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ANALYSIS OF THE INFLUENCE OF HARMFUL ELEMENTS ON THE QUALITY OF CASTINGS IN GREY CAST IRON MELTING

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Abstract

The article proposes a three-stage model for the formation of flake graphite based on [(Mn, X)S-type crystalline nuclei]. In this model, three important groups of elements are involved:

- deoxidizing elements,
- Mn and S,
- modifying elements.

During the pre-treatment of the molten metal, various materials—such as carbon materials and metallurgical silicon carbide—are used to control the level of oxidation and to promote the formation of active graphite nucleation sites.

Keywords: Grey cast iron, S, Al, Zr, Ti, induction furnace, high superheating in the furnace, preconditioning.

Introduction

The quality characteristics of grey cast iron, particularly graphite morphology and the tendency for carbide formation, are directly dependent on the chemical composition of the molten metal and the metallurgical treatments applied to it. In modern foundry practice [1], in accordance with environmental and technological requirements, traditional cupola furnaces are increasingly being replaced by induction furnaces.

Melting in induction furnaces allows precise control of temperature, flexible adjustment of the metal composition, and the production of high-quality castings. However, such furnaces typically produce low-sulphur iron ($S < 0.05\%$), which leads to a reduction in graphite nucleation sites and an increase in eutectic undercooling. As a result, the likelihood of carbide formation and the development of unfavorable graphite forms (types D and E) increases [2, 3].

Effective graphite crystallization mainly occurs through heterogeneous nucleation, where complex sulfide compounds of the (Mn, X)S type play a key role as primary nucleation sites. Therefore, controlling the manganese and sulphur contents within an optimal ratio, particularly maintaining $(\%Mn)\times(\%S)$ in the range of 0.03–0.06, is essential for stabilizing the graphite formation process.

Recent studies have shown that strong oxide-forming elements – aluminum and zirconium – promote the formation of complex oxy-sulfide particles in molten iron, increasing the number of graphite nucleation sites [4, 5]. This reduces eutectic undercooling, facilitates the formation of type A graphite morphology, and decreases the likelihood of carbide formation.

Accordingly, this study investigates the effect of two-stage treatment (preconditioning and modification) using Al and Zr elements on grey cast iron melted in an induction furnace, with particular emphasis on the formation of (Mn, X)S compounds and their influence on the graphite crystallization process.

Properties of grey cast iron

Only when the molten iron is sufficiently undercooled (by about 200÷230 °C), clusters of small elementary particles $((C_6)_n$ can exist as stable homogeneous nuclei for graphite particles. Under normal conditions, achieving such a high degree of undercooling is very difficult. Therefore, graphite nucleation mainly occurs through heterogeneous nucleation.

Various compounds can form in molten cast iron depending on the melting and casting processes. From a thermodynamic point of view, the free energy of formation of oxides/silicates and sulfides (ΔG° at 1723 K) (Fig. 1) indicates that, under industrial conditions, they form more stable particles in the liquid metal compared to nitrides and carbides. Silicate particles are considered favorable nucleation sites for graphite in grey cast iron. This is explained by their hexagonal crystal structure, suitable wettability [6, 7], lattice compatibility, and relatively high stability. The role of sulfides in graphite nucleation is less clear, since graphite has a hexagonal structure, whereas sulfides generally have a cubic crystal lattice.

Foreign particles can act as substrates for nucleation only if they satisfy two conditions: (a) they must meet certain lattice mismatch requirements; that is, a specific crystallographic plane of the foreign particle should have a certain compatibility with the parameters and orientation of the graphite crystal lattice; (b) they must satisfy the interfacial energy requirements between the heterogeneous nucleus and graphite; only particles that are well wetted by graphite can serve as effective nucleation sites on their surface.

