LETTER TO THE EDITOR

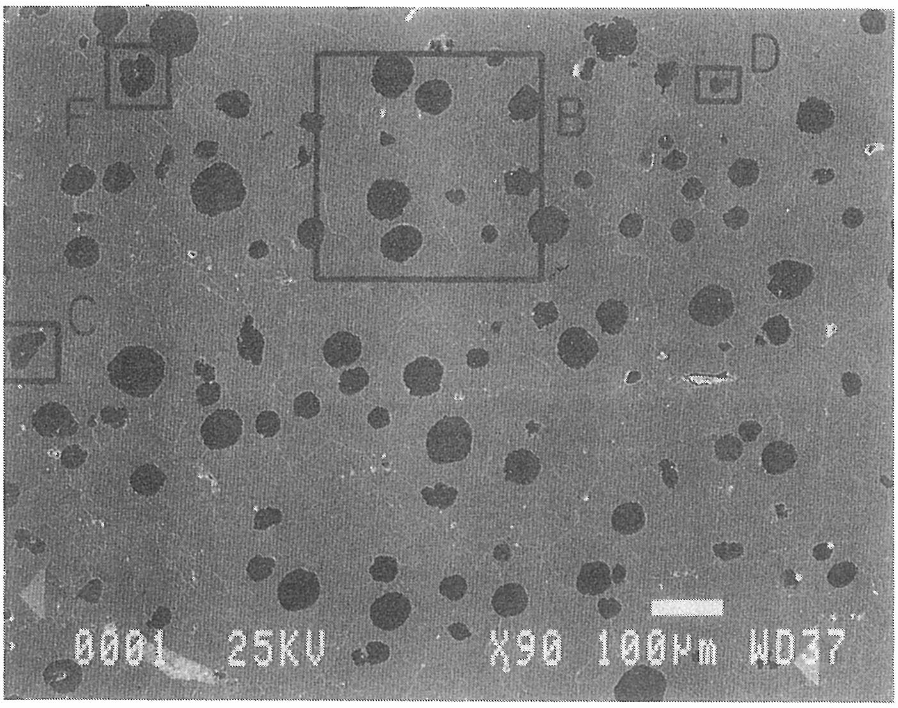
Magnesium Map of the Spheroidal-graphite Structure in Ductile Cast Irons

Sir,

Professor Zhukov posed a number of questions in his letter, contained in your issue of *Cast Metals,* Volume V, No. 3, page 178, relating to my paper entitled "Magnesium Map of the Spheroidal-graphite Structure in Ductile Cast Irons," which originally appeared in Volume V, No. 1, pages 6-19. I would like to attempt to provide some answers.

His first question concerned the precise location of the magnesium halo in relation to the graphite nodules. In reply, I would explain that we recently scheduled further experiments to determine the precise location of the Mg halo, because the precipitation of secondary graphite was not taken into account during the development of the theory. Three steps have to be considered in relation to the nucleation and growth mechanism of spheroidal-graphite during the entire period of growth, both in liquid and in solid iron. The first two steps involve the growth of graphite in liquid iron and in relation to the austenite shell, as the solidification process proceeds. The last step is the growth as secondary graphite at the interface of the pre-existing spheroidal-graphite and the austenite matrix. A. Javid, *et al.*[1] reported that secondary graphite was deposited as a ring on pre-existing spheroidal-graphite during heat-treatment. Although the authors did not comment upon the fact, a discernible gap was to be seen between this ring and the pre-existing spheroidal graphite in their SEM photographs. This means that secondary graphite does not subsequently precipitate directly onto the pre-existing spheroidal graphite, but nucleates anew to grow on the wall of the matrix. In this new series of studies, the graphite ring was also to be found around most of the graphite nodules to be found in the same microstructure as that shown in Fig 2 in the original paper, as a result of re-observation. The graphite ring could be clearly distinguished in a well-polished graphite nodule. The re-observed microstructure, together with the graphite nodule and its associated graphite ring are shown respectively within this correspondence as Fig A and B. The Mg halo may exist between such a ring of secondary graphite and the pre-existing spheroidal graphite. The following two mechanisms are considered as the underlying reason:

