The Future Role of Ferroalloys in Iron and Steel

Øystein Grong[1], Pär Jönsson[2] and Ole-Svein Klevan[3]

1) Department of Materials Technology and Electrochemistry, NTNU, N-7491 Trondheim, Norway.
2) Department of Metallurgy, KTH, S-100 44 Stockholm, Sweden.
3) Elkem ASA, c/o Elkem Thamshavn, PO Box 10, N-7301 Orkanger, Norway

ABSTRACT

In the present paper the future role of ferroalloys in iron and steel has been reviewed, with particular emphasis on how non-metallic inclusions that form during deoxidation affect the resulting microstructure evolution during solidification and in the solid state by a process of heterogeneous nucleation. Traditionally, ferroalloys have been regarded as bulk products where the overriding concern has been to meet the customers' specifications and demands in terms of composition, size and costs. More recently, the important role of ferroalloys in iron and steel manufacturing has been fully recognised; particularly their ability to acts as inoculants and grain refiners through a modification of the inclusion chemistry and crystal structure. This, in turn, has brought about new ideas about ferroalloy product development and collaboration between industry and academia on a multilateral basis. In the paper, results are presented from on-going research projects, where both the potential and success of the approach are demonstrated. Some principal guidelines for new ferroalloy product developments are presented towards the end.

1. INTRODUCTION

Many of the different elements to be added in iron and steelmaking are supplied through ferroalloys. Process developments and product quality shifts in ferrous metallurgy rely much on improved compositional control, in particular the content of impurities and minor alloying elements [1]. This, in turn, has an impact on ferroalloys in terms of stricter quality specifications for greater uniformity and higher purity. Thus, the future role of ferroalloys must be viewed on the background of the needs of the iron and steelmaker because the requests for alloy modifications or possibly new grades clearly derive from these.

The present paper summarises the progress made in developing inoculants and grain refiners for iron and steel. The ideas presented below derive from a broad interest in ferrous materials ranging from ferroalloy production, iron and steel making to fabrication of shaped castings and slabs for further working to standard stocks and finished products by means of thermomechanical processing and welding [1-11]. The essence of the problem is either to create or introduce submicroscopic non-metallic inclusions in the liquid steel that can act as heterogeneous nucleation sites for different types of microstructures during solidification and subsequent solid state transformations (e.g. graphite, ferrite or austenite), without compromising the resulting mechanical properties. In the authors opinion this represents a golden opportunity for the innovative ferroalloy producer to modify the existing qualities to ensure that the overall performance is more in accordance with the future demand for inoculants and grain refiners in shaped castings and wrought steel products.

2. GRAIN REFINING OF STEELS

The demand for higher performance materials with optimum combination of properties is steadily becoming more

critical. Since the grain size in steel controls the resulting mechanical properties, the desired property profile can only be obtained by the development of a properly adjusted microstructure [12]. At present, no grain refiners (or inoculants) are commercially available for steels, as opposed to cast iron and aluminium alloys where such remedies are widely used to control the microstructure and thus the resulting mechanical properties of the final products [4, 13]. This represents a new and interesting marked segment for the ferroalloy industry, but the success relies heavily on the chances of controlling the inclusion chemical composition and size distribution during full-scale steel production by a late addition of a specially designed grain refiner.

2. 1 Characteristics of Candidate Ferroalloys

Traditionally, ferroalloys have been regarded as bulk products where the overriding concern has been to meet the customers' specifications with respect to composition, size and costs.

2.1.1 Alloy cleanliness

It is well established that both FeCr and FeMn, produced by means of conventional casting methods, contain an intrinsic distribution of oxides and sulphides, the former group being the most important one [14, 15]. Figure 1 shows examples of complex MnS and MnO-SiO_2-MnS inclusions commonly found in commercial MC FeMn. These systems are characterised by a high oxygen solubility in the liquid state (up to about 0.5 % O by weight or higher) [14]. The inclusions form naturally both prior to and during the casting operation owing to reactions between O and S and Cr, Si, and Mn present in the alloys. However, because the cooling rate associated with conventional sand mould casting is low, the resulting size distribution of the Cr_2O_3, SiO_2, MnO or MnS oxide and sulphide inclusions is rather coarse, as shown in Fig. 2. Typically, the size of the inclusions in commercial FeCr and FeMn is between 5 and 50μm [14, 15], which makes such alloys unsuitable for grain refining of steel.