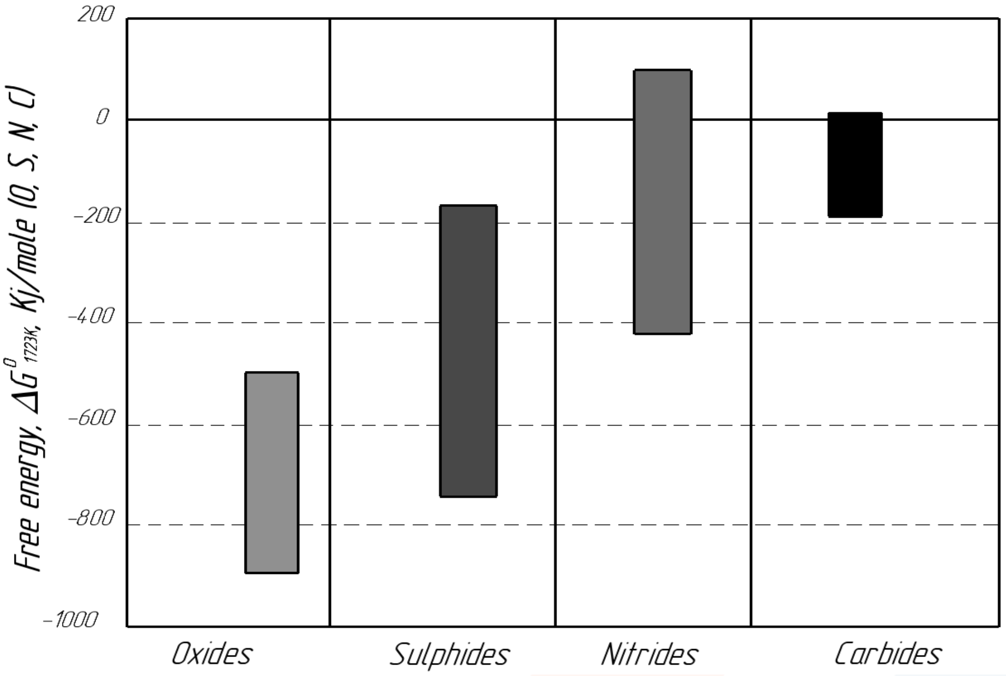

Fig. 1. Range of the free energy of formation (ΔG° at 1723 K) of various compounds of typical elements present in molten iron [8]

The possible sequence of graphite nucleation substrates can be expressed as follows: graphite (highest – requiring the lowest energy), silicates, oxides, sulfides, carbides, nitrides, and austenite (lowest). MnS is considered a moderately effective candidate for graphite nucleation, while other sulfides may exhibit even higher nucleation ability. Conventional modifying elements such as Ca, Sr, and Ba form silicates that also possess good properties as graphite nucleation sites. In addition, elements such as Ca, Ce, La, Pr, Nd [9], and Sr can participate in MnS nuclei to form complex sulfides – (Mn,X)S. These compounds have good lattice compatibility with graphite and are considered among the most effective heterogeneous nucleation sites. For example, although the lattice mismatch between MnS and graphite is relatively large (–12.1%), modified particles such as SrMnS exhibit better compatibility (–5.2%), making them more effective for graphite nucleation.

In grey cast iron, both unmodified and modified states, a three-stage model of graphite nucleation has been proposed (Fig. 2) [10]: (a) small oxide-based nuclei (0.1–3 µm, typically less than 2.0 µm) form in the hեη molten metal; (b) complex (Mn,X)S-type compounds (1–10 µm, typically less than 5.0 µm) nucleate on these particles, where X = Fe, Si, Al, Zr, Ti, Ca, Sr, P; (c) graphite nucleates on the sides of the (Mn,X)S compounds, since their crystallographic mismatch with graphite is relatively small.