A Re-observed microstructure which provides a wider view of the microstructure shown in Fig 2 and 3 of the author's original paper (SEM). (B) shows a graphite nodule with a graphite ring; (C) is the nose-like graphite nodule, referred to by Professor Zhukov in his comparisons of graphite nodules in Fig 3; (D) shows the graphite nodule referred to in a later paragraph as being the nodule on the diagonal traced down at an angle of about 45 degrees from the upper right-hand corner of the maps in Fig 3, and (F) is the graphite nodule containing the inclusion portrayed in Fig 8.



B Graphite nodule surrounded by a graphite ring; ×400.

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1 The Mg halo surrounding a graphite spheroid changes its state from gas to liquid at about 1,100°C, the volume being reduced exceedingly by the time solidification is completed. Therefore it is suggested that the halo-like phenomena appears in the space between the graphite spheroid and the matrix. Since metallic magnesium does not enter into a bonding system with iron atoms and those of graphite, the liquid magnesium may be present at the interface between the matrix and the spheroidal graphite at this time. Secondary graphite may subsequently nucleate at the matrix wall and then grow inwards. As a result, the magnesium may be sandwiched between the secondary graphite and the pre-existing spheroidal graphite.

2 Contrariwise, if the halo-like space is not thick enough to allow the growth of the secondary graphite on the wall of the matrix, then the growth site for the graphite may be provided by the outward diffusion of the iron atoms. In this case, the magnesium might not diffuse outwards, but may remain at the same site because the size of Mg atoms (Ø3.20 Å) is much bigger than that of iron atoms (Ø2.48 Å). Actually, there has been no report of Mg diffusion in solid iron under atmospheric pressure, but only under the pressure of Mg vapour. Even if Mg can diffuse in solid iron, the diffusion velocity of Mg may be slower than that of the iron atoms. In these circumstances, the secondary graphite may nucleate on the wall of the matrix and grow outwards, leaving the Mg on the pre-existing spheroidal graphite. As a result, the Mg halo may exist between the secondary graphite and the pre-existing spheroidal graphite.

The analysed region surrounding the graphite nodule may be wider and deeper than that at the matrix because of the density of the graphite. Therefore, the Mg halo may appear wider than its actual width.

Professor Zhukov pointed out that the dimensions of the 'red' nodule in the author's illustration Fig 3b corresponded to the sum of the 'black+yellow' areas in Fig 3a. Furthermore, the 'black' inner nodule in Fig 3a has no 'nose' on its left side, whilst the same nodule in Fig 3b, c, and d has such a nose on the left side, which corresponds exactly to a protuberance of the 'yellow' halo in Fig 3a.

As a result of the author's re-observation, it was seen that the matrix was trapped in the nose-like graphite nodule shown in Fig C contained within the present text. This was proved by EDS. Elements characterised by low diffusibility might exist at the matrix, but only where such a matrix was left during the growth of spheroidal graphite in an austenite shell. Therefore, the inside of the graphite nodule in Fig 3a showed not only the black colour of the graphite, but also the bright colour of the matrix. The same thing can be said in relation to the nose-like graphite nodule in Fig 3c. The original microstructure was based on the same overall view as that portrayed in each of the coloured map microstructures in Fig 3, and included the nose-like nodule. Unfortunately, in order to accommodate the original microstructure on the page, the Editor trimmed the illustration, thereby cutting away the edge, which included the nose-like graphite nodule.

Professor Zhukov pointed to other examples, including the nodule on the diagonal traced down at an angle of about 45 degrees from the upper right-hand corner of the maps in Fig 3. In Fig 3b, c, and d it was possible to distinctly see a neighbouring small graphite nodule just to the top of it. Yet in Fig 3a, there is only a 'yellow' protuberance on its place – that is graphite impregnated with magnesium.