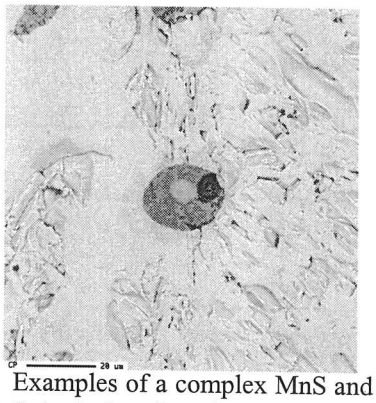


Fig. 1 Examples of a complex MnS and MnO-SiO_2-MnS inclusion found in commercial MC ferromanganese. From Sjöqvist [15].

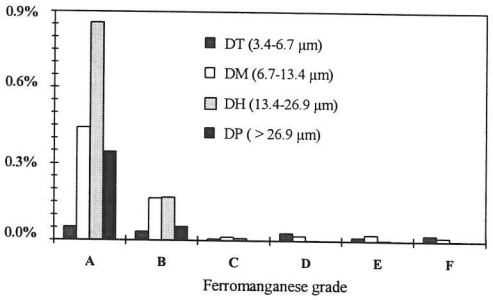


Fig. 2 Size distribution of non-metallic inclusions found in some commercial grades of LC and MC ferromanganese. From Sjöqvist [15].

2.1.2 Dissolution behaviour

When a properly sized ferroalloy containing a given distribution of inclusions is added to liquid steel, the inclusions will be transferred from the ferroalloy to the steel[14, 15]. The inclusions will eventually loose their identity, but their ability to survive in the liquid steel depends on the time of addition of the ferroalloy, the dissolution rate of the ferroalloy and the deoxidation practice applied prior to the addition [11]. By considering and exploring these characteristics, it is possible to control the dissolution and mixing behaviour of the ferroalloy in the liquid steel prior to solidification as well as avoid excessive inclusion coarsening.

2.1.3 Inclusion control

Controlled laboratory experiments have shown that the additions of a strong oxide and sulphide former such as Ce to a liquid ferrous alloy will result in the formation of Ce_2O_3 and CeS [16]. The initial size of the inclusions obtained with this conventional alloying technique is between 1 and 1.5 μm, but coarsening of the inclusion population will occur gradually with time, as indicated in Fig. 3.

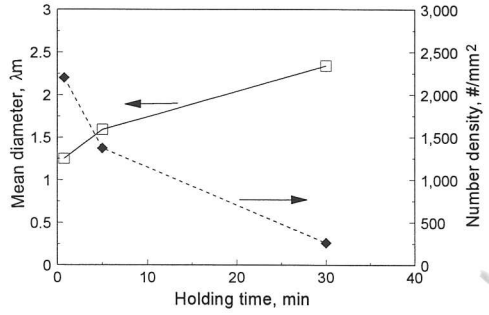


Fig. 3 Coarsening behaviour of cerium-based inclusions (Ce_2O_3) in liquid iron melts at 1600°C. Data from Gou and Suito [20].

Therefore, unless the melt is immediately quenched after the Ce addition the inclusions will grow larger and eventually become detrimental to the steel mechanical properties. On the other hand, if a supersaturated liquid containing the reactive elements in solution is quenched from a high

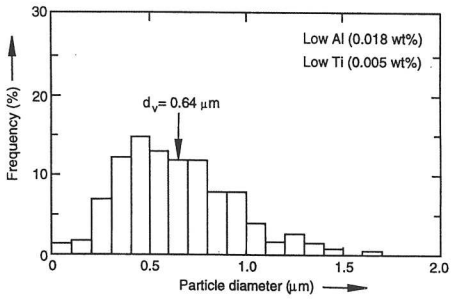


Fig. 4 Size distribution of non-metallic inclusions commonly found in steel weld metals. After Grong [3].

temperature, a fine distribution of submicroscopic inclusions will inevitably form by a process of homogeneous nucleation during cooling, where the number density may exceed 10^8 particles per mm^3. This is readily achieved in steel weld metals, as shown in Fig. 4, owing to the high cooling rates involved [3]. A similar inclusion distribution can also be obtained in ferroalloys by the choice of an appropriate casting technique.

2.1.4 Potential for new product developments

Based on the circumstantial evidence presented above it is possible to point out a direction for modification of the existing ferroalloy qualities, where the overall performance is more in accordance with the future demand for grain refiners in shaped castings and wrought steel products. It is desirable that these alloys contain a high number density of finely dispersed oxides and/or sulphides with the ability to nucleate austenite or delta ferrite at very small undercoolings. Both REM (Ce and La) oxides and sulphides as well as Zr and Ti oxides are known to promote the formation of ferrite or austenite in steels [17-20]. In view of the world-wide steel production of about 800 million tonnes per year, the potential marked for such special treatment alloys is enormous.

