Non-metallic inclusions in steels – origin and control

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ABSTRACT
Non-metallic inclusions (NMIs) play a key role in many important properties of steel, influencing both processing and application of steel products. In this work, the current understanding of the origin and classification of NMIs is reviewed, highlighting the dramatic development of the last decades. This includes the discussion of the thermodynamics of inclusion formation and the current knowledge on the effects of melt shop processing variable on NMIs composition, amount and size distribution. The development of inclusion engineering – tailoring the process to obtain the desired NMIs is highlighted and the development in selected areas – tire cord, springs and bearing steels as well as prevention of nozzle clogging – is used to illustrate this development. The promising field of “oxide metallurgy” is also discussed in the context of inclusion engineering. Finally, the difficulties in meaningfully characterizing and quantifying NMIs are briefly commented. In summary it is concluded that inclusion control in steels has evolved significantly in the last decades. This is due to the progress in understanding the interplay between thermodynamics, steel and slag chemical composition as well as melt shop processing. This made possible the tailoring of non-metallic inclusions via processing, to optimize steel properties. Nonetheless, some important problems remain and must still be solved to improve inclusion control and optimization.

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1. Introduction

Until some 50 years ago, it was not uncommon for a metallurgy student to be told that non-metallic inclusions (NMIs) in steel came mostly from eroded pieces of refractories and entrapped slag. Albeit inclusions in steel were already a theme of important studies at that time, the knowledge of their importance to steel behavior was certainly not as pervasive as it is today. Since NMIs are non-metallic phases in the steel matrix, perhaps it is also understandable that they were not attractive to many physical metallurgists, mostly concerned with understanding the metal behavior and its phase transformations. As steel was challenged by different alternative materials and by more demanding applications, it became clearer that an important part of its behavior is intimately connected to the type, size and distribution of NMIs present in the matrix. This led to intense development in understanding their origin, properties and behavior during product processing. Much improvement also took place in NMIs control and quantification and in the correlation of its features with their effect on properties. Tailoring inclusions to improve properties and performance became an important feature of steelmaking and in the 1980s the term inclusion engineering was coined to describe this process [1]. Inclusion engineering starts with the definition of the desirable properties that inclusions should have. Then, through thermodynamics and adequate processing, a product where these desirable inclusions are dominant is designed and made. In the present work, studies that characterize the origin and control of NMIs are reviewed together with the current understanding of their behavior during processing. A brief overview of the work on quantification of inclusions and characterization of their distribution is presented. The most recent work on inclusion engineering is also reviewed. The effects of NMIs on steel properties are not discussed in depth in the current review. As literature in the field is growing at a fast pace, the reader is directed, whenever possible, to recent reviews on specific topics. The classical references for the subject are the seminal book by Kiessling [2] and the proceedings of the series of International Clean Steel Conferences organized, every 3–5 years, by the Hungarian Mining and Metallurgical Society (OMBKE). The interested reader is directed to these sources for invaluable information on the subject and on the many excellent reviews mentioned in the text.

2. Origin and classification of non-metallic inclusions

2.1. NMIs classification

When modern steelmaking technology started developing, it was soon noticed that oxygen, widely used as refining agent, and sulfur, a ubiquitous impurity coming most from coal and coke, both extensively soluble in the liquid metal had very little solubility in the solid phases of iron. Thus, upon solidification, they were rejected to the liquid and finally formed low melting compounds “FeO” (wustite) and FeS and eutectics involving these compounds. This rendered steel inadequate for hot working [3]. The mutual solubility of the oxides and sulfides of iron and some alloying elements (e.g. Mn) further complicates the problem [4,5]. Hence, the content of oxygen and sulfur in solution must be decreased to produce quality steel. Many elements commercially available and acceptable as part of the steel composition such as silicon, manganese and aluminum, have a high affinity for oxygen and can thus be used as deoxidizers readily forming non-metallic deoxidation products when added to the liquid steel [6]. These products can become important oxide NMIs. In the case of sulfur, on the other hand, only elements with low solubility in iron (such as Ca and Mg) or rare-earths have sufficiently high affinity to sulfur to form non-metallic sulfides at the liquid metal temperatures [6]. Thus, most of the sulfur in steel must be removed from solution by slag refining and the rest, by precipitation reactions occurring mostly during solidification. These differences introduce two of the possible forms of classifying non-metallic inclusions: by their chemical composition (oxides, sulfides, etc.) and by the stage in the process in which they are formed, with reference to the start of the solidification. Inclusions formed before the start of steel solidification are called primary and those formed after solidification starts, secondary. Besides these, another common classification that has contributed significantly to confusion in the field, is concerned with the source of the inclusions. Those originating from the steelmaking process (such as the oxides and sulfides discussed above) are classified as “endogenous” and those appearing from “external” sources (fragments of refractories, entrapped slag, etc.) are classified as “exogenous”. Rarely however, will an “exogenous” volume of material survive long enough in the steel without suffering extensive reaction with the melt and thus changing significantly. In the past there was an important contribution from “exogenous” sources to the inclusionary population, in special large inclusions from
refractories and casting pit material, for instance [7]. This, however, has been significantly reduced in modern steels. Nonetheless, it is still a problem that when students are introduced to the subject sometimes they end up believing that the most important sources of non-metallic inclusions are “exogenous”. This does not mean that the interactions between the metal and refractories, for instance, are not relevant [8,9]. These interactions can indeed have a significant influence on the inclusions present in the steel. If the definition of “exogenous” includes also, for instance, inclusions originated from reoxidation from contact with air and those resulting from entrained slag interacting with the liquid metal, as proposed in [10], the range of “exogenous” inclusions expands considerably. This is probably a more adequate definition of “exogenous” inclusions. However, not only these inclusions are changed to a substantial extent during the process but, in some cases, it can be argued that they are “part of the process”. Thus, it is debatable to which extent the “exogenous”-“endogenous” classification helps or further confuses the issue.