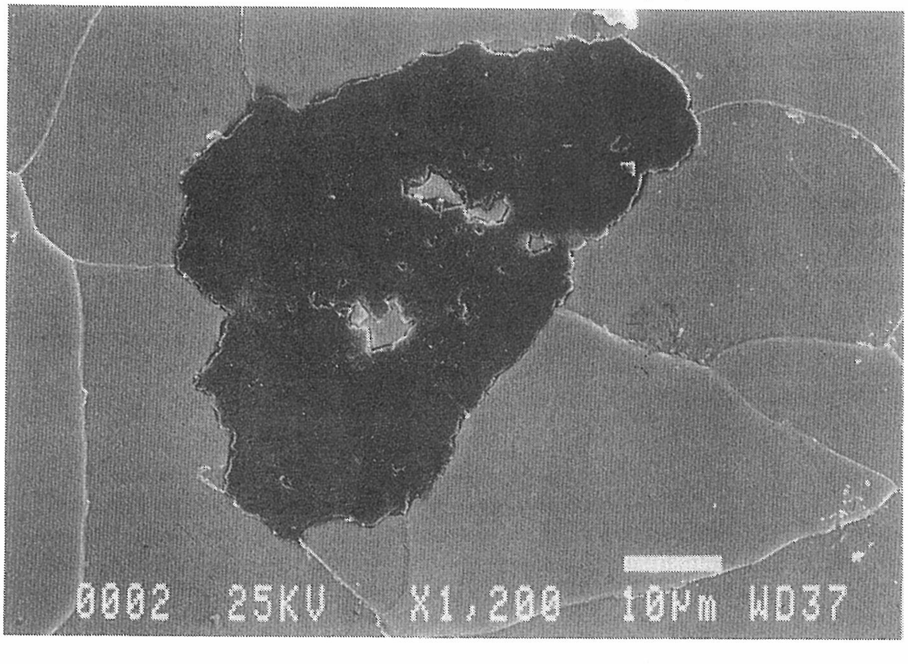
In answer, the author would suggest that the situation might be similar to the nose-like graphite nodule discussed previously. The graphite nodule at the near-right upper corner in Fig 3a has been reproduced in this correspondence as Fig D.

Since, in this case, the matrix contained a graphite nodule, which in turn contained magnesium, an attempt has been made in Fig E to suggest how such nodules might have been intercepted in the sections through the samples.

Professor Zhukov also asked what the author's work really had to do with the magnesium bubble theory which was originated by A. A. Gorshkov.

The author had no intention of ignoring the work of A. A. Gorshkov, but he was unable to locate this paper on the formation mechanism of spheroidal graphite in cast iron in any library in Japan. Indeed, there would appear to be no Russian papers on cast iron anywhere in Japan before December 1955. As a result, the writer was only aware of this study from references contained within another author's paper. Because of this, there was no way of commenting on Gorshkov's findings. More recently, the author was able to obtain the missing work^2 from Mr. E. Nechtelberger, a member of the Editorial Board of *Cast Metals*, based in Austria. According to the paper, A. A. Gorshkov's theory can be summarised as follows: Eutectic graphite is deposited and then grown on a pre-existing graphite nuclei in a magnesium gas bubble. At the same time, with the precipitation, there is also the precipitation of eutectic austenite which surrounds the bubble with graphite.

C The nose-like graphite nodule shown in Fig 3 which contains a section of matrix (SEM).