2.2 Grain Size Control in Steels

A deep understanding of steel microstructures has enabled the steelmaker to exploit systematically the property potential of the soft iron. A major objective has been to increase strength without giving away too much of toughness, with good weldability retained, and all this at minimum costs. In practice, these contradictory requirements can only be met by designing steels with a properly balanced microstructure [3, 21, 22].

2.2.1 As-cast microstructures

As-cast steels are prime examples of materials where the properties achieved depend upon the characteristics of the solidification microstructure. In general, a coarse columnar grain structure will

inevitably evolve upon solidification if potent heterogeneous nucleation sites ahead of the solidifying front are absent. In the presence of effective seed crystals, fine equiaxed grains form directly in the melt, as shown schematically in Fig. 5.

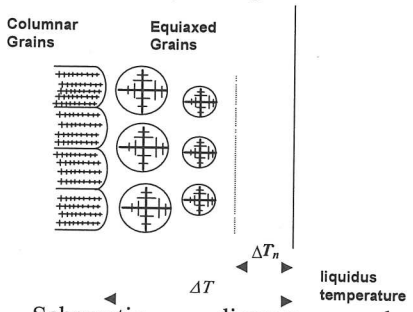


Fig. 5 Schematic diagram showing heterogeneous nucleation and growth of equiaxed grains ahead of columnar grains.

Depending upon the circumstances, the equiaxed grain structure may completely override the inherent columnar grain formation[13], which, in turn, gives rise to an improved castability (e.g. hot ductility and hot cracking resistance) through a smaller grain size and reduced problems with centre-line segregation.

Experience has shown that the as-cast microstructures of high alloyed steels are quite different from those of the pure carbon-manganese or low alloy steels due to their higher alloy content and broader span in chemical composition. Four distinct solidification modes are commonly observed:

- Primary ferrite formation
- Primary ferrite formation followed by a peritectic transformation to austenite
- Primary ferrite and austenite formation
- Primary austenite formation

Due to the absence of subsequent solid state phase transformations, there is a particular need of grain refining in fully austenitic or ferritic steels. Both the castability and the quality of shaped castings and slabs for further working to standard stocks (i.e. sheet, plate, tube, bar, wire and rod) will be significantly improved by a reduction in the initial grain size.

2.2.2 Grain refinement by inoculation

Inclusions are known to play an important role in development of the steel solidification microstructure and substantial grain refining has been observed in a number of systems, including [2, 3, 12, 16-24]:

- Aluminium-titanium deoxidised low alloy steels due to nucleation of delta ferrite at titanium oxide/nitride inclusions.
- Aluminium-titanium deoxidised ferritic stainless steels due to nucleation of delta ferrite at titanium oxide/nitride containing inclusions.
- Rare earth metal (REM) treated low alloy steels due to nucleation of delta ferrite at Ce/La containing oxides and sulphides.
- Rare earth metal (REM) treated ferritic stainless steels due to nucleation of delta ferrite at Ce/La containing oxides and sulphides.
- Rare earth metal (REM) treated austenitic stainless steels due to nucleation of austenite at Ce/La containing oxides and sulphides.

The specific effect of Ce on the microstructure evolution in ferritic and austenitic stainless steel castings is shown in Fig. 6.

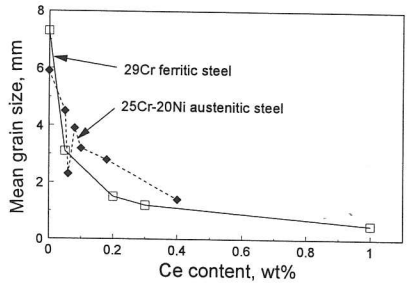


Fig. 6 Effect of cerium on the solidification microstructure of 29Cr ferritic and 25Cr-20Ni austenitic steel, respectively. After Figenschuh [23].

In all cases the effectiveness of the grain refiner is related to the ability of the nucleus to adopt a rational orientation relationship with the seed crystals, which provides a

small lattice disregistry δ across the solid/solid interface [25]:

$$\delta^{(hkl)_s}_{(hkl)_n} = \sum_{i=1}^{3} \frac{1}{3} \left(\frac{\left| (d_{uvw_s^i} \cos\gamma - d_{uvw_n^i} \right|}{d_{uvw_n^i}} \right) \qquad (1)$$

where $(hkl)_s$ is a low-index plane of the substrate, $[uvw]_s$ is a low-index direction in $(hkl)_s$, $(hkl)_n$ is a low-index plane in the nucleated solid, $[uvw]_n$ is a low-index direction in $(hkl)_n$, $d_{[uvw]s}$ is the interatomic spacing along $[uvw]_s$, $d_{[uvw]n}$ is the inter-atomic spacing along $[uvw]_n$ and γ is the angle between the $[uvw]_s$ and the $[uvw]_n$.

