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On the crystallization of graphite from liquid iron–carbon–silicon melts

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ABSTRACT

Extensive SEM work was carried out on deep etched specimens to reveal the evolution of graphite shape in Fe–C–Si alloys of industrial composition during early solidification and at room temperature. The samples had various magnesium and titanium levels designed to produce graphite morphologies ranging from coarse lamellar to interdendritic lamellar to mixed compacted – spheroidal. The present findings were then integrated in previous knowledge to produce an understanding of the crystallization of lamellar, compacted and spheroidal graphite.

It was demonstrated that most forms of graphite grow radially from a common center, most of the time as foliated dendrites (see Figure). The basic building blocks of the graphite aggregates are hexagonal faceted graphite platelets with nanometer height and micrometer width. During solidification, thickening of the platelets occurs through growth of additional graphene layers nucleated at the ledges of the graphite prism. In the magnesium-free irons that graphite platelets assemble into foliated crystals and dendrites, forming graphite plates that grow along the *a*-axis. In the magnesium-modified melts the graphite platelets stack along the *c*-axis, producing clusters with random orientation. The clusters are then assembled into quasi-cylindrical shapes connected to more or less curved walls to form tadpole graphite, compacted graphite, or chunky graphite. If enough magnesium is added, conical sectors made of platelets stacked in the *c*-direction grow from the same nucleus. The conical sectors may occupy the whole volume of the sphere forming a graphite spheroid, or only part of it like in chunky graphite. The large number of cavities observed between the platelets is consistent with growth of foliated dendrites.

1. Background

Multicomponent Fe–C–Si–Mn–S-etc. alloys, known in industry as cast irons, solidify with a stable austenite/graphite (γ/Gr), or metastable γ/Fe_3C eutectic. Although the use of these alloys in the panoply of materials employed by humans dates as far back as 502 B.C., and in spite of the extensive research started at the beginning of the 18th century and continued to these days, unanswered questions regarding the mechanism of formation of various graphite shapes are still waiting for answers.

1.1. Graphite morphologies and crystal lattice

Depending on composition and cooling rate, three main graphite morphologies crystallize from the Fe–C–Si melt during solidification: lamellar (LG), compacted or vermicular (CG) and spheroidal (SG), as exemplified in Fig. 1 [1–3]. The internal structure of SG exhibits conical sectors of parallel graphite planes growing radially from the center (Fig. 2-a). The sectors may be partially broken (Fig. 2-b) in extreme cases causing “exploded” graphite. The annular rings may exhibit zig-zag steps of the (0001) planes, suggesting columnar crystals of graphite with different orientations [4].

The compacted graphite is considered to be an intermediate shape between LG and SG. The highly 3D branched morphology of CG was revealed as early as 1979 through successive polishing and reconstruction of the two-dimensional (2-D) microstructure [5]

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(Fig. 3-a), and then confirmed through deep etching (Fig. 1-b), and graphite extraction through focused ion beam nano-tomography [6] (Fig. 3-b).

The LG is further classified as a function of size and distribution. The most common shapes of lamellar graphite are coarse lamellar (type-A) and interdendritic (type-D, and type-E often referred to as undercooled graphite). Very fine interdendritic graphite can be obtained for example in irons with normal sulfur content of 0.03–0.08wt%, high titanium (0.5–1%) and high cooling rates [7].

Other intermediate graphite shapes have been identified, such as coral graphite, a highly branched fibrous type of graphite [8,9], and superfine interdendritic graphite (SIG), which is short (10–20 μm) and stubby, exhibiting round edges similar to the coral graphite. It was obtained in low-S and moderate-Ti content irons (*e.g.* <0.01%S, ~0.3%Ti) [10].

