrix as nanoplatelets, the polymer nanocomposites have improved mechanical, thermal, and barrier properties depending upon the type of nanoplatelets [8–11]. During the last several years, a number of nanocomposite systems have been widely studied with many different polymers and layered silicates [12]. However, the expanded graphite flake studied here can be applied primarily for providing electrical conductivity in polymer nanocomposite systems using a similar nanoplatelet reinforcement concept [13, 14].

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