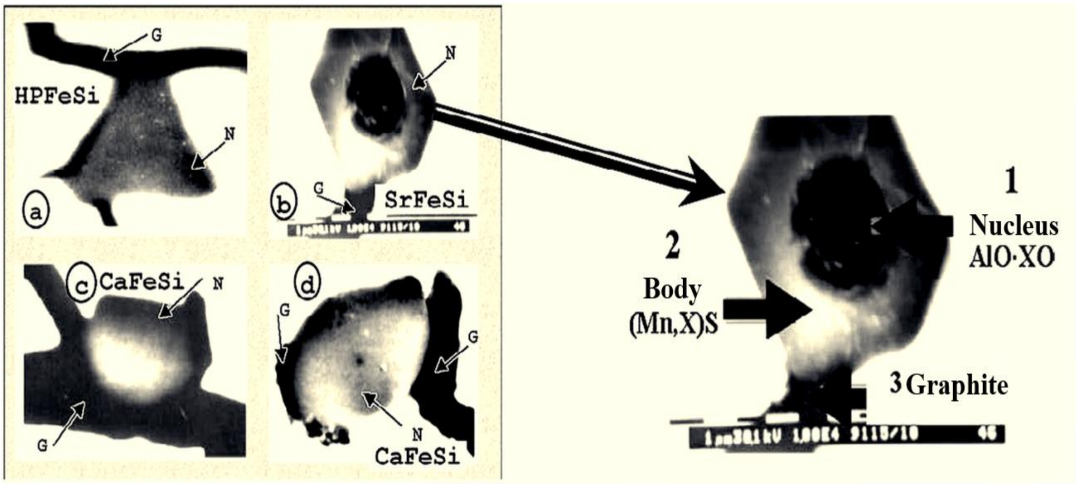

Fig. 2. Typical morphologies of graphite nuclei in differently modified grey cast irons [G – graphite; N – nuclei]. [a) high-purity (HP)–FeSi; b) Sr–FeSi; c and d) Ca–FeSi]

It has been observed that Mn and S are the main constituents of all micro-additions identified in cast irons from industrial production, regardless of their location in the microstructure, chemical composition, or the type of treatment applied to the molten metal. Under all the conditions described above, manganese sulfides are not simple but have a complex structure. In modified cast irons, (Mn, X)S compounds become even more complex; they form at lower Mn/S ratios and exhibit a higher compatibility for the initiation of graphite crystallization. This effect is especially pronounced when one or more modifying elements such as Ca, Sr, or Ba are present.

The initiation of graphite crystallization on MnS particles has also been confirmed through microstructural modeling. Recent studies have shown that silicon-rich oxide double-layer films can act as substrates for the formation of oxy-sulfide particles, thereby initiating graphite crystallization. The presence of such films provides a favorable base for graphite growth. As a result, flake graphite is formed, whereas undercooled graphite represents a true coupled growth form, which develops at lower temperatures when suitable film-type substrates are absent in the molten metal.

In foundry practice, grey cast irons with low sulphur (S) content typically solidify with a high degree of eutectic undercooling. This, especially in thin-walled castings widely used in the automotive industry, leads to carbide formation and the appearance of undercooled graphite structures.

The formation of white layer/carbides in cast iron and the characteristics of the eutectic structure are strongly dependent on the sulphur (S) content. For example, grey irons melted in an electric furnace (acid-lined, medium-frequency induction furnace) with 3.8÷3.9% carbon equivalent and 0.001÷0.003% Al exhibit different “white layer/carbide formation” behaviors (Fig. 3) at two sulphur levels: the base melt (0.024% S) and after sulphur addition (0.072% S). These differences are related to both the sulphur content and the modification treatment. The white layer formed in the sample consists of several zones. The region completely free of grey areas is referred to as the fully white zone. The region extending from the grey fracture zone to the apex, where the white layer first appears, is defined as the total white layer. In both cases, the very low residual aluminum content in the melt adversely affects the initiation of graphite crystallization.

