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Trace elements and graphite shape degeneracy in nodular graphite cast irons

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Graphite degeneracy in spheroidal graphite cast iron is just a common feature faced by foundries. It is generally associated with the presence of so-called poisoning elements, and may in some cases be suppressed by addition of other elements. Mastering these additions is all except simple in practice since industrial alloys do generally contain many elements that can affect graphite shape even when present at low or trace level. In this work, trace and low level elements are considered in relation with the three successive steps of microstructure formation: i) nucleation of graphite; ii) growth of graphite; and iii) solid-state transformations.

Keywords: *nodular cast iron, graphite degeneracy, trace elements.*

1. Introduction

The role of low level elements on solidification of cast irons has been the subject of many reviews, e.g. by Lux [1]. One obvious problem is quantifying low level elements as they may be effective below the detection limits of standard or even advanced analytical means. Further, chemical analyses are global and do not give any hint on where and how trace elements have affected microstructure formation. Emphasis has thus often been put on characterizing compounds in which they are tied and to make some assumptions on the mechanism of their action. This work will first discuss this aspect when dealing with nuclei formation, then the discussion will be extended to graphite growth during solidification. Finally, some comments will be made on redistribution of elements during solid-state transformation.

2. Graphite nucleation

The inoculation mechanism in spheroidal graphite cast irons has been studied by Skaland et al. [2] who proposed a three-step model where a core of sulfide gets surrounded by a shell of oxide on top of which a complex $XO.MgO.SiO_2$ oxide precipitates, where X may be Al, Ca or Ba. The understanding of the role of oxi-sulfides in the building up of appropriate nuclei led to the definition of new inoculants doped with S and O and containing elements reacting with them such as Al, Ba, Ca, Ce, Mn, Sr, Zr [3]. A somehow simpler mechanism involving a core made of MgO encapsulated in MgS has been proposed [4]. In this work, particles of (Mg,Si,Al)N nitride were also found at the periphery of the nuclei, which could eventually turn to become nuclei in low-S melts [5, 6].

Figure 1 shows the nucleus of a graphite spheroid found in an industrial nodular cast iron [7]. The same phases as mentioned above could be identified as well as RE-bearing phases already reported [6]. This nucleus consists mainly of (Ca,Mg)S, but is amorphous. Further, no epitaxy could be found between any of the dark crystalline spots and the graphite around [7]. It thus appears that graphite could certainly nucleate on any heterogeneous substrate, and that the most important step in the spheroidizing process is graphite growth.

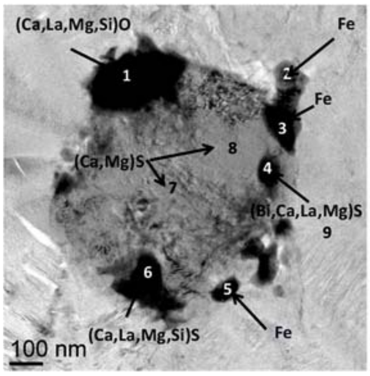

Fig. 1 Graphite nucleus
with an amorphous sulfide core.

3. Graphite growth

Provided spheroidizing elements (Mg and RE) are present, graphite will easily surround these foreign particles due to its recognized high capability to bend. A consensus has been raised that this is due to the fact spheroidizers are prone to pick up oxygen and sulfur out of the melt. It may then be easily accepted that half-treatment of the melt would lead to a mix of lamellar and spheroidal graphite (the so-called compacted graphite), but it should be stressed that overtreatment leads to degenerate graphite [1]. In other words, magnesium and RE not only ties O and S as stable compounds precipitating in the melt, they also affect graphite growth.

As reviewed previously [8], many attempts have been made since long not only to quantify the amount of trace elements in graphite precipitates but also to locate them at a smaller scale. The conclusions are that any element present in the melt is prone to enter to some level in graphite, and that there is no significant accumulation at the graphite melt interface.

To get further insight in the growth mechanism of graphite, Fe-C-X samples have been prepared with excessive X addition [9]. With Ce, it is possible to get graphite growing as isolated sectors or exploded nodules, see Fig. 2. It could thus be concluded that spheroidizing elements adsorb on graphite and slow down the growth along the prismatic directions. From such results, growth of spheroids may be described by continuous nucleation of new blocks at the circumference of the spheroids that then grow along the prismatic planes [10].

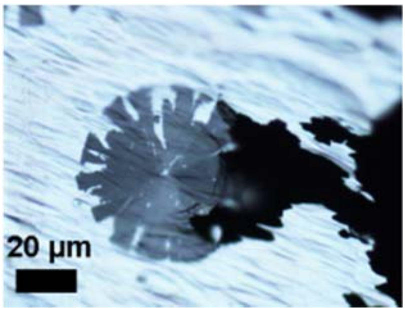

Fig. 2 Thin foil of an exploded nodule.

4. Solid-state transformations

An increase in concentration of trace or alloying elements at the graphite/matrix interface has sometimes been reported to explain graphite degeneracy or pearlite promoter effect. If such a film had formed during solidification, it should have quickly stopped transfer of carbon to graphite spheroids leading to metastable solidification. In other words, this enrichment if it exists must have appeared in solid-state, which seems difficult to imagine in the case of substitutional solutes such as Cu, Sn and Sb. This appears still controversial but other explanations have been offered to the pearlite promoter effect of these elements [11]. However, no explanation has been suggested up to now for the effect of many trace elements as reported long ago by Thielemann [12].

5. Conclusion

Plotting the critical level of various elements for graphite degeneracy in nodular irons versus the corresponding atomic mass shows a clear correlation: the heavier are the atoms the lower is their critical limits (Fig. 3). As the atomic weight relates to the size of the atoms and to the number of their outer electrons, such a relationship can be easily associated with adsorption of these elements on the graphite surface. This confirms that the main role of so-called "active" elements is modifying graphite growth by simple adsorption and absorption.

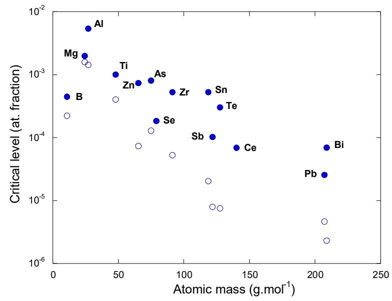

Fig. 3 Relation between atomic mass of elements poisoning nodular irons and their reported critical levels [12]. Open symbols relate to minimum values seen to affect graphite shape, solid symbols to maximum admissible values.

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