The undercooling ΔT_n, which is a measure of the energy barrier to heterogeneous nucleation, has been shown to increase monotonically with increasing values of the planar lattice disregistry [3, 25]. Accordingly, the most potent catalyst particles are those that also provide a good epitaxial fit between the substrate and the embryo, as indicated in Fig. 7. These data refer to nucleation of delta ferrite at different inclusion constituent phases, but sulphides

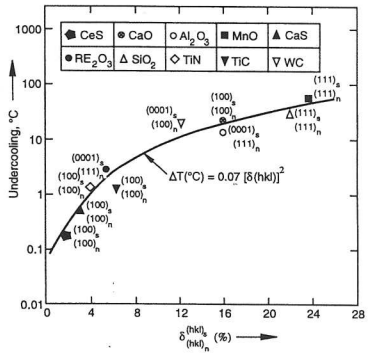


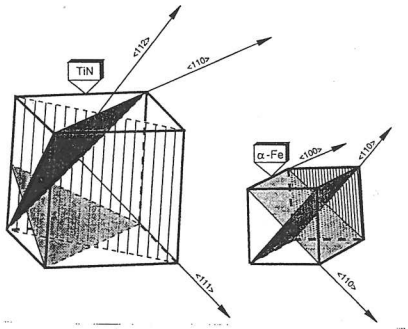
Fig. 7 Relationship between planar lattice disregistry and undercooling for different inclusion constituent phases in ferritic steel. Data compiled by Grong [3].

and oxides of the CeS, CaS, RE_2O_3 type appear to be the most favourable nucleation sites. In fact, Fig. 7 shows that the undercooling required to trigger a nucleation event is of the order of 1°C when the atomic misfit across the interface is 5% or lower. This degree of undercooling is sufficiently low to promote the formation of an equiaxed microstructure during solidification (see sketch in Fig. 5), provided that number density of the nucleating inclusions ahead of the advancing solid/liquid interface exceeds a certain threshold. On this basis it is not surprising to find that Ce additions to steel promote grain refining, as shown previously in Fig. 6.

2.2.3 Solid state transformation behaviour

The same inclusions that give rise to grain refinement during solidification can also influence the microstructure evolution in the solid state by affecting the recrystallisation and grain growth behaviour and/or by promoting intragranular nucleation of acicular ferrite [2, 3 12, 22].

Fig. 8 Conditions for intragranular nucleation of acicular ferrite at inclusions in low alloyed



steels [26].

Since these particles are thermodynamically stable up to the steel melting point, they can restrict recrystallisation and grain growth through Zener pinning. In addition, they can affect the recrystallisation and solid state transformation behaviour of steels by providing favourable nucleation sites for specific microstructures within the austenite grain interiors. In the latter case the development of a faceted ferrite nucleus, which exhibits a rational orientation relationship with both the austenite and the inclusions, would require that the substrate and the austenite have similar crystal structures and identical lattice orientations [26]. The catalyst particles must therefore be

cubic and bear an orientation relationship with the austenite that lies within the Bain orientation region, as shown in Fig. 8. However, under such conditions even multiple intragranular nucleation of acicular ferrite at inclusions is feasible, as illustrated in Fig. 9.

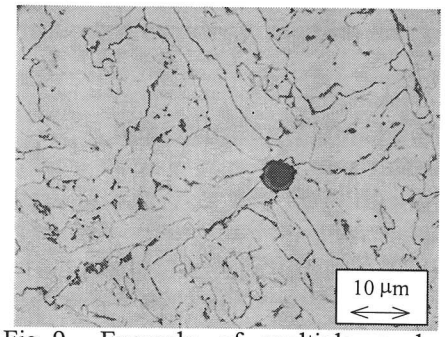


Fig. 9 Example of multiple nucleation of ferrite laths at a Ti-containing inclusion in a low carbon microalloyed steel. Courtesy of Casper van der Eijk, SINTEF.

2.2.4 Trends in steelmaking practice

Over the past decades, significant improvement of steel properties has been achieved through strict control of the chemical composition, volume fraction and size distribution of non-metallic inclusions. This has been made possible by the introduction of secondary steelmaking as an integrated step in the production route and the use of advanced ladle refining techniques for deoxidation and desulphurisation [27, 28]. The detrimental effect of inclusions on steel properties arises from their ability to act as initiation sites for microvoids and cleavage cracks during service. Hence, the use of clean steels is considered to be an advantage, both from a toughness and a fatigue point of view.

