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# Reexamination of crystal growth theory of graphite in iron-carbon alloys

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ABSTRACT

Most analysis of graphite morphology in cast iron-carbon alloys is performed on samples cooled to room temperature. This raises the concern that the crystallization of graphite is obscured by subsequent recrystallization and growth in solid state. To bring clarity to this issue, the authors used Field Emission Gun Scanning Electron Microscopy on deep-etched interrupted solidification (quenched) specimens to reveal the morphology of graphite growing in contact with the liquid at the very beginning of solidification.

To understand the complexity of graphite crystallization in iron alloys, the analysis included evidence from the crystallization of materials with analogous hexagonal structure, such as of snowflakes and metamorphic graphite, and from the crystallization of diamond cubic structure silicon crystals in aluminum-based alloys. Information from research discussing graphite produced through gas-solid (chemical vapor deposition) and solid-solid (graphite in steel) transformations was also exploited.

The large variety of graphite solidification morphologies described in this and earlier papers derives from the complexities of its faceted growth during crystallization, a diffusion-limited crystal growth process, in the presence of anisotropic surface energy and anisotropic attachment kinetics. It was confirmed that the basic building blocks of the graphite aggregates are hexagonal faceted graphite platelets generated through the growth of graphene layers. As solidification advances, the platelets thicken through layer growth through two-dimensional or screw dislocation nucleation. Depending on bulk composition, local supersaturation and undercooling, the platelets aggregate through a variety of mechanisms including tiled-roof and foliated crystals and dendrites, curved-circumferential, cone-helix, helical (macro-spiral), and polyhedral pyramidal (or conical) sectors growth. The final graphite shape of graphite spheroids is affected by the crystallography of the nucleus, as it affects the initial growth of the graphite platelets.



## 1. Introduction

Graphite, is one of the two naturally-occurring forms of crystalline carbon, the other one being diamond which is transformed into graphite above 900 °C. While diamond has a face-centered cubic lattice, graphite has a layer-structure of graphene sheets in which the carbon atoms are arranged in a honeycomb lattice. The strong sigma-bonds within layers, and weak Pi-bonds between layers produce the faceted morphology and high anisotropic behavior of graphite.

At least two mechanisms appear to be responsible for the formation of graphite: i) growth of two-dimensional (2-D) graphene sheets with subsequent aggregation and recrystallization in graphite platelets [1]; and ii) crystallization of graphite platelets from amorphous carbon deposited on the growth surface of graphite [2,3]. Typically, graphite grows faster along the tightly-bond *a*-axis directions [1010], rather than the loosely-bond *c*-axis direction [0001]. This explains the graphite flakes in natural graphite and the graphite lamellae in gray cast iron. However, under certain conditions, in nickel-carbon, cobalt-carbon, and iron-carbon alloys such as steel and cast iron, the graphite aggregate appears to extend in the *c*-rather than the *a*-direction producing

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spheroidal/nodular graphite.

Room temperature graphite morphology in cast Fe–C alloys is the results of crystallization from the liquid followed by solid-state carbon diffusion growth. The chemical complexity of the iron melts, and the transitory nature of nucleation and local segregation produced by melt treatment, are the main complicating factors. The interplay between these variables can produce a large variety of graphite shapes including lamellar/flake (LG), compacted/vermicular (CG), spheroidal/nodular (SG), and temper graphite, as well as some "degenerated" morphologies, such as spiky, exploded, or chunky graphite [4–6].

Spheroidal graphite can crystallize in high purity Ni–C and Fe–C–Si melts [7–9], as well as in "impure" industrial melts, where the level of surface-active anti-compacting elements (O and S) is drastically reduced through additions of reactive compacting elements (e.g. Mg, Ce, Ca). To achieve spheroidization in high purity melts, much higher solidification rates are required as compared to the industrial melts. Low solidification rates in directionally solidified Ni-2.1% C, produced lamellar graphite [10]. With increasing purity and solidification rate, a transition from plate-like to spheroidal graphite occurs.

Metallographic specimens of cast and cooled to room temperature Mg– or Ce-treated melts frequently exhibit a multilayer structure, associated with up to three stages in their formation. Two-stage (duplex) spheroids have also been observed [11]. They will be further discussed later in this paper.