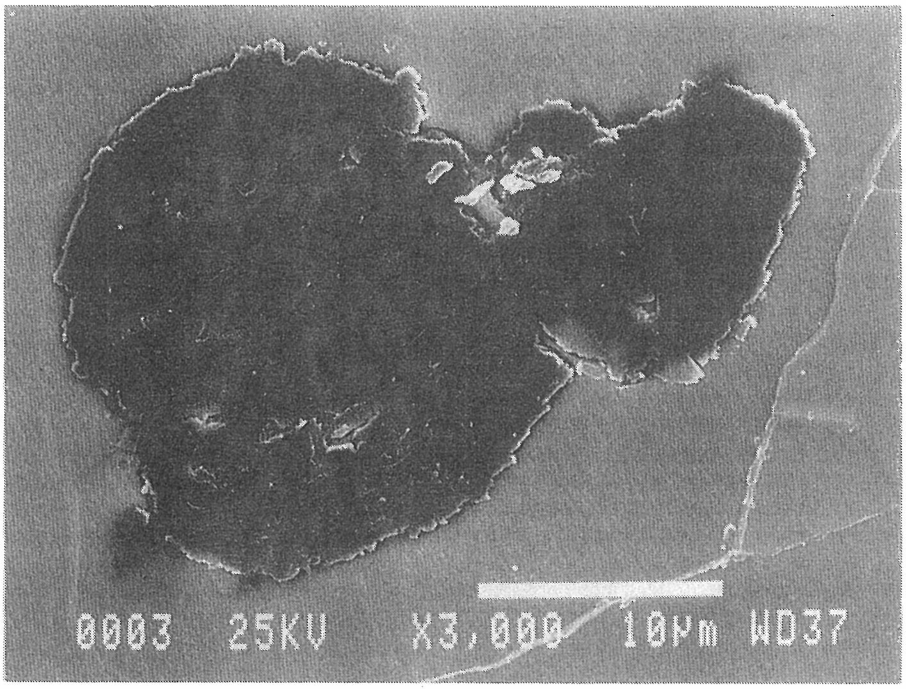
At first, graphite occupies the site of the gas bubble, and as a result the graphite can assume the spheroidal form. Subsequently, the spheroidal graphite grows evenly within the austenite shell, receiving carbon atoms through the surrounding shell. The graphite nuclei forms in the magnesium gas bubble according to the following formula:

$$\text{Mg gas bubble}+\text{CO gas}\rightarrow\text{MgO Solid}+\text{C solid}+117446\ \text{Cal/mol}$$

The initial Mg gas bubble (1.5-2.0 mm) is reduced in size by reaction with the CO gas and becomes smaller in dimension (1-3 μm). The new version of the Mg gas bubble contains the reaction products MgO solid and C solid (the graphite nuclei). Furthermore, this secondary Mg gas bubble does not undergo further reduction in diameter because it has been stabilised by diffusion of hydrogen gas from the liquid iron into the bubble. Every graphite nodule contains metallic magnesium and MgO within its structure. However, upon analysis, only MgO is detected in spheroidal graphite. Although the same mechanism might be considered in relation to Ca and Ce, these elements have a higher vapour pressure than Mg. As a result, their spheroidising abilities are weaker than those of Mg.

From the above explanation, it will be seen that the theory of A. A. Gorshkov is basically the same as the nuclei theory, although a Mg has bubble is seen to contribute to the formation of the spheroidal graphite. The Gorshkov theory requires the simultaneous existence of CO and H_2 gases in the liquid iron in order to, respectively, nucleate the graphite nuclei and stabilise the Mg gas bubble.

On the other hand, the site theory suggests that every graphite form which arises in cast iron is dependent on the site where the graphite precipitated whilst the substructure is dependent on the nature of the growth behaviour of the graphite crystal structure at that site. That is to say, the site of the graphite precipitation dictates the form of the graphite and its substructure. For the nucleation and subsequent growth of spheroidal graphite in magnesium-treated liquid iron, the first site will be a free surface and an Mg gas bubble. The second site will be the interface between the pre-existing spheroidal graphite and the austenite shell.



D The graphite nodule at the near right upper corner of Fig 3 (SEM).

Graphite grows according to the nature of these sites, as shown in Fig 10 of the author's original paper. As a result, the graphite spheroids are composed of thin graphite 'plates' with a polycrystalline substructure. The author found that it was also possible to explain the nucleation and growth mechanism of compact vermicular and chunky graphite by the site theory.[3-6]

From this, it will be seen that the site theory is fundamentally different from that of A. A. Gorshkov's as regards the nucleation and growth mechanism of spheroidal graphite.

