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Reply to the Letter to the Editor

*Regarding the Paper “Study of the Eutectoid Transformation in Nodular Cast Irons in Relation to Solidification Microsegregation”
A Freulon, P De Parseval, C Josse, J Bourdie,
J Lacaze: MMTA 2016*

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In his discussion of our paper,^[1] Doru M. Stefanescu first stresses that the presence of carbides in the as-cast samples he investigated with Guo was mentioned in one of their other papers,^[2] not the one^[3] we referenced. It is agreed that the presence of carbides was clearly stated in the first paper by Guo and Stefanescu,^[2] however, the authors mentioned that “When the segregation of Cr and/or Mn reached a certain level, complex carbides of the (Fe,Mn)₃C or (Fe,Cr)₃C may form” in their second paper^[3] on page 439. As the alloys and experimental conditions were exactly the same in both of their studies, it was presumed—perhaps improperly—that both studies therefore dealt with the same samples, and this sentence was understood to mean that the authors indicated the possible presence of some carbides in their samples.

Unless stated by D.M. Stefanescu, the conduct of the experiments was very similar in his study with Guo to that of our own work, in that commercial cast irons were used, re-austenitized, and then cooled at controlled rates. In our experiments, the cooling rate varied from 2 to 20 K/min but that of the observed samples were 2 and 5 K/min as clearly indicated in the paper.^[1] In the work of Guo and Stefanescu, the cooling rate was either 12 or 24 K/min. The difference between Guo and Stefanescu’s two papers is that in the first one,^[2] they used energy-dispersive spectrometry (EDS), while in the second one^[3] they carried out microanalyses with wavelength-dispersive spectrometry (WDS).

Even if decreasing the cooling rate truly favors ferrite formation, this does not mean it could help smoothing compositional differences due to the eutectoid transformation as claimed by Stefanescu in his discussion. There are two reasons for this:

1—It is known that any chemical heterogeneities such as microsegregation issued from the solidification step are hardly smoothed out by heat treatment in the case of cast irons, and this must be due to the low diffusion coefficient of substitutional solutes (Cr, Cu, Si substitute to iron in the fcc and bcc matrices) as well as to thermodynamic interactions. For a cooling rate of 12 K/min as illustrated in Figure 1(B) of Stefanescu’s discussion, the eutectoid transformation proceeds at about 1023 K (750 °C) and takes a time of $t = 600$ seconds. Following Fridberg *et al.*,^[4] an upper estimate of the diffusion coefficient of substitutional solutes D can be taken as 10 times the self-diffusion coefficient of iron for light elements such as silicon, and 5 times for elements such as chromium and copper. The self-diffusion coefficient of iron was given for austenite as $7.0 \times 10^{-5} \cdot \exp(-286000/RT) \text{ m}^2 \text{ s}^{-1}$ and for ferromagnetic ferrite as $1.6 \times 10^{-4} \cdot \exp(-240000/RT) \text{ m}^2 \text{ s}^{-1}$, where R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T the temperature in Kelvin. Diffusion is much faster in ferrite, and the silicon diffusion coefficient is thus evaluated to about $10^{-15} \text{ m}^2 \text{ s}^{-1}$ at 1023 K (750 °C) in this phase. Within the time t , the distance that silicon atoms could move in ferrite is given as $(D \cdot t)^{0.5}$, *i.e.*, less than $1 \mu\text{m}$ which is even lower than the size of the volume excited with the electron beam (see below). In austenite, the distance would be about 10 times smaller.

2—There cannot be any compositional differences setting up in the matrix during the stable and metastable eutectoid transformations because this would need long-range diffusion of substitutional solutes within austenite. For the same cooling rate as above (12 K/min) and assuming an average half-distance between nodules of $80 \mu\text{m}$ as seen on the micrograph of Figure 3(b) in Guo and Stefanescu’s paper,^[3] an average growth rate of the transformation front V of $1.3 \times 10^{-7} \text{ m s}^{-1}$ is found. With the silicon diffusion coefficients in austenite indicated above, a solute spike developing in austenite would have a thickness of $(D/V)^{0.5} = 1.3 \times 10^{-11} \text{ m}$. Such a value is totally unphysical (lower than atomic distance), meaning that no spike develops ahead of the transformation front and it also implies that there is no long-range redistribution of substitutional solutes between ferrite and austenite or pearlite and austenite.

Another aspect of the work discussed by Stefanescu relates to the analyses themselves. For spot counting with a standard microprobe, the diameter of the electron beam is around $1 \mu\text{m}$, but the volume of matter that is affected is much higher as the electrons penetrate the material for some distance. In our case, observing the contamination marks allowed us to consider that the

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effective diameter of the analyzed spot was 2 μm . As both studies were performed at 15 kV, there is no reason to think there was any difference. Doing our best to use WDS to increase the signal-over-noise ratio, the detection level was clearly indicated as was the associated standard deviation for all analyzed elements. Even with the optimized conditions used for counting, a standard deviation of 0.2 wt pct for silicon was determined which is the easiest alloying element to quantify due to its content. Although this information was not provided by Guo and Stefanescu, one can presume that they used conditions to reach a similar detection level and standard deviation. This means that changes in silicon content of ± 0.2 wt pct as seen in Figure 2(C) of Stefanescu's discussion which are related to ferrite/pearlite or pearlite/austenite interfaces are within the range of statistical variations. Furthermore, if analyses have been carried out on etched samples effectively, as seems to be the case according to the next to last sentence of Stefanescu's discussion, then they would be best considered as semi-quantitative and small differences such as those mentioned above could hardly be considered for any quantitative use.

Following the suggestion in the last sentence of Stefanescu's discussion, there is a result that cannot be ignored in the work by Guo and Stefanescu.^[3] This result is reproduced in Figure 2(D) of Stefanescu's discussion. The distributions in Cr, Cu, and Si (and also Mn in the original paper) show abrupt and high composition changes between austenite and pearlite that are much higher in amplitude than the detection limits and should be significant even if recorded on etched

samples. It is because of their abruptness that it was suggested these composition changes could have resulted from previous carbides solutionized during the re-austenitization process. In Figure 2(D), it can be seen that Cr and Cu (and also Mn in the original work) are higher on the pearlite side of the pearlite/austenite interface, while Si is lower. Cr and Mn are known to be carbide stabilizers and thus enrich in cementite, and this compares favorably with Stefanescu's statement. On the contrary, copper does not enter in cementite and has a much lower solubility in ferrite than in austenite. Thus, if there were a long-range redistribution of copper during pearlite growth, it would have been expected to be associated with a copper enrichment in austenite and not in pearlite. A discussion of the possible reason(s) for such a paradox would have been welcome in the second paper by Guo and Stefanescu.^[3] The lack of such a discussion is made even more striking by the fact that in their first analysis^[2]—page 540—Guo and Stefanescu stressed they did not find any copper in the pearlite of the copper-bearing pearlitic alloy they investigated.

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