Finally, a common way of classification of NMIs is related to the inclusion size: thus, inclusions can be classified as macro and micro inclusions. One must be aware that, to have a sensible cutoff between sizes, Kiessling’s proposal should be used, when adopting this classification [2,11]: i.e., an inclusion is a macro inclusion if it is large enough to cause immediate failure of the product either during processing or use, as for instance, the inclusion shown in Fig. 1. All other inclusions should be classified as micro inclusions. Thus, while important, this is a difficult classification to apply. Frequently, sizes are defined arbitrarily to separate macro and micro inclusions and the classification becomes difficult to justify.

2.2. Thermodynamic basis

As steelmaking temperatures are high, inclusion formation reactions approach equilibrium. For this reason, thermodynamics is an important tool in understanding their formation. The thermodynamic fundamentals of NMI formation have been the subject of study for a long time [13,14] and are quite well known, e.g. refs. [6,15–18]. Nonetheless, it is worth mentioning that there are still important discrepancies in the thermodynamic data related to the formation of, for instance, alumina inclusions [19,20]. This may not be a problem for the usual range of aluminum application as deoxidant, but it does introduce important uncertainties in the processing of the new generation of high Al high Mn steels, for instance [21]. The problem is also complicated in the case of elements with limited solubility in iron such as Mg and Ca [18,22]. For these elements, significant discussion still prevails with respect to key thermodynamic data relevant for the study of reactions in steelmaking. The application of computational thermodynamics has provided, in recent decades, important insight in the solution of complex problems. These used to be rather difficult to handle with more conventional calculation techniques. General aspects and examples of the application of this technique to steels and steelmaking have been discussed, for instance, in refs. [23–27]. Examples of the application of the technique to problems related to NMIs can be found in many publications such as refs. [28–32].

3. Formation, removal and control of NMIs

The classification as primary and secondary is useful in the discussion of inclusion formation and removal. Removing
primary NMIs from the liquid steel is, in principle, possible. Conversely, secondary inclusions, that form during solidification, are probably impossible to remove and can only be “engineered” to result in the less detrimental possible effect on the product.

3.1. Primary inclusions

3.1.1. Nucleation and morphology

Primary inclusions form in the liquid steel and follow closely the thermodynamics of the process. Thus, two important aspects should be considered: their nucleation and the correspondent morphology.

In general, nucleation is rapid when deoxidants are added. This may be due to the large supersaturations observed during the dissolution of the deoxidant additions. Nonetheless, Sigworth and Elliott, for instance, carefully evaluating the conditions for nucleation of silica [33] observed the need for supersaturation. The results of Miyashita [34] and industrial observations do not indicate, however, that supersaturation is significant in silicon deoxidation during steelmaking. Miyashita also observed that “comparison of changes of the dissolved and the total oxygen shows that the rate of decrease of the total oxygen is determined by the rate of removal of the deoxidation products”, Fig. 2.

The dependence of the amount of oxide inclusions on the difference between total oxygen and soluble oxygen in steel has been highlighted in many deoxidation studies (for instance ref. [20]). This is shown schematically in Fig. 3.

