Progress in the Development and Use of Grain Refiner Based on Cerium Sulfide or Titanium Compound for Carbon Steel

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A fine-grained microstructure yields the optimum combination of strength and toughness of steel. Moreover refinement of the as-cast structure can reduce the tendency for hot-cracking during forging and rolling. This paper describes how small inclusions can be used to control the microstructure of steels. These small inclusions (dispersoids) are oxides, sulfides, nitrides and carbides which are in the 1 μm size range and capable of promoting grain refinement during solidification by a process of epitaxial nucleation or in the solid state through intragranular nucleation of ferrite. Such particles are sufficiently small to be harmless from a toughness point of view, but at the same time large enough to act as potent nucleation sites during phase transformation. The dispersoids can either be created by balanced additions of strong oxide and sulfide forming elements to an impure steel melt or be added directly into the liquid steel through a specially designed master alloy containing the nucleating particles. In both cases it is possible to manipulate the steel microstructure in a positive direction, but the latter method, involving the use of a master alloy, has probably a wider industrial application.

KEY WORDS: steels; solidification structure; oxides, sulfides; inclusions; nucleation.

1. Introduction

The demand for higher performance materials with optimum combinations of properties is steadily increasing. For steels, the microstructure controls the resulting mechanical properties and hence, the desired property profile requires the development of a properly adjusted microstructure. The traditional way of producing a fine-grained microstructure yielding the optimum combination of strength and toughness is through thermomechanical processing. During the past decades, it has become clear that some non-metallic inclusions can have a profound influence on the grain size of steel. These inclusions (also called dispersoids) are usually oxide, sulfides, nitrides or carbides.1,2)

Non-metallic inclusions in steel can influence the microstructure evolution in three different ways:
1) By acting as nucleating agents for the solidifying steel resulting in a refinement of the solidification structure. It is generally accepted that these inclusions must have a low planar lattice disregistry with respect to the nucleus in order to serve as potent nucleation sites during solidification.3,4)
2) By contributing to pinning of the grain boundaries, thereby inhibiting austenitic grain growth. To function optimally, the pinning inclusions should have a size below 100 nm and be finely distributed.5)
3) By promoting nucleation of intragranular acicular ferrite during the austenite to ferrite transformation. The mechanism behind these nucleation events is not yet fully understood. However, both the crystal structure, as well as, the formation of a manganese-depleted zone adjacent to the inclusions seem to play a role.6–8)

Oxides, nitrides and sulfides of Ti and Ce are most commonly used as dispersoids in steels. Some of these compounds have a low planar lattice disregistry with respect to ferrite.9) It has been reported in the literature that TiN can promote grain refinement during solidification of ferritic steels.3,10–13) A fine distribution of TiN will also retard austenite grain growth through Zener pinning.5,14) Moreover, Ti-oxides along with Ti-nitrides are known to enhance the formation of intragranular acicular ferrite in low alloyed steels.7,8,15) Ce is a very strong sulfide and oxide former when added to steel. Ce additions to steel are known to grain refine a cast structure which solidifies in a ferritic manner.16–18) The most probable cause is the low planar lattice disregistry between ferrite and the Ce compounds. When the distribution of Ce-oxides is fine enough, then the growth of austenite grains is impeded.19,20) Ce-sulfides are also reported to enhance the formation of intragranular acicular ferrite.21,22)

A strict control of the balance between the deoxidizing/desulfurizing agent on the one hand and oxygen, sulfur and nitrogen on the other hand is necessary to tailor the right type of inclusion that can improve the microstructure.
Therefore, and for the sake on inclusion size control, a number of special “grain refiner alloys” for steels is now under development.

2. First Generation Grain Refiner Alloys

In order to utilize the inclusions for grain refinement purposes, it is essential to have control over their size distribution. An average size of about 1 \(\mu\)m is desirable. This is a compromise between two conflicting requirements. On the one hand, a submicron particle size implies that the dispersoids start to lose their potency because a curved interface increases the associated energy barrier against nucleation. On the other hand, if the particle size is significantly larger than 1 \(\mu\)m the dispersoids may become detrimental to toughness. At the same time the particle number density drops rapidly, which makes grain nucleation at such sites less likely.1)

So far, the new steel developments have been hampered by the fact that the nucleating dispersoids used to control the microstructure evolution must be created within the system as a result of deoxidation or desulfurization reactions. The problem is the uncontrolled coarsening of the inclusions, with subsequent loss of toughness. Elkem has developed23) a Ce containing ferroalloy that can be added as a cored wire at a late stage during steelmaking reducing the time for coarsening. The advantages of using such a ferroalloy to add Ce contra the addition of pure Ce metal are 1) a higher Ce yield and 2) no oxidation of such a ferroalloy in air. This is a so-called first generation grain refiner.