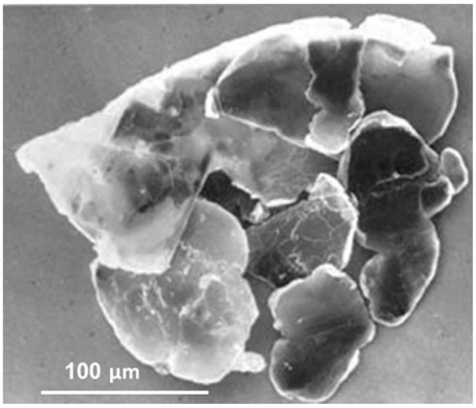
Several irregular and undesired graphite shapes are considered to be the outcome of degeneration of SG. Chunky graphite (Fig. 4) appears as a result of extensive branching of graphite spheroids [11,12]. It is a highly interconnected form of graphite that does not include broken pieces of graphite spheroids.

A transition LG-to-CG-to-SG can be triggered through the addition of small amounts of Mg, Ce or lanthanides to a low sulfur iron. The process is reversible: SG will revert to LG with sulfur addition or through loss of magnesium by evaporation and/or oxidation.

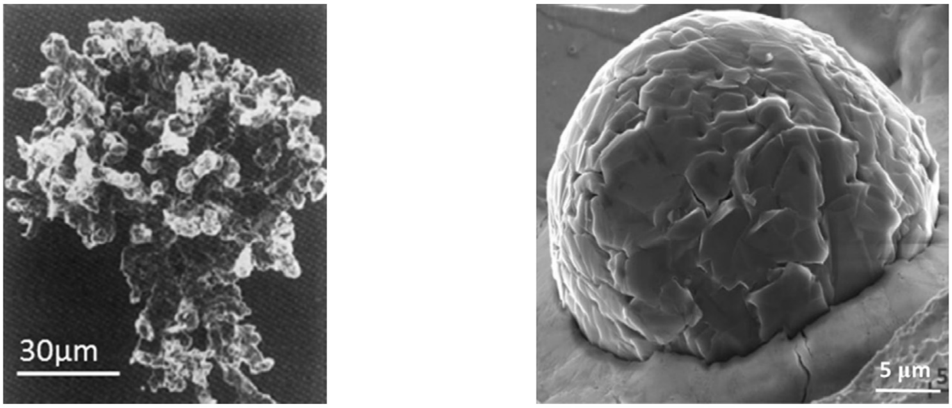
Alternatively, similar structural changes can be achieved by holding molten iron in vacuum for long periods (days or weeks) prior to casting to remove elements such as oxygen, sulfur and phosphorus, leaving a “clean” melt [13,14]. Dhindaw and Verhoeven [15] observed SG in vacuum-melted high purity Fe–C–Si alloys of hypoeutectic and eutectic compositions solidified at high cooling rates. These observations lead some researchers to suggest that the spheroidal form is actually the preferred habit for growth from a metallic solution, in the absence of surface active elements such as O, S and P, and that LG is an impurity-modified form [16].

While in industrial practice the transition between these graphite shapes is controlled reasonably well, in spite of the many years of research, the transition mechanism is not clearly understood. In particular the growth mechanism of graphite from the liquid is still a subject of much debate.

The crystal lattice of graphite is hexagonal, with A-B-A-B stacking of semi-infinite hexagonal monolayers [17] (Fig. 5). The bonding is strong covalent in the plane of the layers and weak van der Walls between them as the large axial ratio, $c/a \approx 2.7$, indicates. Each monolayer is a 2-D polymeric graphene sheet [18] to which carbon atoms can attach easily in the monolayer plane (*a*-directions), but with a much lower probability normal to the monolayer (*c*-direction). The A and B layers are displaced by half of the *c*-axis spacing. Because of the difference in the bonding forces between the *a*- and *c*-directions, it is reasonable to assume that the



a) lamellar graphite– lettuce growth [1]



b) compacted graphite – cauliflower growth [2] c) spheroidal graphite– cabbage growth [3]

Fig. 1. Typical graphite shapes obtained from commercial cast iron through deep etching and extraction.