The effects of non-metallic inclusions on properties relevant to the performance of steel in structural and mechanical applications

André Luiz Vasconcellos da Costa e Silva

EEIMVR-UFF, Volta Redonda, RJ, Brazil

Abstract
Non-metallic inclusions (NMIs) occur typically in low or very low volume fractions (from $10^{-2}$ in a high oxygen weld deposit to $10^{-5}$ in very clean bearing steels) but play an important role in many properties of steel. NMIs play a decisive role in processes involving ductile fracture, fatigue and corrosion, for instance. These are some of the properties more relevant to the performance of steel in structural and mechanical applications. Furthermore, NMIs may influence nucleation during phase transformations of steel. In this work, the relation of these properties to NMIs is reviewed, highlighting progress and difficulties in each area. Perhaps because of their very low volume fraction, NMIs are sometimes overlooked in the basic physical metallurgy education and their study is left to the realm of those interested in steelmaking. In the last decades a dramatic evolution in the understanding of their relationship to properties, however, has led to significant improvements in many steel products: the outstanding increase of fatigue life in automotive springs and in bearings is one of many such examples. It is concluded that steel improvement in many cases requires “inclusion engineering” and this can only be achieved through close collaboration between physical metallurgy, process metallurgy and steelmaking. Those who realized this have made significant progress in steel development in recent decades as highlighted in this short review.

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Andre Luiz Vasconcellos da Costa e Silva graduated as Metallurgical Engineer from the Military Institute of Engineering (IME), Rio de Janeiro, in 1976. Obtained his M.A.Sc. from the University of British Columbia, Vancouver, in 1979 and his Ph.D. from the University of Florida, Gainesville, in 1994. His career started as an engineer in Eletrometal Aços Finos S.A. (currently Vila Yellow, Brazil) and has taken part on pioneer projects on deepwater oilfield completion and production. Has been the Technical Director of the Brazilian Institute for Nuclear Quality, where he has been certified both as Level III Inspector and Level III Expert in Materials Engineering. He is Professor at the Metallurgical Engineering School in Volta Redonda, of Universidade Federal Fluminense. And is the Chairman of the Alloy Phase Diagram International Commission (APFID) from 2008 to 2015. In 2014 he received from IOM, England the Hume Rothery Award, for distinguished achievements in relation to phase transformations and in 2017 became the 15th recipient of the triennial ABM, Brazil “Hubertus Colpaert” Silver Medal for his contribution in metallography and physical metallurgy. He is a member of ABM, ASM and TMS.

1. Introduction

While a large emphasis is given to the importance of steel microstructure in the education of metallurgists and materials scientists, the influence of non-metallic inclusions (NMIs) on steel properties is comparatively neglected. In industry, on the other hand, the attention to the importance of NMIs on steel performance is pervasive and the focus of constant studies and improvements. This has become especially important as steel has been challenged by different alternative materials and by more demanding applications. The improvement of many properties only became possible with the understanding of their relationship to the type, size and distribution of NMIs present in the matrix. In the last decades, the steelmaking industry developed significant process improvements that lead to much better control of inclusion volume fraction, size and composition (e.g. Refs. [1–6]). Tailoring inclusions to improve properties and performance is an important feature of steelmaking and the term “inclusion engineering”, coined in the 1980s [7] is widely used. Inclusion engineering starts with the definition of the desirable properties the inclusions should have. Then, through the definition of adequate processing conditions, a product is made where these desirable inclusions are predominantly formed. Controlling inclusion distribution in the final product, in special those NMIs formed after the beginning of solidification (secondary inclusions, see item 2) remains a significant challenge. The tools for modeling and understanding this issue have been recently reviewed [8]. The origin and control of NMIs have been reviewed in a previous publication [1]. In the present work, the status of understanding NMIs properties and behavior during processing is first considered. Then, the current understanding of the relationship between NMIs properties, size, distribution, and properties that are critical for the performance of steels in structural and mechanical applications are summarized. As literature in the field is growing at a fast pace, the reader is directed, whenever possible, to recent reviews and important publications on specific topics.

2. Classification of non-metallic inclusions – a brief overview

Many commercially available elements that are acceptable in steel composition have a high affinity for oxygen and can thus be used as deoxidizers, forming non-metallic deoxidation products when added to the liquid steel [9]. Examples are silicon, manganese and aluminum. Deoxidation 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 for sulfur to form non-metallic sulfides at the liquid metal temperatures [9]. 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. The most common sulfide precipitating during solidification is MnS. Based on these observations two possible classifications for NMIs emerge: (a) using their chemical composition (oxides, sulfides, etc.) or (b) considering the moment they form with respect to the start of the solidification: primary, before solidification starts, and secondary, after solid steel starts forming in the mold. Furthermore, inclusions originating from the steelmaking process 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. These reactions produce changes in the NMIs. Thus, this classification can, sometimes, be confusing [1].