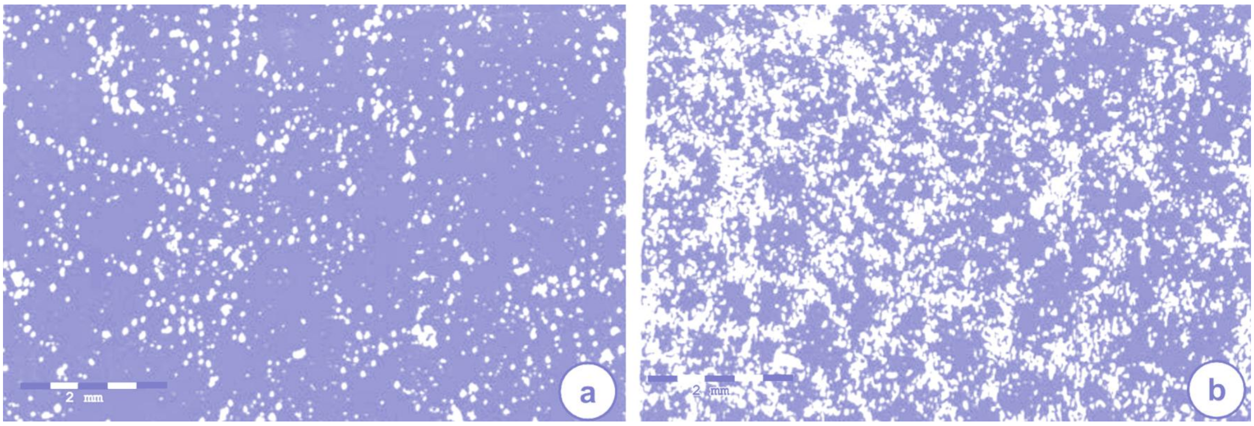

Fig. 3. Eutectic cell structure in Ca-modified cast irons: low sulphur (a – 0.024% S, 16 eutectic cells/cm) and high sulphur (b – 0.071% S, 34 eutectic cells/cm) conditions [30 mm diameter sample, 20:1, Stead reagent]

The effect of sulphur, either individually or in combination with manganese, has a long history in cast iron research. It is widely recognized that, in grey cast iron, a controlled relationship between manganese and sulphur contents is necessary, and this relationship can be expressed in various forms.

$$\%\,\mathrm{Mn} = 1.7(\%\mathrm{S}) + 02\ 04 \tag{1}$$

$$\%\mathrm{Mn}/\%\mathrm{S} = 5 - 15 \tag{2}$$

$$(\%\,\mathrm{Mn}) \times (\%\mathrm{S}) = 0.03 - 0.06 \tag{3}$$

Equation (3) was recently proposed by R. Gundlach as a result of reviewing the most important historical data on the influence of manganese and sulphur in grey cast irons. This equation is also based on the three-stage model of flake graphite nucleation in commercial irons, taking into account the major role of (Mn, X)S compounds.

For example, the results shown in Fig. 3 correspond to grey cast irons with the following compositions: 0.024% S and 0.75% Mn [(%Mn)·(%S) = 0.018] and 0.071% S and 0.77% Mn [(%Mn)·(%S) = 0.055]. A considerable amount of laboratory and industrial data has confirmed the usefulness of Equation (3). It enables effective control of manganese and sulphur contents within the ranges of 0.4÷1.2% Mn and 0.04÷0.12% S.

CONCLUSION

The conducted studies have shown that the quality characteristics of grey cast iron melted in induction furnaces are primarily determined by the chemical composition of the molten metal and the applied metallurgical treatments. In low-sulphur melts, eutectic undercooling increases, which leads to carbide formation and the development of unfavorable graphite morphologies (types D and E).

It has been established that graphite crystallization mainly occurs through heterogeneous nucleation, where complex (Mn,X)S-type compounds act as the primary nucleation sites. Controlling the manganese and sulphur contents within an optimal ratio, particularly maintaining $(\%Mn)\times(\%S)=0.03–0.06$, is a key factor in stabilizing the graphite formation process.

The results also indicate that strong oxide-forming elements such as aluminum and zirconium promote the formation of complex oxy-sulfide particles in the melt, increasing the number of graphite nucleation sites. This reduces eutectic undercooling, facilitates the formation of type A graphite, and significantly decreases the tendency for carbide formation.

Furthermore, the use of crystalline carbon materials and metallurgical silicon carbide has been shown to enhance graphite nucleation, thereby improving the microstructure and overall quality of grey cast iron.

Thus, achieving high-quality castings in induction-melted grey cast iron requires optimal control of chemical composition, effective formation of (Mn, X)S nucleation sites, and the application of complex metallurgical treatments based on Al and Zr.

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