Suito and co-workers [37] discussed the possibility of supersaturation in an experimental study of the formation of alumina in iron. As in the case of silicon deoxidation, this does not seem to be a problem in steelmaking. In actual steel processing, heterogeneous nuclei will probably be abundant. Hence, the laboratory conditions observed by [33,37] cannot be reproduced in the industrial environment.

Significant work has been done on the nucleation and growth morphology of alumina in steel, because of the importance of aluminum killed steel to the industry. Several authors [38–43] have looked in detail into the evolution of alumina

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**Fig. 2** – Change in total oxygen and dissolved oxygen in steel as a function of time after addition of silicon to deoxidize the bath. Total oxygen was measured in four different heats. Data from [34].

**Fig. 3** – (a) A simple example of the dependence of the amount of oxide NMIs on the difference between total oxygen and soluble oxygen. In the example, deoxidation starts in point “a” with the addition of Al to a steel with an initial content of dissolved oxygen %O₂. In the absence of nucleation barriers, alumina will be formed to bring the dissolved oxygen and aluminum contents to point “c”. The total oxygen content in the steel will correspond to the oxygen in solution (%O₂) added to the oxygen in the alumina inclusions still present in the bath, corresponding to point “b”. From “a” to “c” deoxidation proceeds according to the stoichiometry of the reaction 2Al + 3O = Al₂O₃. Note: Usually the difference between soluble Al (%Alₐ) and total Al is small and difficult to measure. (b) The relationship between the amount of inclusions and total oxygen (%O₂) in steel determined by [35]. When inclusion and total oxygen content is lower, extreme care is necessary to obtain reliable measurements, as shown in (c). (c) Relationship between oxide inclusion density in chemical samples versus total oxygen in pin samples collected after completion of ladle furnace treatment. Oxide inclusions quantified by automated SEM (adapted from [36]).
Fig. 4 – Oxide growth shapes as a function of the local activities of oxygen and aluminum (adapted from [40]).

Fig. 5 – A summary of morphologies of alumina observed in steel with different estimated local O activities and Al concentrations. Adapted from [44]. For the source of the individual observations, see ref. [44].

Fig. 6 – Some examples of alumina inclusion morphologies. Inclusions extracted by dissolving the as-cast matrix. In (a) the dendritic structure is circles with a dashed line [45]. The fibers of the filter used to retain the inclusions during the dissolution process are visible in the background. (b) Polygonal alumina inclusion, courtesy of A. Mitchell, UBC [12].

3.1.2. Removal

The possibility of floating out inclusions formed in a stagnant liquid bath can be ruled out by simple calculations, mostly due to the limitations of Stokes’ law [38]. Small inclusions reach limit floating velocities that require unrealistic processing times for usual ladle depths. Clustering of the inclusions [38,39] thus significantly helps on the possibility of floating. The importance of clustering, in special in the case of alumina inclusions, has been noted for a long time [40]. Important progress in understanding of the processes occurring during clustering of inclusions has been made possible by in situ observation [39,47]. Emi and co-workers [47,48] observed in situ the behavior of inclusions at the steel–gas interface. They demonstrated that in this condition, alumina clusters readily. Calcium aluminate inclusions, on the other hand, seem to have little tendency to move closer to each
other, clustering only when a full collision happens in the liquid. Wikström and co-workers (e.g. [49,50]) expanded the in situ observations to the steel–slag interface and to inclusions within the slag. They confirmed the results of Emi for the metal–gas interfaces. Emi and co-workers [47] observed that while these observations are relevant for phenomena at gas–steel interface (for instance, at bubble surfaces) they do not give direct indication about how agglomeration happens within the liquid steel. This is especially important for liquid inclusions, where other forces may be relevant. In any case, whether the inclusions are solid, or liquid plays a role on agglomeration. For a long time now, it has been established that stirring is essential to promote clustering but, perhaps more important, to bring the inclusions to their most important sinks, the slag and the ladle walls. The work of Lindskog and co-workers [51,52] using radioactive tracers has been very important in understanding the importance of these sinks. With the current limitations on the use of radioactive tracers, BaO has been adopted as a tracer when it comes to evaluating the eventual entrapment of slags and fluxes [53] and its influence on steel cleanliness. The use of BaO tracers has also been very effective in determining the effect of ladle glaze on subsequent heat cleanliness [53,54]. IRSID has developed the use of lanthanum as a tracer for oxide inclusions. Since La₂O₃ is very stable, the alumina inclusions present at the moment of La addition were marked by this element. Hence, re-oxidation inclusions formed afterwards could be identified [55]. In the case of “exogenous” inclusions originated from mold flux, the presence of alkali oxides can be used as “tracer”. Mold fluxes are usually the only additions in steelmaking that contain significant amounts of alkali oxides [56].