Finally, a common way of classification of NMIs is related to the inclusion size: inclusions can be classified as macro and micro inclusions. A sensible cutoff between sizes should follow the proposal by Kiessling [10,11]: an inclusion is a macro inclusion if it is large enough to cause immediate failure of the product either during processing or use. All other inclusions are 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.

3. Properties of NMIs relevant to their effects on steel properties and performance

Some properties of NMIs have a key importance on how they influence the behavior of steels. These include plasticity or hardness as a function of temperature, coefficient of thermal expansion (CTE), crystallization behavior (in the case of glassy inclusions) and to a lesser extent, solubility of metallic solutes. NMIs have ionic, covalent or mixed bonding character. As such, they are in general brittle at room temperature and have no strong bonding to the metallic matrix. As temperature increases, some inclusions become more plastic. Many measurements of hardness and plasticity of inclusions have been performed (e.g. Refs. [12–15]). The observed changes are,
Fig. 1 – Effect of temperature on relative plasticity of NMIs, depending on their chemical composition. The curves are of semi-quantitative nature. Adapted from Ref. [11].

Fig. 2 – Schematic illustration of the behavior of NMIs after thermomechanical treatment, depending on their relative plasticity at the working temperatures.

Fig. 3 – Alumina cluster in steel after deep etching with nital. Scanning electron microscope (SEM), Secondary electrons (SE) [21] Courtesy of C. Cicutti, Tenaris-Siderca.

However, too complex to describe in a simple way. A significant amount of work in simulation of the deformation of imbedded phases and associated voids is also available (e.g. [14,16–18]). Nonetheless, one of the most widely used concepts to describe deformation behavior continues to be inclusion “relative plasticity”. This concept is especially useful when there is a lack of accurate knowledge of NMIs properties. The concept of relative plasticity was introduced in the 1960s as the ratio of the true deformation of inclusions to the true deformation of the steel [19]. Kiessling [11] summarized the relative plasticity of inclusions in steel in a classical graph (Fig. 1).

The graph in Fig. 1 gives an overview of the complexity of the behavior of inclusions when steels are deformed. Depending on temperature and inclusion composition, their relative plasticities vary, and these particles may deform, crack or have mixed behavior, as illustrated in Fig. 2.

In many cases, the combination of low bonding strength to the matrix and matrix deformation leads to void creation and separation (or debonding, as commonly used in the composite literature). Furthermore, hard inclusions will typically break and redistribute in the steel under these conditions. This has been discussed by Robinson and Pickering [20] in the case of alumina, for instance. Understanding the breakage and redistribution of alumina is further complicated by the fact that alumina inclusions frequently cluster during the processing in the liquid state, as shown in Fig. 3 [21]. Predicting the behavior of hard inclusions or inclusions that become less plastic at lower temperatures has been a challenge to modeling the behavior of steel. Attempts to correlate NMIs behavior with their elastic moduli or hardness, in drawing tire cord wire at room temperature, for instance, have not been successful [22]. Nonetheless, these are the basic parameters needed to quantitatively describe the mechanical behavior of inclusions and hence their effects on steel properties via modeling (e.g. [23]).

Inclusions that are plastic at the working temperature will deform when steel is worked. This will result in elongation of the inclusions along the major working directions. This introduces, in many cases, shape anisotropy in the inclusions. This results in anisotropy of the properties influenced by NMIs [24]. Bernard and co-workers did the most comprehensive experimental study of oxide plasticity to date [25]. Recently Zhang and co-workers [22] have confirmed the relationship between high temperature plasticity and melting point of oxide inclusions, by correlating the calculated liquidus temperature of the inclusions with their aspect ratio measured in rolled and drawn tire cord wire. In some modeling work of NMIs deformation during hot working, the plastic deformation of the inclusions is associated with its viscous flow...
and reasonable prediction of anisotropy is achieved. In other cases, elastic-plastic behavior is assumed [23], using data determined some decades ago [25]. On a more quantitative study, Matsuoka [26] and co-workers demonstrated that the ratio of flow stress of the inclusion to that of the matrix will define the elongation of the inclusions. Interestingly, the properties of MnS used in modeling were those determined in the 1960s [27]. They also modeled the behavior of composite inclusions, having alumina surrounded by MnS. The behavior is as sketched for “complex” inclusions in Fig. 2. The results confirmed the experimental observations of [28] who showed that as sulfur content falls below 60 ppm, the aspect ratio of these Al₂O₃/MnS inclusions decreases substantially. These results are of special importance for modern high purity, clean steels.