The room temperature graphite spheroid is the product of three successive events: 1) nucleation and growth in the liquid; 2) growth during the eutectic transformation via carbon diffusion through the austenite shell; 3) growth during cooling to room temperature as the solubility of carbon in austenite decreases. This lead some researchers to assume that the stages in Fig. 1 correspond to the three events above. Yet, stage II in TEM images [12] appears very different than in the other two figures where conical sectors are seen in stage II. The separated graphite conical sectors indicate the beginning of formation of degenerate graphite. As the graphite in Fig. 1-b was obtained from the graphite flotation zone in a large casting, it is reasonable to assume that it has grown mostly in the liquid. Pockets of iron entrapped behind the growing sectors support this supposition. Then, the occurrence of the conical sectors in stage II is the result of increased instability at the growth interface. This hypothesis finds support from columnar graphite structures found on spheroids obtained in rapidly solidified Ni–C alloys [9]. Thus, stage II may be the result of growth through the austenite shell, but also of growth in contact with the liquid.

Because of the extensive recrystallization of the amorphous carbon deposited on the crystalline graphite during cooling to room temperature, extending the results of the TEM analysis on this type of samples to explain crystallization from the liquid, appears risky. As it will be demonstrated throughout his paper, significant differences in graphite microstructure are found when the experimental sample is obtained through interrupted solidification versus from the as-cast sample. Nevertheless, it should be noted that interpretation of quenching experiments requires careful analysis, because transformation continues during quenching. Thus, it is not always possible to distinguish between the microstructure immediately before quenching and that formed during quenching. The goal of this paper is to integrate results of new research on interrupted solidification and room temperature specimens, with the current information on the crystallization of graphite and of analogous faceted systems (ice crystal, silicon-base alloys, iron-nickel alloys, metamorphic graphite), and with evidence from other processes producing graphite spherulites through gas-solid and solid-solid transformation.

## 2. Analysis of most accepted mechanisms for the crystallization of graphite

The complexity of the problem of graphite crystallization and growth iron melts is illustrated by the large number of postulated models, periodically reviewed in the literature, e.g. Refs. [4–6,13,14]. Because of space limitations, the current discussion will cover only models that found support in graphite growth in iron and nickel-based alloys, in analogous faceted systems, as well as in other graphite producing processes.

A consensus appears to have been reached in that the building blocks of graphite aggregates are graphite platelets resulting from the stacking of graphene layers. Platelet-type nano-fibers obtained by Yoon et al. [15] through catalytic routes appeared to be sets of 5–25 graphene stacks. The graphene sheets were also found to stack in a "herringbone" arrangement. Examination of spheroidal graphite obtained by heat treatment of medium carbon steel by Li et al. [16], also concluded that the building blocks of the radial sectors of the spheroids are graphite platelets about 10–30 nm thick and hundreds of nanometers in length. The HRTEM image of such a platelet presented in Fig. 2 shows straight 002 fringes. The bright interplatelet region shows wavy fringes indicating a low degree of graphitization. Double and Hellawell [10] concluded that the graphite flakes in a eutectic Ni-2.1% C alloy are composed of layers of 10 μm thick, fault free crystals, stacked together. Hexagonal faceted graphite platelets with nanometer-height in the *c*-

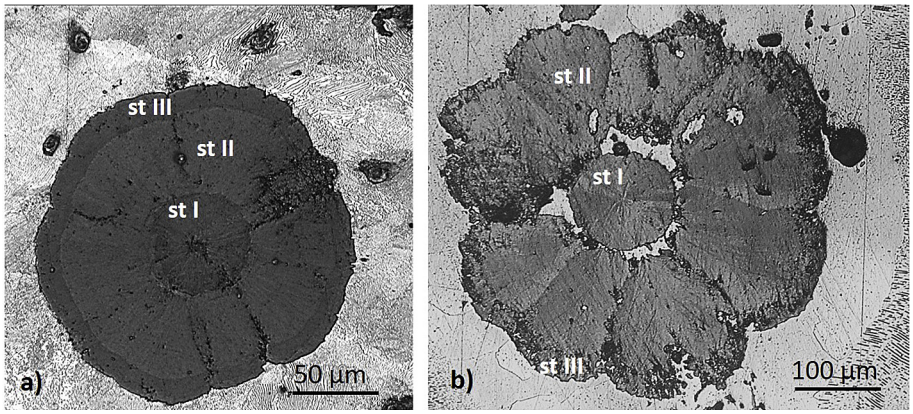


**Fig. 1.** Optical images of three-stage graphite aggregates: a) optical image of well-formed graphite spheroid (compliments of J. Barlow and A. Catalina, Caterpillar Inc.); b) optical micrograph of a degenerated (exploded) graphite spheroid (compliments of A. Udroiu).