The overall process of inclusion removal in ladle processing, where most of primary deoxidation inclusions are formed, involves at least three steps: the growth and/or clustering of individual inclusions, the movement of the inclusions to the sinks (ladle slag and ladle walls) and their attachment to these sinks. Two factors are important for the movement of the inclusions: bath stirring, which is probably the dominant factor, and dragging by rising bubbles. It has been shown that in most ladle processes, the gas bubbles in steel are too large to effectively remove a significant number of inclusions, unless a very large volume of gas is used [57]. The calculations of Zhang and Taniguchi [57] indicate that this tool is only effective in regions where the steel velocity is high and fine bubbles are possible. This is typically the case for submerged entry nozzles (SEN) [58] or similar configurations such as the ladle nozzle shroud [59]. Some advantage is also observed in the ascending leg of RH vessels.

Stirring has been recognized to promote the agglomeration and the transport of the inclusions or their clusters to sinks. Fig. 8, [60] is one of the first studies that clearly showed that increasing the stirring energy (in this case the current in electromagnetic stirring) increases the kinetic constant for the removal of inclusions (measured by total oxygen content).

Industrial observations seem to indicate that the efficiency of inclusion removal passes through a maximum at a certain agitation energy. The first report of this observation is probably the one by Suzuki and co-workers [61]. Their results were presented as a function of specific work of agitation, but they recognize the importance of agitation energy: “The reason for the decrease [of inclusion removal] seems to be due to the erosion of brick or entrapment of the slag... because CaO and MgO type inclusions are found increased with stronger stirring energy.” Their results are shown in Fig. 9.

Later, Neifer and co-workers [62], and Ek and co-workers [63] used computational fluid dynamics and physical modeling to study the removal of oxides as a function of the rate of gas flow in the ladle. The modeling results of Neifer [62] indicated an optimum gas flow for the removal of oxide NMIs. They observed that the decrease in total oxygen was less efficient with increased gas flow rate. They ascribed this to reoxidation from slag or from the atmosphere. These results are consistent with the results of Suzuki and co-workers [61]. The results of Ek and co-workers [63] showed relatively low influence of the argon flow rate on the rate of inclusion removal. The authors suggested that rinsing (for inclusion removal) is best achieved with a low argon flow rate. Interestingly, the industrial measurements of Neifer and co-workers [62] indicated that the rate of total oxygen reduction decreased with the increase in gas flow. They suggested that natural convection gave the best results in their industrial tests. As there is very limited data
on the industrial heats where measurements were made, it is difficult to speculate on the causes of this observation.

More recently, Zhang and Thomas [64] collected many results of the kinetic constant for the removal of oxide inclusions as a function of agitation energy in a single graph (Fig. 10). They included an envelope around the measurements, to stress the existence of an optimum agitation. They also performed simulations that reproduced the expected behavior [65] represented by the envelope in Fig. 10.

The existence of an optimum agitation may be caused by reoxidation. Excessive stirring leads to the opening of an “eye” in the slag causing steel exposure to the atmosphere [64] and slag entrainment, mostly at the edge of the “eye” [68–70], as suggested by Suzuki and co-workers [61]. Fig. 11 illustrates the change in NMI’s chemistry when strong stirring is used for desulfurization. The increase of Ca and Mg content in the inclusions is evidence of probable slag emulsification [71].

In the absence of a slag, excessive agitation with argon was observed to cause re-entrainment of alumina inclusions [70]. Thus, it seems clear that rinsing operations aimed at the removal of NMI’s from the liquid metal in the ladle, should be performed at optimum selected agitation energies.

The importance of reoxidation for steel cleanliness cannot be overemphasized. Nadif and co-workers recently reviewed the importance of reoxidation and the measures to control it [72]. In recent decades, manufacturers have added many measures to control the most important sources of reoxidation in and after ladle metallurgy: flat products producers regularly use submerged entry nozzles (SEN) and ladle shroud to prevent contact of the steel stream with air. Tundish inertization [73] and mold protection with inert gas, in special in long products casting, are becoming standard for high quality steels. Special attention is also given to shroud and valve design to control air ingress caused by negative pressures in valve systems [74].

