NEW FORMATION ROUTE FOR CARBIDE-CORE, GRAPHITIC-CARBON MANTLE GRAINS BASED ON FULLERENES. Yuki Kimura and Joseph A. Nuth III, Code 691, Astrochemistry Laboratory, NASA’s Goddard Space Flight Center, Greenbelt MD 20771 (ykimura@sstedmail.gsfc.nasa.gov).

Introduction: The formation environment of TiC-core, graphitic-mantle spherules was calculated after their discovery in acid residues derived from the Murchison carbonaceous meteorite [1]. The graphitic spherules including metal carbide crystals such as TiC were identified as presolar grains from their isotopic content and assumed to form within the circumstellar envelopes of carbon-rich asymptotic giant branch (AGB) stars [1,2]. The metal carbide crystals were composed of Ti and/or Zr-Mo carbide, were generally located at the center of individual spherules and are surrounded by well-graphitized carbon. Therefore, it has been assumed that TiC condensed prior to carbon. These composite spherules have been called core-mantle grains. The radii of the metal carbide core and of the graphitic mantle layer are 5-200 nm and 0.3-9 µm, respectively. Constraints on the formation conditions and environment, such as the C/O abundance ratio and total gas pressure, of the TiC-core, graphitic-mantle spherules can be derived from the size of the TiC core and graphitic mantle, and depend on the vapor density and the cooling rate of the grains.

Most of the carbon in the outflow of carbon-rich AGB stars is in the form of CO and C2H2 [3]. Carbonaceous materials such as polycyclic aromatic hydrocarbons (PAHs) and fullerenes are believed to form from C2H2 and its derivatives because CO is a very stable molecule [4,5]. Therefore, all of the theoretical calculations were carried out based on C2H2 gas abundances, i.e., no one has ever considered CO gas as a carbon source. If carbonaceous materials are formed not only from C2H2 molecules but also from CO gas, then most predicted formation constraints such as gas outflow velocity, stellar mass loss rate, total gas pressure, temperature and C/O abundance ratio will require reconsideration. Here we demonstrate the production of carbonaceous materials from CO gas in the laboratory and present a possible new formation route for TiC-core, graphitic-mantle spherules around AGB stars.

CO gas as the source of carbonaceous grains: We found that single-shell, large-cage-structure, carbon particles are produced by the Boudouard reaction, which is the disproportionation of CO molecules into solid carbon and CO2 gas. In the 1970’s, the Boudouard reaction was used to produce graphite flakes, lamellar graphitic crystallitles and filamentous graphite using Mg, Ni, Fe, Co and Mo as catalytic metals [6,7]. Subsequently, the Boudouard reaction has been widely used in the production of carbon nanotubes using Mo, Ni, Co, Ni-MgO and Fe as catalytic metals [8-10].

Recently, we produced large-cage carbon particles by resistive heating of carbon rod at a total pressure of 200 Torr in a gas mixture of He and CO. Since there is no report that fullerenes or nanotubes of this size are produced by the common evaporation of a carbon rod, we believe that our large cage carbon particles were produced by the Boudouard reaction, but in a catalytic metal free system. The high temperature (~3000K) of the evaporation source would provide sufficient energy to induced the Boudouard reaction.

As a result of high-resolution transmission electron microscope (TEM) observations, many large cages, which appear to be short nanotubes or large fullerenes, were visible. We concluded that the large cages are single shell structures, i.e., fullerenes of many sizes, but most are larger than C70, which was determined by the TEM observations including the electron diffraction pattern, by sublimation at temperatures as high as 800°C and by their infrared spectra.