2.1. Application of the First Generation Grain Refiner to Austenitic Steels

Grain refinement of highly alloyed austenitic steels is important because these steels maintain their solidification microstructure during cooling due to the absence of a phase transformation in the solid state. An example of the application of a Fe–Si–Ce grain refiner alloy to this type of steel is the microstructure modification of austenitic high Mn steel. The base alloy is called Stromhard. This is a modified Hadfield steel produced by Scana Steel Stavanger. It contains 1.3% C, 0.3% Si, 18% Mn, 0.004% S and 0.005% O. A series of (80 kg) castings of this steel were done under basically similar conditions with varying additions of Ce and Al. The Ce additions were done using a Fe–Si–Ce grain refiner alloy.24)

There are significant differences in the microstructure after various additions. The microstructure of two of the steels is shown in Fig. 1. The steel without Ce addition shows a chill zone close to the surface of the casting and a coarse dendritic structure some distance (ca. 2 mm) from the block’s surface. After addition of 0.02% Al and 0.05% Ce, the steel has a much finer dendritic microstructure close to the surface of the block, as well as, in the center of the block. Analyses of the inclusions of the steels reveal that both steels contain Ti-nitrides. Steel with Ce additions contain Ce-oxides and Ce–Al-oxides. The inclusions have been analyzed by quantitative WDS measurements. On basis of the ratio between Ce, Al and O in these inclusions, it is assumed that these are CeO\(_2\) and CeAlO\(_3\) respectively. Some larger inclusions consist of more than one phase. An X-ray mapping of such a multiphase inclusion in a Ce added steel is shown in Fig. 2. The mapping shows that the core contains Ce-oxide while the surface phase is a mixture of Ce and Al oxide, presumable CeAlO\(_3\).24)

The planar disregistry between the austenitic steel and the different inclusions can be calculated3) in order to make a prediction about which inclusion might be the most potent nucleation site for austenite. The main weakness with the disregistry data available is that it is calculated for the case at room temperature and without correcting for the influence of alloying elements on the lattice spacing of the steel. The lattice parameter for austenite in this case was corrected for the high Mn and C contents and the temperature.25,26) The influence of temperature on the lattice spacing of TiN,27) CeO\(_2\)28) and CeAlO\(_3\)29) is available in the literature while crystallographic data for Ce\(_2\)O\(_5\)S\(_3\)30) is only available for conditions at room temperature. The planar lattice disregistry between austenitic steel and these nonmetallic inclusions versus temperature is shown in Fig. 3. It is seen from the figure that CeAlO\(_3\) has the lowest planar disregistry with austenite in the whole temperature range and that it is about 3% at 1 600 K where the steel is solidifying. This same oxide has been identified in austenitic

![Fig. 1. Microstructure of high Mn steel casting. Micrographs are taken close to the surface of the casting, a) reference casting without Ce, b) casting with 0.05 wt% Ce and 0.02 wt% Al.](image-url)
stainless steels that show a finer solidification structure after addition of a Ce containing grain refiner.\textsuperscript{31)}

3. Second Generation Grain Refiner Alloys

So far, the new steel developments have been hampered by the fact that the nucleating dispersoids used to control the microstructure evolution must be created within the system as a result of deoxidation or desulfurization reactions. The problem is the uncontrolled coarsening of the inclusions, with subsequent loss of toughness. This barrier may be overcome by the use of specially designed grain refiners (in the following designated second generation grain refiner alloys) containing a fine distribution of the dispersoids, analogous to that done in grain refinement of aluminium alloys.\textsuperscript{31)} Provided that the resulting particle number density and volume fraction are of the correct order of magnitude, these master alloys can be added late in the process, either in the tundish or the casting mould, and thus enable full-scale production of new steel grades without changing the steelmaking process itself.\textsuperscript{1)}

There are two different ways the master alloys can be produced. The melting and quenching route means that the alloy components first are mixed and melted in an induction furnace and then superheated to make sure that all elements, including oxygen and sulfur, are in solution. This superheated melt is then rapidly quenched to achieve the desired distribution of the dispersoids in the grain refiner. Alternatively, a powder metallurgy route can be employed. This method involves mixing of iron oxide powder (optionally iron powder) with other metals or oxides. The pellets made from these blends are subsequently reduced in a controlled atmosphere at high temperatures to remove excess oxygen from the master alloy, leaving behind a fine dispersion of stable oxides in the iron matrix.\textsuperscript{33)}

The second generation of grain refiners is still in an early stage of development and the effect of their addition to steel is under investigation.

3.1. Development of New CeS-based Grain Refiners for Steels

Based on crystallographic-data, CeS emerges as some of the most promising nucleating agents with a lattice disregistry between ferrite and CeS of less that 1\%\textsuperscript{,21)} It is therefore attempted to produce an alloy containing a fine dispersion of CeS in a metallic matrix that will easily dissolve in molten steel and does not change the steel composition too much.