Professor Zhukov also pointed out that one could obtain perfect nodules in ductile iron treated with yttrium and high-boiling point RE metals.

The author would suggest that the nucleation and growth mechanism of spheroidal graphite in liquid iron treated with RE metals has been well verified in work by S. Yamamoto *et al.*[7] According to their findings, the absorbed hydrogen in RE metals can be the source of the gas bubbles.

However, one more possibility might be considered in relation to the role of RE metals. Their liquid droplets and inclusions might act as sites for the nucleation and growth of spheroidal graphite.

Professor Zhukov also pointed out that perfect nodules are formed in white iron which contains no gas bubbles. Here, the iron is supersaturated with spheroidising elements and then subjected to a graphitising anneal. He suggested that the works of P. I. Stiopin (Moscow) and Essen and Tavadge (Tbilissi) were almost forgotten. These workers placed a small piece of magnesium inside a cavity in a cylindrical specimen of flake graphite cast iron, which itself was inserted into a thick-walled hermetically-sealed steel bomb. Using this equipment, the specimen was subjected to high temperatures – but lower than the solidus – and internal Mg-vapour pressure. The graphite flakes in the diffusion zone developed semi-spherical edges and many such flakes completely transformed themselves into perfect nodules.

It must be confessed that the author did not know of the works of P. I. Stiopin and Essen and Tavadge. If Professsor Zhukov has access to these papers, he would welcome copies.

The formation mechanism of temper graphite and its morphology were studied in detail by Y. Lee[8] and K. Kawano.[9] According to their studies, temper graphite nucleated, in a dominant manner, at the free surfaces and subsequently grew along these, such as in the case of voids in the solid state. As a result, the morphology of the secondary graphite depended on the morphology of the free surfaces where temper graphite precipitated. The author suggests that this is just such a phenomena which can be explained by the site theory. It is felt that the works of P. I. Stiopin and Essen and Tavadge will also be explained by the site theory.

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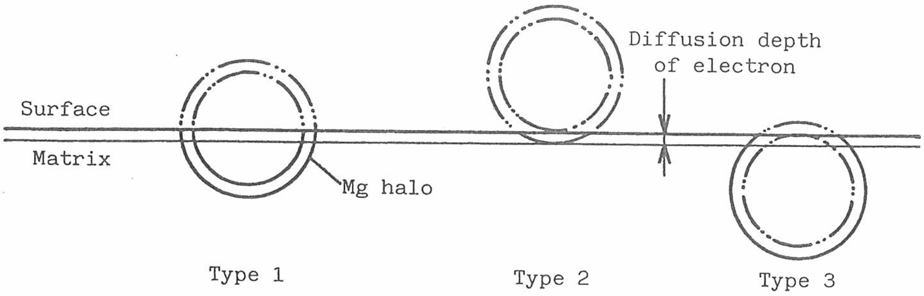
Professor Zhukov also asks why certain graphite nodules have a high magnesium content in their inner core? Was it that these nodules were intersected exactly through their centre? Furthermore, why were these cores, mainly composed of graphite, nevertheless very hard, and why did they not flatten during the hot rolling of ductile iron (R. G. Gvetadze, Tbilissi)? And why were certain elements having a diamond superstructure observed in these graphite cores?

The author would point to the correctly numbered and captioned Fig 8 in his paper, which was also mentioned in the discussion. Here, a high magnesium content present at the centre of a graphite nodule demonstrated the existence of an inclusion. Such an inclusion might be trapped by the magnesium gas bubble before the commencement of solidification, as illustrated in Fig 10. As described in the author's paper, inclusions consisted of a system based on Mg-Ca-Si-S-O. This looks like a compound ceramic. Perhaps this is the reason why the inclusion in the graphite nodule is so hard.

Professor Zhukov also asked if there really were carbon filaments in graphite polycrystalline structures?

