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Comment on Stefanescu, D.M.; Alonso, G.; Suarez, R. Recent Developments in Understanding Nucleation and Crystallization of Spheroidal Graphite in Iron-Carbon-Silicon Alloys. Metals 2020, 10, 221.

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In an article published in this journal in February 2020, Stefanescu et al. reviewed recent developments in understanding nucleation and growth of spheroidal graphite in cast iron [1]. The intention of the present comment is not to discuss the merits and limits of this highly documented paper in general, but to correct erroneous statements made by the authors in their Section 5.1. One of the approaches reviewed in this section is the work by Theuwissen et al. [2], who suggested that the 2-D poly-nucleation-growth (PNG) mechanism applied by Amini and Abbaschian [3] to describe the formation of polyhedral graphite plates in Ni–C alloys might also be operational for flake and spheroidal graphite in cast iron melts. This hypothesis has been supported by the analytical calculations of Lacaze et al. [4], and it is this latter work which is severely criticized by Stefanescu et al. in section 5.1 of their paper [1]. In the following, we detail that the supposed numerical incongruities and seemingly shortcomings of the work by Lacaze et al. [4] are not real, but are based on a severe misinterpretation of the analytical model parameters and results.

The 2-D nucleation-growth model for spheroidal graphite by Lacaze et al. [4] expresses the overall growth rate of a nodule from the liquid, \( G_{PNG} \), as (Equation (14) in [4]):

\[
G_{PNG} = a \left( \frac{\pi}{3} \cdot J_a \cdot (V_l)^{2/3} \right)^{1/3}
\] (1)

where:
- \( a \) is the height of the nuclei, which is set equal to the distance between basal planes of graphite.
- \( J_a \) is the nucleation rate of new growth units at the outer surface of the nodule and is described by a classic approach for 2D nucleation [5].
- \( V_l \) is the lateral spreading rate of the growth units.

A first approach to express \( V_l \) was to consider a general kinetic law derived by Cahn et al. [6], which leads to the following equation (Equation (17) in [4]):

\[
G_{PNG} \approx 0.05 \cdot (\Delta T)^{5/6} \cdot \beta \cdot \left( 2 + \frac{\xi}{\Delta T} \right)^{2/3} \cdot \exp \left( - \frac{7200 \cdot \xi}{\Delta T} \right) \text{ m.s}^{-1}
\] (2)
where $\Delta T$ is the undercooling with respect to the graphite liquidus, $\beta$ denotes a structural parameter and $\xi$ is the diffuseness of the interface as defined by Cahn et al. [6].

The structural factor was set to 1, as it should be for single atoms (as opposed to molecules) [5], and $\xi$ was varied between 0.1 and 1 which is its maximum value (sharp interface). This gave the curves plotted with dotted lines in Figure 1a.

A second way to express $V_l$ was based on carbon diffusion from the liquid to the growing units. The solution proposed was according to Bosze and Trivedi [7], which is more precise than the approach used by Amini and Abbaschian [3]. This led to the following equation (numbered 29 in [4]):

$$G_{PNG} = 2.6 \times 10^{-11} \cdot (\Delta T)^{17/6} \cdot (\beta)^{1/3} \cdot \exp\left(-\frac{7200 \cdot \xi}{\Delta T}\right) \text{ m}^{-1}$$

The structural factor was set to 1 as before, and the same values were used for the diffuseness, giving the solid curves in Figure 1a.

Lacaze et al. calculated growth rates in the range of undercooling of 0–250 °C in agreement with the fact that experiments on primary graphite growth from the liquid are carried out on melts having been carbon saturated at high temperature—typically 1350–1550 °C—to get a large enough temperature interval before bulk eutectic solidification occurs, following in this many previous authors [3,8,9].

The first criticism of Stefanescu et al. is the choice of the range of the undercooling $\Delta T$. The authors claim that an “undercooling higher than about 50 K will be conducive to metastable structure in Fe-C-Si alloys”. Stefanescu et al. [1] obviously misunderstood the undercooling as a technical undercooling evaluated with respect to the eutectic instead of with respect to the graphite liquidus.

Then, referring to the figure reproduced here in Figure 1a, Stefanescu et al. “also notice some numerical incongruities: At a reasonable undercooling of 25 K (thin vertical line on the figure) it will take 3 hrs”. These authors thus also mixed up the plots, as our final discussion was dealing with results calculated with Equation (3) which appear as solid lines in Figure 1a. To avoid any further misunderstanding, the curve calculated with Equation (3) and the selected value of 0.1 for diffuseness is reproduced in Figure 1b.

Finally, Stefanescu et al. claimed “Such unrealistic calculation results are not surprising given the number of parameters that have to be estimated (e.g., the height of the nucleating disk, diffuseness, the correction for the structural factors)”. Thus, these authors wrongly accused us of using a high number of fitting parameters, while there was only a single one, the interface diffuseness, and the impact of this one has been discussed.

The appropriateness of our approach was checked against a few available experimental results [10] in the last section of our paper [4]. To sum up, we certainly think that analytical approaches could still be of some help for understanding metallurgical processes and in particular, spheroidal graphite growth.
Figure 1. Overall growth rate of a graphite spheroid according to the PNG model as a function of the undercooling with respect to the graphite liquidus. The horizontal line represents the experimental value estimated by Amini and Abbaschian for the thickening rate of lamellar graphite (growth along the basal-c direction). \( \xi \) is the diffuseness of the interface. In (a) is shown the figure as reproduced by Stefanescu et al. [1] with dotted and solid lines associated respectively to equation (2) and equation (3). In (b) has been drawn the same figure but with the single curve that should have been considered when discussing our calculation results.

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**Conflicts of Interest:** Page: 3

The authors declare no conflict of interest

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