The attachment of the inclusions to the sinks depends mostly on surface tension and, on a secondary level, on the ability of the sink to dissolve the inclusions. Most steelmaking slags, regardless of their composition, will wet oxide inclusions. This is due to the magnitude of the difference in the surface energy between inclusion and steel and inclusion and slag. This issue has been discussed for a long time, at least since the work of [75] and others and has been summarized by Olette in ref. [76]. The importance of the liquid fraction of the slag in promoting NMIs removal was clearly understood very early [75] and was confirmed by clever experiments [77]. There remains, however, some controversy on the effect of the slag viscosity. Nakajima and Okamura [78] proposed a

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Fig. 9 – Effect of stirring work on the degree of deoxidation. Circled points have reached less than 20 ppm total oxygen content. Adapted from [61].

Fig. 10 – Oxygen removal constant $k$ in equation $\frac{d[SO_2]}{dt} = -kt$ as a function of specific stirring power in different secondary metallurgy reactors. Data mostly from [60,66,67] adapted from [64].

Fig. 11 – Effect of ladle stirring on average chemistry of all inclusions observed in samples collected from ladle, mold and slabs. According to Kaushik and co-workers, strong stirring was performed during desulfurization and probably promoted slag emulsification as evidenced by the higher Ca and Mg content in the inclusions. Adapted from ref. [71].
model to describe the process of inclusion transfer across the metal–slag interface. This has been later discussed in detail and used in many studies [79-82] and has been considered in a recent review on the topic of absorption of inclusions by slags [83]. Nakajima and Okamura proposed that under certain conditions the inclusion transfer from the metal to the slag may include the drainage of a film of metal from the interface, while in other cases, in special in the case of solid inclusions, such a film may not exist [80] (Fig. 12).

They concluded that the viscosity of slag and the relevant surface energies were the critical parameters to define the efficiency of the passage of the inclusion, and of reducing the risk of it being re-entrained in the metal. This could be summarized by a condition defined by the Reynolds number at the inclusion approach. More recently Sridhar and co-workers [81,82,84,85] have concluded that their in situ observations indicated film drainage to be a pervasive phenomenon, delaying the passage of inclusions to the slag in most cases.

Once the inclusions leave the metal, their dissolution has been considered immediate, in the case of liquid inclusions (see, for instance, ref. [65]). With the possibilities of in situ observation, interesting work has been performed in the dissolution kinetics of solid inclusions [86–88]. In some cases, the kinetics of dissolution is controlled by transport (“diffusion in a boundary layer”). In other cases, such as MgO inclusions, the formation of intermediate layers that depends on slag composition may hinder the dissolution introducing a chemical step in the process. This confirms previous results [89] obtained by more conventional techniques. More recently, Yan and co-workers [90] assessed the dissolution rate of MgO in slags, indicating that all available data agrees with mass transfer control.

Holappa and co-workers [91] investigated the development of active tundish slags in which inclusion absorption is a “key property”. They observed that the efficiency with which a given slag will dissolve solid non-metallic inclusions depends on the complex interplay between slag composition, thermodynamics, surface tension and viscosity. Holappa and co-workers concluded, “further systematic research is needed to get better knowledge...and to develop optimal slags”. The attachment of NMs to ladle refractories can be favorable [51] but ladle glaze from previous heats may also be a source of inclusions [53], depending on the slag composition of the heat previously processed in that ladle [54,92]. Furthermore, inclusion attachment to valve refractories can be disastrous if it happens during casting causing nozzle clogging, for instance. The subject has been well reviewed (e.g. refs. [93,94]) and will be discussed later. It is interesting to note, however, that, in the case of clogging caused by alumina, the possible important effect of FeO formed during reoxidation on the agglomeration of the inclusions was clearly demonstrated [95].

A significant number of publications on the possibilities of removal of primary inclusions by casting powders or mold fluxes, both in conventional ingot casting [96,97] and in continuous casting [56,98–100], is available but the main issues are not different from those discussed above. Casting powders or mold fluxes (similar to tundish slags) must perform a multitude of functions [56] and flow conditions in the mold are defined by various constrains, including the avoidance of powder entainment on the product surface [101]. This somewhat limits the extent of inclusion removal and retention by the mold casting powders [102]. Optimizing the flow of steel in the tundish or in the mold to enhance the chances of inclusions reaching the slag surface can conflict with other relevant metallurgical objectives [103]. It seems that the conventional approach of eliminating inclusions as much as possible in the ladle and then preventing the formation of new ones (by reoxidation, for instance) may still be the most promising one for clean steel.

An additional concern is the movement of primary inclusions inside the strand. The asymmetry of inclusion distribution in the cross section of products of curved casting machines, for instance, is well established [12]. Asymmetry of inclusion distribution can also appear due to partial nozzle clogging [103].