Formation of core-mantle grains: Since the large cages are present only on the particles’ surface in the case of production in a gas mixture of He and CO, the large cages are deposited after production of the amorphous carbon particles. Although the evaporation temperature of carbon is quite high (~3000 K), the sublimation temperature of fullerene-like carbon particles is very low. For example, the sublimation temperatures of C60 and C70 are 300 and 350°C, respectively [11]. Therefore, even if amorphous carbon particles formed by the evaporation of the rod and large cages are simultaneously produced around the carbon rod by the Boudouard reaction, the amorphous-core, large-cage-mantle structure would be produced due to the large difference in condensation temperature (i.e., the large cages will remain in the gas-phase until the gas cools down to a considerable degree).

In order to make analogs of the TiC-core, graphitic-mantle spherules found in meteorites, TiC grains were produced by coevaporation of carbon and Ti in a CO gas atmosphere. Although we do use Ti wire, the production of large fullerenes was also observed to occur in Ti-free gas mixtures of He and CO and their formation was confirmed using TEM observations. The sizes of the TiC grains are similar to the size of the TiC grains produced in He gas, distributed between 20-40 nm whereas the thickness of the mantle layer is drastically different. Although the production condi-
tions for both samples of TiC grains were the same except for the composition of the gas, the mean thickness of the carbon mantle layer of TiC produced in CO gas is approximately 20 nm versus 2 nm for particles formed in He gas. Although the number density of Ti atoms is 10^4 times smaller than that of carbon atoms, as estimated from the relative volumes of the particles, TiC grains still grew to 20-40 nm. During gas evaporation, since the growth of TiC is terminated by the deposition of lots carbon atoms onto the surface of the growing TiC grains, TiC grains cannot be grown larger than 20 nm in a carbon rich environment (see Fig. 1 in [12]). Therefore, we believe that the growth of TiC was not prevented due to later deposition of fullerenes at low temperature. Although the expected pressures in circumstellar environments is 2-5 orders of magnitude lower than in this experiment, there is much more chance to grow a carbon mantle layer by the deposition of fullerenes onto the TiC grains due to their low sublimation temperature, if fullerenes are produced in earlier stages of grain formation, i.e., in the outflow of a carbon star or in the superwind phase terminating the life of the AGB star.

The mantle layer over TiC grains found in meteorites consists of graphitic carbon while the carbonaceous mantle produced in our experiments is composed of large cage structures. Although buckminsterfullerene, C_{60}, is thermally stable up to over 4000°C, as shown by the molecular dynamics study [13], C_{60} is transformed to amorphous graphitic carbon at only 400°C in the presence of water [14]. Indeed, since the Murchison meteorite is classified as a CM2, we know that these TiC-core, graphitic-mantle spherules were exposed to a hydrothermal environment that could have transformed the large cage structures into amorphous graphitic carbon. Of course nothing precludes the earlier transformation of such cage structures to amorphous carbon by exposure to water vapor: such exposure could have occurred in the expanding atmosphere of the AGB star, in the molecular cloud core from which the Solar Nebula collapsed, or in the nebula itself. Therefore, we propose a possible new formation route; namely, that TiC-core, graphitic-mantle spherules are produced by the deposition of large prenucleated carbon cages onto TiC grains in the atmosphere of an AGB star and the subsequent hydrothermal alteration of the fullerenes to a graphitic structure. Nanocrystalline-core, well-graphitized carbon mantle spherules were also found in the Murchison meteorite [2]. The nanocrystalline cores are constructed from randomly oriented graphene sheets with little graphitic layering order. Our hypothesis would also apply to the formation of this composite carbon grain. Since there are many types of carbonaceous materials, such as PAHs, graphite with various degrees of order, amorphous carbons, fullerenes and carbidic and their composite structures have been found in meteorites and in stellar sources, there could be basic building blocks that eventually form carbonaceous grains. Although it has been assumed that CO gas is very stable, it might actually be a very important source for the formation of carbonaceous grains. Since the Boudouard reaction is accelerated by small metallic particles, large fullerene-like cages would be produced quite easily around AGB stars. We expect that new constraints on particle formation in AGB stars via the Boudouard reaction could be derived from detailed theoretical calculations based on our study.

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