However, due to the increased emphasis on weldability attempts have been made to improve the heat affected zone (HAZ) toughness by exploiting the beneficial effects of inclusions on the solid state transformation behaviour of steels. The phenomenon of intragranular nucleation of acicular ferrite at inclusions is well known from low-alloy steel weld metals, where the best properties are achieved at elevated oxygen and sulphur levels owing to the development of a more fine-grained microstructure [2, 3, 12]. The same observations have also been made in wrought steel products deoxidised with titanium and zirconium [8, 30-38], although the conditions existing in steelmaking are more challenging due to the risk of inclusion coarsening and entrapment of large particles that can act as initiation sites for cleavage cracks. This makes grain refining by inclusions in such steels rather hazardous. Nevertheless, the main features of the concept are widely recognised and substantiated to an extent which makes it highly attractive to the steel industry.

2.2.5 Potential for new steel product developments

In addition to the productivity increase and the improved quality of the existing products, the concept of inclusion-stimulated ferrite nucleation provides a fertile opportunity for the design of new steel grades for different applications. Both in Japan and in Europe a number of research programmes and patents have been scheduled to develop steels with catalytic inclusions that can contribute to grain size control and microstructure refinement during thermomechanical processing and welding [8, 30-40]. At present, the development is hampered by the fact that the inclusions must be created within the system as a result of deoxidation reactions, leading to problems with a coarse inclusion size distribution as mentioned before. This barrier may be overcome by the use of a grain refiner containing a fine distribution of the nucleating particles, analogous to that done in grain refining of aluminium alloys. If extensive inclusion coarsening can be avoided prior to solidification, a new generation of oxide dispersed steels may emerge from such a technology.

3. GRAPHITE FORMATION IN DUCTILE IRON

FeSi-based inoculants and treatment alloys for cast iron are commercially available and commonly used in the foundry industry.

These alloys contain balanced additions of strong oxide and sulphide formers such as Mg, Ca, Al, Ce, La, Ba or Sr [4, 41-43]. It is well established that the major role of the minor elements is to modify the chemical composition and crystal structure of the existing inclusions in the liquid iron, thus promoting the graphite formation during solidification. In general, a high number of small graphite nodules is aimed at in the iron, since this will improve the castability as well as the resulting mechanical properties of the finished product [44].

3.1 Inoculation Mechanism

Graphite formation in ductile cast iron occurs by a process of heterogeneous nucleation analogous to that documented for grain nucleation in steel [4]. The inclusions which form in the liquid iron after the magnesium treatment (e.g. by using a FeSi alloy containing about 5wt% Mg, 0.5wt% Ca and 0.5wt% Al) are complex magnesium and calcium containing sulphides and oxides.

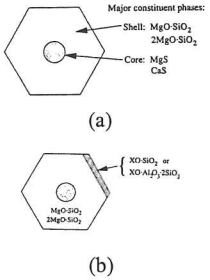


Fig. 10 Schematic representations of non-metallic commonly found in ductile cast iron; (a) Constituent phases observed after nodularizing with FSM, (b) Phases formed after inoculation with Ca, Ba or Sr-containing FeSi. After Skaland *et* al [4].

As shown in Fig. 10(a), the dominating constituent phases are MgS, CaS, $MgO{\cdot}SiO_2$ and $2MgO{\cdot}SiO_2$. After inoculation with a Ca, Ba or Sr containing ferrosilicon (X denotes Ca, Ba or Sr), hexagonal silicate phases of the $XO{\cdot}Al_2O_3{\cdot}2SiO_2$ or the $XO{\cdot}SiO_2$ type form at the surface of the inclusions where an exchange reaction with MgO is probably involved, Fig. 10(b). The presence of phases of this nature will enhance the nucleating potency of the inclusions with respect to graphite. As illustrated in Fig. 11, the (001) basal planes offer particularly favourable sites for graphite nucleation because these facets represent a good match for development of coherent/semi-coherent low energy interfaces between the substrate and the nucleus. This conforms to a small planar lattice disregistry δ, according to the definition in equation (1). The results in Fig. 11 highlight the fundamental importance of the minor elements contained in the ferrosilicon alloy, and in search of more efficient inoculants for ductile iron the recognition of nucleation theory as a guiding principle should be duly observed [1].

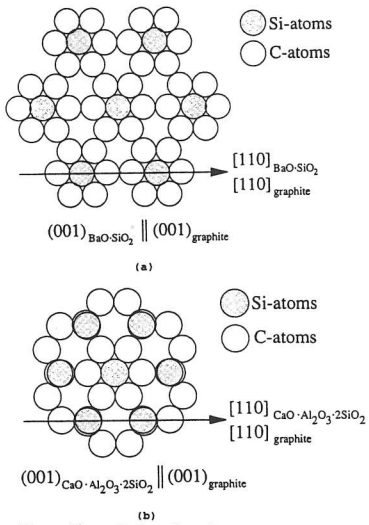


Fig. 11 Details of the lattice arrangement at the nucleus/substrate interface after inoculation; (a) Coherent graphite/$BaO{\cdot}SiO_2$ interface, (b) Coherent graphite/$CaO{\cdot}Al_2O_3{\cdot}2SiO_2$ interface. After Skaland *et* al [4].