The CeS-based grain refiners are produced using the melting and quenching route. Specifically, this means that the different components first are charged and melted in a tantalum crucible under the shield of a protective gas (e.g. cleaned argon) and then superheated to make sure that all elements, including sulfur, are in solution. The superheated melt is subsequently rapidly cooled to achieve the desired distribution of the particles in the grain refiners.

The CeS-based grain refiner shown in Fig. 4 is produced using the melting and quenching route in the laboratory by mixing small (centimeter-size) chips of Ce metal with FeS to achieve the target sulfur content of about 5\% by weight.
This mixture is then melted and superheated in a tantalum crucible under the shield of pure argon employing induction heating. The melt is subsequently quenched against a fast rotating copper wheel. It follows from Fig. 4 that the chilled metal ribbons reveal a very fine dispersion of CeS particles being embedded in a matrix of Ce+Fe. The mean diameter of the CeS particles is about 2 μm. This shows that control of the particle size distribution in these grain refiners requires the use of rapid solidification, either through melt spinning or atomizing. This type of CeS dispersed alloy has also been produced with a matrix of Ce–aluminides.34,35

3.2. Development of Ti-oxide/Nitride Based Grain Refiners for Steels

As stated earlier Ti-oxides and Ti-nitrides can have a profound influence on the microstructure. The objective is at this point to produce a combination of Ti-oxides and Ti-nitrides in an iron matrix. The basis for the experiments rest on reported investigations of many alternative routes for the production of TiN from ilmenite (FeO·TiO2).36–43 The production of grain refiners directly from ilmenite ore eliminates the need of mixing of different powders; it is economically attractive and can easily be scaled up to industrial scale in a DRI-type of installation.

The method to produce a Ti-oxide/Ti-nitride grain refiner alloy is to crush an ilmenite ore to a fine (<3 μm) powder. Ilmenite samples are oxidized before reduction to bring the iron to its highest oxidation state (Fe3+). This is done at 800°C for 2 h. The FeO·TiO2 is transformed during this operation to Fe2O3·TiO2. Afterwards, the materials are reduced in a furnace with a thermo gravimetric analysis (TGA) system. The TGA system allows the operator to follow the degree of reaction by recording mass of the sample as a function of time and converting it to a suitable measure for the conversion of the solid. The solid reaction products obtained in these experiments were characterized and analyzed by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive Spectrometers (EDS) and Electron Probe Mapping Analysis (EPMA).44

Figure 5 shows the evolution of the process over time. In Fig. 5, the conversion is related to oxygen transfer from the solid to the gas phase corresponding to amount of oxygen (in wt%) bound to trivalent iron in the sample. It can be seen that at the early stage of the reaction (during the first hour approximately), the conversion of oxygen is rapid, which means the reduction rate is high. The reduction rate slows down over time. At the initial stage of the reduction, the reduction of ilmenite pellets at 1 000°C and 1 100°C proceeds faster than that at 850°C. After 4 h of reduction, the conversion of oxygen are more than 100%, which indicates that the complete reduction of Fe3+ to Fe can be achieved and that TiO2 is also reduced partially.

Figure 6 shows a backscattered image of the produced material. EDS analyses show that there are iron-rich (spectrum 1) and titanium-rich (spectrum 2) particles. The XRD patterns of reduced ilmenite pellets indicate that there are phases of Fe, TiN, Ti2O5 and Fe2TiO5. The amount of TiN present is small, but the presence is confirmed in the optical microscope where it is visible as gold colored cubes. The existence of Ti2O5 in the reduced ilmenite pellets indicates that rutile was also reduced slightly.

4. Conclusions

The present review summarizes the progress made in developing new grain refiners for steels. It is demonstrated how a latent grain refining potential can be released during solidification through a modification of the existing deoxidation and desulfurization practice. In a real casting situation this is best done using novel treatment alloys being tailor made for the purpose. Such grain refining alloys, which contain cerium as the reactive element, are now commercially available and can be used in replacement of misch metal to enhance the nucleation potency of the endogenous inclusions with respect to austenite or ferrite in a given steel.

In industrial steelmaking a sensible level of addition is between 0.2 and 0.5% by weight. Hence, further increase of the grain refining potential for improved microstructure control requires the use of novel master alloys containing a high number density of the nucleating oxides or sulfides. These “second generation grain refiners” should preferentially be added to a clean steel melt being low in oxygen and sulfur. Such grain refiners, where the dispersoids occupy about 50% of the volume, can only be produced through smart alloy design in combination with novel man-
ufacturing methods. Two types of such alloys are under development: An alloy with a high density of Ce-sulfides which is produced through rapid solidification and an alloy with Ti-oxides and Ti-nitrides which is produced through powder metallurgical route.

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