Sichen [104] has recently reviewed the efforts to model secondary steelmaking, in special ladle processing. The attempts at modeling slag-metal interfacial reactions, eye opening, inclusion generation, nucleation, growth and segregation/removal have been carefully reviewed indicating the most promising techniques. Sichen [104] cautions, however, about the difficulties of relating important ladle process variables (mass transfer coefficients, inclusion removal rate, open eye size, etc.) to the stirring gas flow rate since “industrial ladle involves many uncertainties, e.g., the blockage of the porous plug and the leakage of the gas line.” The difficulties in controlling eye opening via cameras and image analysis...
3.2. Secondary inclusions

The driving force for precipitation of secondary inclusions increases as solutes segregate during solidification and the solubility of oxides and sulfides in steel diminishes as temperature decreases.

The precipitation of inclusions due to changes in solubility in steel has been discussed for a long time (see, for instance, the discussion in [108]). Around the beginning of the 1960s the denomination primary and secondary inclusions was firmly established [109] and the relations between segregation and inclusion precipitation were becoming evident. At that time, the first models to describe the phenomenon were established [110]. Turkdogan (e.g. refs. [111–113] and Flemings (e.g. refs. [114–116]) made important contributions to the understanding of the combined effects of segregation and change of solubility with temperature on the genesis of secondary inclusions. In the 1980–90s more sophisticated models were developed by Nippon Steel [117–121] and by IRSID [122–126]. The same techniques are also applied successfully to the precipitation on microalloying nitrides during the solidification of HSLA steels (see [127,128], for instance). These models opened the way to the development of inclusion engineering, as it is known today, by coupling thermodynamic databases, and later kinetic ones, to solidification modeling and the calculation of inclusions formation. These calculations started from the knowledge of the desired steel composition for the precipitation of the envisaged inclusions followed by the design of slag constitution to properly achieve these steel compositions during ladle processing.

One important issue is the interaction of inclusions formed in the interdendritic liquid and the advancing solidification front. In situ observation [129] has shown that the solidification conditions play an important role on whether inclusions formed ahead of the interface are pushed or engulfed. Theories have been formulated and adjusted to properly describe these results, considering additionally the effects of surface tension and density [130]. The theoretical developments [131–133] were more focused on metal matrix composites, but presented good agreement with the results on NMIs in steels. The results indicate that the critical growth velocity, \( V \), of the advancing interface for the transition between engulfment and pushing of inclusion of radius \( R \) may be approximated by \( V = k/R \) where \( k \) is dependent of the inclusion type.

The morphology of secondary inclusions can be specially influenced by reactions occurring during their precipitation. The case of sulfides is probably the best characterized since Sims observed the effect of deoxidation on sulfide morphology in the 1930s [108] and later proposed a classification into three main types of sulfides. This has been addressed in detail by many authors (e.g. [134]). More recently, Ishida and co-workers [135–137] concluded that, besides the type of reaction associated with sulfide formation, surface tension plays a critical effect on sulfide morphology.

4. Inclusion engineering

Gaye and co-workers [124] present one of best overviews of the conceptual process in the application of thermodynamics to inclusion engineering in steel. Fig. 13 presents the concept in a simplified way, over two ternary isotherms. Once the desired inclusions are defined, the steel composition that will generate these inclusions is calculated. Then, the ladle slag that will establish this steel composition through steel-slag equilibrium is calculated and used in the ladle furnace. The classical aphorism “Look after the slag, and the metal will look after itself” [138] is fully considered, in these cases. The concept has been successfully applied to a wide range of steels. These include steels in which hard alumina and alumina containing inclusions (such as spinel) must be avoided, as bearing steels, and steels where the inclusions must act as nuclei for phase transformation during steel cooling. Calcium treatment to form liquid inclusions