3.2 Effects of Ce and La on the Inclusion Formation

If rare earth metals (REM) such as Ce and La are added to the liquid iron via the magnesium ferrosilicon (FSM) treatment alloy, slightly different inclusions will form. Referring to Fig. 12, they can be grouped into three main categories [43]:

i) Type A inclusions, which contain Ca, Mg, Si, S and O as the main

constituent elements along with Ce and La.

ii) Type B inclusions, which contain Mg and Si as the main constituent elements.

iii) Type C inclusions, which contain P, Mg and/or Ce.

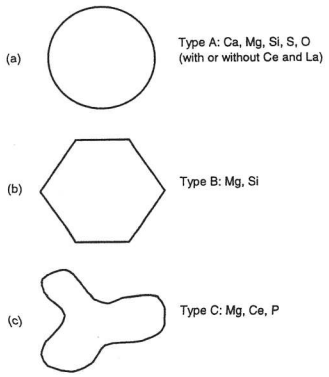


Fig. 12 Grouping of inclusions found in Ce and La treated ductile cast iron; (a) Type A inclusions, (b) Type B inclusions, (c) Type C inclusions. After Onsøien *et* al [43].

The type A inclusions probably originate from reactions occurring during the magnesium treatment and the subsequent inoculation stage. They may also absorb Ce and La if these elements are present in the liquid iron. The type B inclusions contain the strong oxide forming elements Mg and Si but not Ce or La. Finally, the phosphorus-rich inclusions (type C) stem from reactions occurring during the final stages of the solidification process. As a result, they do not take part in the graphite formation and are therefore of minor interest in the present context [43].

3.3 Conditions for Graphite Formation

In the absence of Ce and La, the temperature for graphite nucleation at the type A inclusions $T_{n,A}$ is thought to be just below the stable eutectic temperature of the iron, as illustrated in Fig. 13(a) due to a favourable crystal structure. Conversely, the type B inclusions are less potent sites for graphite formation and are therefore characterised by a lower nucleating temperature $T_{n,B}$. During solidification the resulting release of latent heat implies that the temperature of the supercooled liquid in the REM-free iron will never reach the point where the type B inclusions become active. This corresponds to the situation described in Fig. 13(b) (region A).

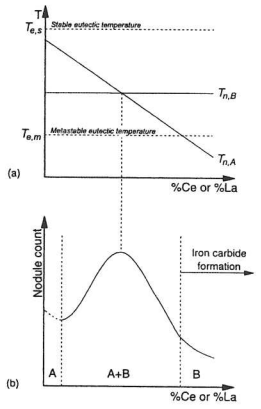


Fig. 13 Schematic representation of the mechanism of graphite formation in ductile cast iron containing Ce or La; (a) Nucleation conditions during solidification, (b) Resulting change in nodule count with increasing Ce or La additions. After Onsøien *et* al [43].

When Ce or La is added to the liquid iron the energy barrier against graphite nucleation at type A inclusions increases because of a modification of their chemical composition and crystal structure, as indicated in Fig. 13(a). At low Ce/La levels, this increase is not large enough to promote graphite nucleation at type B inclusions. Nevertheless, the interaction between the type A inclusions and Ce or La gives rise to a slight reduction in the graphite nodule count after solidification, as illustrated in Fig. 13(b). At higher Ce/La levels the undercooling required for graphite nucleation at type A inclusions increases and reaches the level of the type B inclusions. This implies that that both types of inclusions will act as nucleation sites for graphite during solidification, conforming to the A+B regime in Fig. 13(b). As a result, the total nodule count increases.

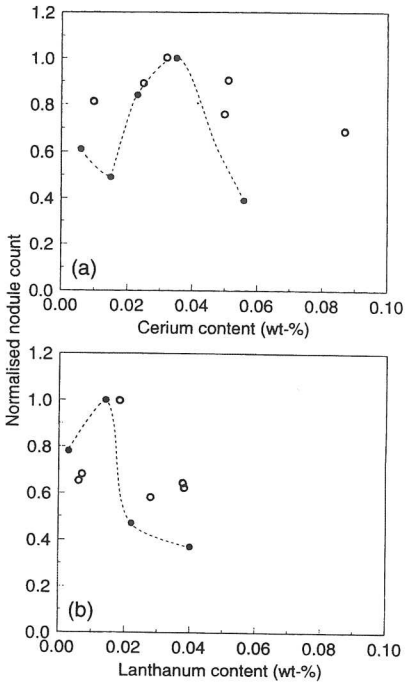


Fig. 14 Effect of rare earth metal (REM) additions on the graphite formation in ductile cast iron: (a) Cerium, (b) Lanthanum. Data compiled by Onsøien *et* al [43] (from two independent sources).