In fact, the author would suggest that spheroidal graphite is composed of thin graphite 'plates',[3,10] not carbon filaments. In a previous paper,[3] this was verified by observing the appearance of a nodule using SEM, and examining the electron diffraction pattern. In a recent observation, the eutectic graphite cell of spheroidal graphite was broken down into a single plate of graphite or into a block of such plates using ultrasonic vibration. These were then directly observed by SEM.[10] The same experiment carried out on spheroidal graphite was also conducted on compacted vermicular and chunky graphite with identical results.[3,5,10]



E Some projected sections of spheroidal graphite surrounded by an Mg halo.

References

1 A. Javaid and C. R. Loper, Jr, "Solid graphitisation in Normalised and Annealed Ductile Cast Irons,"The 94th AFS Congress, Paper No. 90-143 (1990).

2 A. A. Gorshkov, "On the Formation Mechanism of Spheroidal Graphite," *Liteinoe Proizvodstvo* (1955), 3, 17.

3 H. Itofuji, Y. Kawano, S. Yamamoto, N. Inoyama, H. Yoshida and B. Chang, "Comparison of Substructure of Compacted/Vermicular Graphite with Other Types of Graphite," *AFS Trans.*, **91** (1983), 313.

4 H. Itofuji, Y. Kawano, N. Inoyama, S. Yamamoto, B. Chang and T. Nishi, "The Formation Mechanism of Compacted/Vermicular Graphite in Cast Irons," *AFS Trans.*, 91 (1983), 831.

5 H. Itofuji and H. Uchikawa, "Formation Mechanism of Chunky Graphite in Heavy-Section Ductile Cast Iron," *AFS Trans.*, 98 (1990), 429.

6 H. Itofuji, A. Masutani, N. Hashimoto and H. Yamada, "Formation process of Chunky Graphite Structure," The 121st National Foundry Congress in Japan, Oct. (1992), Resume No. 16. (This will be reported as an English paper in the near future.)

7 S. Yamamoto, B. Chang, Y. Kawano, R. Ozaki and Y. Murakami, "Producing Spheroidal Graphite Cast Iron by Suspension of Gas Bubbles in Metals," *AFS Trans.*, 83 (1975), 217.

8 Y. Lee, "Action of Gas and Vapor Elements on Change of Microstructure in Cast Irons-Mechanism of Inoculation and Precipitation of Temper Graphite," Thesis of Kyoto University (1986).

9 Y. Kawano and T. Sawamoto, "Production of Cast Iron with Fine Granular Graphite," *AFS Trans.*, 88 (1980), 463.

10 H. Itofuji, "Observation of Spheroidal Graphite Decomposed by Ultrasonic Vibration," The 119th National Foundry Congress in Japan (1991), Resume No. 41. (This will be reported as an English paper in the near future.)

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NEWS

Ukrainian Workers investigate Production of Graphitic Steels

There has been a resurgence of interest in the properties and application of graphitic steels at the Vinnitsa Polytechnic Institute in the Ukraine. Professor A. A. Zhukov, together with his post-graduate student A. I. Karnaukh, has resumed work on graphitic steels, a project which was interrupted in the early 1950s.

This early work had demonstrated that inoculation of a graphitic steel with calcium promotes the formation, in the as-cast state, of very small, but perfect nodules of graphite. These emerge and grow during a very short first-stage annealing.

Today, this almost forgotten investigation is being re-examined because a high silicon content (e.g. in grades 125S2, 200S2 and 175S2) promotes, on the one hand, a high rate of graphitisation, and on the other, ensures such a level of silicon is no longer a hindrance with respect to low impact problems of silicon-enriched ferrite, especially at low temperatures. This change in direction is the result of recent findings, according to which silicon when used as an alloying element is propitious to the formation during austempering of Bela Kovacs' ausferrite – a structure with high impact strength.

Major improvements are listed as:

1 The introduction of most of the silicon (and calcium) into the melt at the last moment before casting;

2 integration into one operation of a very short graphitising anneal with austenitisation (prior to austempering), and

3 "wetting" the austenitised castings for a few seconds in cold, then hot, water before austempering in a non-atmosphere-controlled furnace, or else a short "wetting" immersion in low-melting-point zinc alloy.