**Fig. 13** – A schematic representation of the inclusion engineering process, from the thermodynamic point of view, for a Si–Mn killed steels in which low melting low Al₂O₃ inclusions are desired. The desired inclusions are represented in a simplified form on the ternary system MnO–SiO₂–Al₂O₃. The diagram on the left presents this system isotherm at 1470 °C. The region of 100% liquid phase is delimited by the thinner lines on the diagram, as indicated. The aluminum content of steels in equilibrium with liquid inclusions in this system is given by the thick “iso-aluminum” lines at the selected temperature. The dashed line indicates the composition of inclusions (as a function of the Al content of the steel) for a 0.35%Si, 1%Mn steel composition, at this temperature. From this diagram, it is evident that the steel aluminum content should not go above the composition of the gray circle (8 ppm) if liquid inclusions are desired. The diagram on the right presents a simplified representation of the ladle slag in the CaO–SiO₂–Al₂O₃ system. The 1520 °C isotherm corresponds to the ladle furnace conditions and shows the region of 100% liquid slag delimited by the thinner lines. The aluminum content of steels in equilibrium with these slags is given by the thick “iso-aluminum” lines at the selected temperature. The gray lines give the corresponding oxygen content of the steel being studied. Ladle slag compositions must be selected among those that will guarantee steels with less than 8 ppm aluminum, indicated in the diagram, if the desired liquid inclusions (in diagram on the left) are to be formed. Adapted from [124].
and avoid clogging during casting along with sulfide modification with calcium are also discussed in this section, albeit they may be considered simpler cases of inclusion engineering.

4.1. Tire cord and spring steels

Tire cords are usually made of silicon manganese steel wires. Many automotive springs are made from similar steels. The presence of hard NMIs (in general alumina or other high alumina NMIs) is very detrimental to the wire drawing operation of tire cords (Fig. 1) and has an important influence on the fatigue life of springs [139–141]. Steel composition must be adjusted to prevent the formation of alumina or alumina-rich NMIs, and to favor low melting, plastic silicates. This requires rigid control of the alumina content of the slag, control of raw materials to prevent undesired aluminum additions together with low slag basicity, which contradicted the prevailing ladle furnace practice when the problem was first solved [140]. There are many excellent examples and reviews focusing on the thermodynamics of inclusion engineering in tire cord and spring steel [140,142–147].

4.2. Bearing steel

While there is still controversy concerning the effect of the individual types of NMIs on the fatigue life of bearing steels [141,148–151] it is clearly established that the size and quantity of the NMIs present in steel is of paramount importance for the fatigue performance of the bearings [151]. Some general agreement seems to prevail in that calcium aluminates and spinel NMIs are detrimental. There is also agreement that very low total oxygen, sulfur and aluminum contents are required to guarantee small size and low volume fraction of NMIs. Furthermore, reversion of magnesium from the slag, which may lead to the formation of spinel inclusions, must be avoided [152]. Different processing conditions to achieve these objectives are used at different plants [10,149,152,153]. The control of slag composition is, however, always one of the key points in controlling NMIs in bearing steels. Fig. 14 presents calculations of the effect of slag composition on aluminum, oxygen and magnesium contents in 100Cr6 (AISI 52100) steel and a comparison of calculated and measured aluminum and oxygen contents in this steel [154].

4.3. Calcium treatment and alumina clogging prevention

Calcium addition to steel was initially developed to modify sulfides and control anisotropy in hot rolled and forged parts [155]. The inclusion modification achieved with calcium treatment has also been used to control machinability [156]. One can argue, however, that in recent decades calcium has found most extensive application in modifying alumina inclusions to prevent nozzle clogging in continuous casting. In this respect, the operational complexities associated with calcium solubility, variabilities in yield when added to steel and “fading” effects possibly associated to calcium high vapor pressure have been extensively studied (e.g. [157–160]). The mechanism of inclusion modification and the correct amount of calcium needed to achieve the desired changes have also been studied to a large extent [161–165] and are currently relatively well understood. The inclusions formed are complex, frequently forming layers of sulfur rich compounds around oxides as well as other distributions, as exemplified in Fig. 15.

Since the objective of the treatment is to have a significant fraction of the inclusions in the liquid state as they pass the casting valves and nozzles, the process becomes more difficult as steels are cast at lower temperatures [166]. The distribution of phases in the formed NMIs is further complicated by their solidification, as shown in Fig. 16.

The amount of calcium needed to modify oxides depends on the total oxygen content in the steel. To date, there is no method of determining total oxygen in time to use it for the decision on the amount of calcium to be added. This poses an important problem in industrial practice. The use of thermo-
dynamics to understand clogging and define the “castability window” is routine [28,163,164,167–169]. As soluble oxygen can be readily measured, it can be used as tool to control the efficiency of calcium treatment, as shown in Fig. 17.