A further increase in the Ce or La content makes the graphite nucleation at type A inclusions more difficult, which, in turn, promotes nucleation at type B inclusions, as illustrated in Fig. 13(b) (region B). Thus, the net effect of these changes is that the nodule count passes through a maximum when the Ce or La content of the iron is progressively increased, in agreement with the experimental observations in Fig. 14.

3.4 Practical Implications

Although Ce and La behave in a similar manner, lanthanum is a stronger oxide and sulphide former compared with cerium. Hence, the observed peak in the nodule count is shifted towards lower concentrations in the case of La, as shown in Fig. 14. At the same time the peak of lanthanum curve is sharper, and therefore more difficult to achieve. Both factors weigh against the use of La as an alloying element in ductile cast iron, either alone or in the form of misch metal additions. This makes Ce the most promising element by virtue of its ability to enhance the nodule count and restore the graphite nodularity in impure iron within a sensible composition range [43]. Product developments along these lines have lead to the introduction of new Ce-containing treatment alloys for ductile cast iron with improved inoculation performance.

4. CONCLUDING REMARKS

The purpose of the present paper has been to summarise the progress made in developing inoculants and grain refiners for iron and steels. The essence of the problem is either to create or introduce submicroscopic non-metallic inclusions in the liquid iron that can act as heterogeneous nucleation sites for different types of microstructures during solidification and subsequent solid state transformations (e.g. graphite, ferrite or austenite), without compromising the resulting mechanical properties. In cast iron inoculation is a well-established technology, but improvements and optimisation of existing treatment alloys are still within reach. Thus, the search for new element combinations and better technical solutions should be continued.

The concept of grain refinement by inclusions is also applicable to steel, but, at present, the potential and limitations of the approach have not yet been fully explored. Possible candidate ferroalloys for steel grain refining are FeCr and FeMn, which are characterised by high oxygen solubility in the liquid state. This provides a basis for obtaining a fine distribution of catalytic oxide inclusions in the alloy after quenching which, following a late addition to liquid steel, can lead to grain refinement both during solidification and in the solid state. Future developments within this field will certainly have an impact on the ferroalloy industry, and it has been demonstrated that the existing theoretical framework is sufficiently relevant and comprehensive to serve as a guiding tool.

5. ACKNOWLEDGEMENTS

The authors acknowledge the financial support from Elkem ASA and the Norwegian Research Council. Grants have also partly been provided by the Norwegian Ferroalloy Research Organisation (FFF). In addition, they would like to thank Dr. Casper van der Eijk and Dr. Morten Onsøien (both SINTEF), Mr. Thobias Sjöqvist (KTH) and Dr. Torbjørn Skaland (Elkem) for many fruitful and stimulating discussions.

6. REFERENCES

1. Grong Ø, Grong T, Skaland T. *Principle Guidelines for New Ferroalloy Product Development*, Proc. Int. Confr. INFACON 7, 11th to 14th of June, 1995, Trondheim, Norway. Publ. The Norwegian Ferroalloy Research Organisation (FFF), pp. 697-707.
2. Grong Ø, Matlock DK. Int. Mater. Rev., 31 (1986), 27-48.
3. Grong Ø. *"Metallurgical Modelling of Welding"*, 2ed, 1997, London, The Institute of Materials.
4. Skaland T, Grong Ø, Grong T. Metall. Trans. 24A (1993), 2321-2345.
5. Skaland T, Grong Ø, Grong T. Metall. Trans. 24A (1993), 2347-2353.
6. Onsøien MI, Grong Ø, Gundersen Ø, Skaland T. Metall. Trans. 30A (1999), 1053-1068.
7. Onsøien MI, Grong Ø, Gundersen Ø, Skaland T. Metall. Trans. 30A (1999), 1069-1079.
8. Eijk C van der, Grong Ø, Walmsley J. Mater. Sci. Techn., 16 (2000), 55-64.
9. Alexis J, Jönsson P. Scan. J. Metall., 26 (1997), 48-54.
10. Alexis J, Jönsson P, Jonsson L. ISIJ International, 39 (1999), 772-778.
11. Berg H., Laux H, Johansen ST, Klevan OS. Ironmaking and Steelmaking, 26 (1999), 127-139.
12. Bhadeshia HKDH. *Bainite in Steels*, 1992, London, The Institute of Materials.
13. Grong Ø., Dahle AK, Onsøien MI, Arnberg L. Acta Mater. 46 (1998), 5045-5052.
14. Kiessling R. *Non-Metallic Inclusions in Steel,* Parts I-IV, 1978, London, The Metals Society.
15. Sjöqvist T. *Effect of Ferro-manganese and Calcium Carbide Additions on Inclusion Characteristics in Steel*, Lic. Techn. Thesis, 1999, Department of Metallurgy, Royal Institute of Technology, Stockholm, Sweden.
16. Guo M, Suito H. ISIJ International, 39 (1999), 678-685.
17. Nuri Y, Ohashi T, Hiromoto T, Kitamura O. Trans. ISIJ, 22 (1982), 399-407.
18. Nuri Y, Ohashi T, Hiromoto T, Kitamura O. Trans. ISIJ, 22 (1982), 408-416.
19. Wilson, WG, Heaslip, LJ, Sommerville ID. Journal of Metals, 37 (1985), 36-41.
20. Guo M, Suito H. ISIJ International, 39 (1999), 722-729.
21. Nicholson A, Gladman T. Ironmaking and Steelmaking, 13 (1986), 53-69.
22. Honeycombe RWK, Bhadeshia HKDH. *Steels-Microsrtucture and Properties*, 2ed, 1995, London, Edward Arnold.
23. Figenschuh H. *Einfluss von Kornfeinenden Zusätzen auf Korngrösse und Mechanische Eigenshäften Umwandlungsfreier Austenitischer und Ferritischer Stahlgusslegierungen*, Dr. Ing. Thesis, 1980, Technischen Universität Berlin, Germany.
24. Westin L. *Grain Refinement of 18 Chromium 8 Nickel Type Steel by Melt Inoculation*. Technical Report, 1980, Swedish Institute of Metals Research, Stockholm, Sweden.
25. Bramfitt BL. Metall. Trans., 1 (1970), 1987-1995.

26. Grong Ø, Kluken AO, Nylund HK, Dons AL, Hjelen J. Metall. Trans. 26A (1995), 525-534.
27. Turkdogan ET. *Fundamentals of Steelmaking*, 1996, London, The Institute of Materials.
28. Lange KW. Int. Mater. Rev., 33 (1988), 53-89.
29. Hanamura T, Shibata H, Waseda Y, Nakajima H, Torizuka S, Takanashi T, Nagai K. ISIJ International, 39 (1999), 1188-1193.
30. Janke D, Zhongting MA, Valentin P, Heinen A. ISIJ International, 40 (2000), 31-39.
31. US Patent 4629504 and EP Patent 177851 *Steel Material for Welded Structures,* 1995, Nippon Steel.
32. US Patent 4842816 *High Toughness Steel*, 1987, Nippon Steel.
33. US Patent 5336339 and EU Patent *589435 Refractory Shape Steel Material Containing Oxide and Process for Producing Rolled Shape Steel of Said Material*, 1993, Nippon Steel.
34. US Patent 5421920 and EU Patent 589424 *Process for Producing Rolled Shape Steel Material Having High Strength, High Toughness and Excellent Fire Resistance*, 1993, Nippon Steel.
35. JP Patent 8041589A *PC Steel Wire or PC Bar Having Excellent Weldability*, 1994, Nippon Steel.
36. EP Patent 849372 A1 *Low Alloy Construction Steel Having Active Particles*, 1996, Dillinger Hüttenwerke.
37. EP Patent 839921 A1 and WO Patent *9739157 Steel Having Improved Toughness in Welding Heat Affected Zone*, 1997, Nippon Steel.
38. EP Patent 906960 A1 *Titanium Killed Steel Sheet and Method*, 1998, Kawasaki Steel.
39. Ma Z, Franke A, Janke D. *Improvements of Castability and Quality of Continuously Cast Steels by Alternative Deoxidation Techniques*, Technical Report, 1999, TU Freiberg, Germany.
40. Ma Z, Janke D. *Improvement of Non-Metallic Inclusions and Fine Grain Structures of Continuously Cast Steel by Oxide Metallurgy*, Technical Report to the European Coal and Steel Commmunity (ESCS), 1997, TU Freiberg, Germany.
41. Onsøien MI, Grong Ø, Rørvik G, Normark A, Skaland T. Int. J. Cast Metals Res., 10 (1997), 17-26.
42. Onsøien MI, Grong Ø, Skaland T, Olsen SE. AFS Trans., 105 (1997), 147-152.
43. Onsøien MI, Grong Ø, Skaland T, Jørgensen K. Mater. Sci. Techn., 15 (1999), 253-259.
44. Elliott R. *Cast Iron Technology*, 1988, London, Butterworths.