4.4. Oxide metallurgy

One of the concerns in near net-shape continuous casting is the need for techniques of microstructural control that do not rely heavily on thermomechanical processing. The use of tailored NMIs as nuclei for ferrite in weld metal has been well demonstrated [170–172]. Based on the current theories for the effect of inclusions on nucleation, inclusions that would deplete the surrounding matrix on manganese seem to be effective. Thus, the development of NMI oxides that have high solubility for or nucleate MnS and will hence cause the desired effect has been demonstrated [121,173–175]. Furthermore, the titanium deoxidation of silicon manganese steels, changing inclusions to titanium oxides [176] or oxides and nitrides [177], has also been demonstrated to be highly effective for the nucleation of ferrite. The work of Koseki, Inoue, Suito and Park demonstrated that titanium nitride can be a powerful nucleation agent promoting the formation of a larger equiaxed grain region in stainless steels both in cast products [30,178,179] and in welds [180,181]. Park and Kang [182] have recently reviewed the developments in this area. It is evident that alloy and process design in oxide metallurgy can greatly benefit from computational thermodynamics [183–185] and modeling [186].

5. Inclusion quantification

By the last decades of the XX Century it was clear that the classical methods of measuring and quantifying inclusions by comparison of images with charts were not fulfilling the needs of the steel community. To improve inclusion quan-

Fig. 15 – Complex calcium alinate inclusion found in slabs treated with calcium to ensure good castability. Sulfide and MgO were probably dissolved in the liquid inclusion during casting. Mg source is probably reduction from MgO in slag (see discussion in item 4.2). Courtesy of C. Cicutti, Tenaris-Siderca.

Fig. 16 – Complex calcium alinate inclusion in fractured sample from as-cast slab. Dendritic solidification is visible in the outer layer of the inclusion. Courtesy of C. Cicutti, Tenaris Siderca.

Fig. 17 – Calculated oxygen in solution steel containing 0.025%Al, 0.01%S, and various contents of O; (15, 20 and 30 ppm, left to right) as a function of the Ca content at 1540 °C. Non-metallic phases present indicated for each region of composition. Calculated with Thermo-Calc® and SLAG3 database. Points are experimental measurements of oxygen in solution in heats without clogging events. Adapted from [45].
tification (size, volume fraction and composition information) several new methods and practices have been proposed and have been reviewed in [64,187–192]. It is apparent that in many cases more than one practice must be used to properly characterize and understand the effect of process on NMIs and then to correlate their effect with properties. This is understandable since some properties seem to depend on the overall distribution of inclusions and others, such as fatigue, depend on the maximum sized inclusion. Furthermore even excluding low-end products, the range of cleanliness of steel products varies significantly. Low-carbon aluminum killed (LCAK) steel have around 40 ppm total oxygen content while bearing steels with around 5 ppm total oxygen are now typical. This results in a dramatic difference in volume fraction of oxide inclusions, not to mention sulfides. Extreme value statistics and its application are of paramount importance in fatigue. These methods are seldom included in usual reviews. For a review including these methods, the reader is referred to ref. [188]. The method of inclusion rating using statistics of extremes adopted in the procedure proposed by Murakami [193] is widely used in the area of fatigue, with very good results. It must be mentioned that, in this method, there would be no limit to maximum inclusion size, since it increases with the volume of steel used in the calculation [188]. This is somewhat incompatible with the expectations of steelmakers.

6. Conclusions

Never the classical aphorism “Look after the slag, and the metal will look after itself” has been so well understood and followed in the processing of steels. In the last decades, the understanding of the effects of NMIs in steel properties has caused steelmaking process to evolve from preventing “unavoidable” contamination to the optimization of NMIs composition, amount and distribution in the steel products.

This has affected all steps in melt shop processing. Raw material selection (e.g., to avoid aluminum contamination), slag composition design, optimization of secondary refining conditions (e.g., time of processing and fluid dynamic conditions), rigorous control of tundish and mold operations and rigorous measures to control reoxidation in all steps of processing have become standard in quality steelmaking.

In this development, thermodynamics has played a decisive role. The understanding of the interplay between thermodynamics, steel and slag chemical composition, and melt shop processing conditions has evolved dramatically. The modeling tools available have also improved significantly, so that important knowledge for inclusion control in steels can now be developed on a scientific basis. These techniques are now widely used in process development and in tailoring NMIs. This ability places a continuous demand on the improvement of the understanding of slag and NMIs properties.

Inclusion engineering is now a reality in a great number of steels and steel plants and steel cleanliness has improved at least an order of magnitude in the last decades. This improvement has posed significant challenges to those involved in NMI qualification and quantification, essential to relate quantitatively NMI population to product properties and behavior. This is a vast field and will be discussed in a future publication.

Thus, notwithstanding all the advances summarized in this review, important problems and questions remain if the quality of steels is to continue improving in the next decades.

Conflicts of interest

The author declares no conflicts of interest.

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