The anisotropy introduced by NMIs shape change cannot be eliminated by further heat treatment. The deformation of NMIs and of segregates is normally responsible for the “fiber” appearance observed during the macrographic examination of steels [29]. An eventual crystallization of the NMIs during steel processing can complicate the prediction of the extent of their deformation and the variation of plasticity with temperature. Inclusions that are initially "glassy" or amorphous have been shown to crystallize when subjected to treatments at temperatures in the range of hot working temperatures of steels [30,31] (Fig. 4).

The crystallized inclusions have different rheological behavior (or relative plasticity) when compared to the "glassy" ones [30]. This can be especially important when NMI plasticity is critical, as in the case of tire cord and spring steel, as will be discussed later.

The coefficients of thermal expansion (CTE) of NMIs are different from that of steel. Brooksbank and Andrews [32] evaluated how these differences in CTE could influence residual stresses around inclusions, in what is now a classical work. They indicated inclusions that could be more deleterious by being surrounded by a tensile stress field associated with these tessellated stresses. In their view, this could be especially important under fatigue conditions [32]. These stresses are also considered relevant to machinability [33]. It is believed that the formation of stress fields, cavities and pores in the steel matrix around the inclusions has a favorable effect on machinability. Inclusions having higher CTE than the steel separate from the matrix on cooling from steel processing temperatures. This may also cause problems in metallographic sample preparation and difficulties with size determination. When automatic methods are used, a gray-level threshold is set to differentiate between oxides and sulfides [34]. Depending on the selected threshold, the dark region between matrix and inclusion can contribute differently to the measured inclusion size.

Significant differences exist in the use of the expression “inclusions” in the discussion of fracture modeling. Many authors include carbides, carbonitrides and other second-phase particles together with NMIs in the definition of “inclusions” (e.g. [35,36]). When considering the ductile fracture process, it seems important to take in account both type of particles [37,38]. Special attention must be paid to the difference of the strength of the matrix–inclusion interface, and the size and distribution of the different types of particles. The interface between NMIs and steel has, in general, very low or no strength [13,14,39,40]. Conversely, the strength of the interface between carbides and steel, for instance, has been estimated in the range of 1200–2000 MPa [41]. This difference has great importance on the effect of NMIs on the steel properties, particularly fracture. The distinction between NMIs and second phase particles can become blurred. In some steels, titanium is used as a nitrogen getter, and TiN inclusions may be formed in the liquid state [29]. On the other hand, in electro steels MnS is formed as a fine precipitate to control grain boundary movement [29]. Gladman [42], using Al₂O₃ particles in steel, demonstrated the controlling role of particle size and volume fraction in affecting grain boundary movement.

4. Effects of NMIs on some important steel properties

4.1. Effects on processing – hot and cold working and forming

It is sometimes convenient to separate the influence of NMIs during processing from that during application, as the conditions in processing are normally not the ones envisaged for the steel application. This is true even considering that most of the problems associated with NMIs discussed in this section are related to their relative plasticity and their influence on steel ductile fracture, the subject of Section 4.2.

Inclusions that occupy a significant portion of the material cross section during hot or cold work or that are in regions where processing deformation is high may cause fracture during processing. Fig. 5 illustrates the fracture of a tire cord wire during cold drawing, caused by the presence of a large inclusion [29]. Controlling the volume fraction, size and distribution of NMIs is thus important. Furthermore, inclusion engineering is of paramount importance [43] on the wire making operations of tire cord and springs. Inclusion engineering is also important for fatigue properties [44] and will be discussed later.
Inclusion distribution in steel products greatly influences how they affect steel properties. A cluster of relatively large alumina inclusions has caused the defects shown in Fig. 6 in a cold rolled foil [45]. Thus, in the case of tin foil, for instance, it is necessary to perform 100% inspection for perforations caused by NMIs [45]. Similarly, NMIs that could be acceptable in a foil for drawing and ironing forming operations (D&I) for can manufacture may cause failure if they are located in the highly deformed can flange region [46,47] (Fig. 7). The behavior of flange cracking in D&I steels for cans has been known to be critical for some time but still requires proper processing control to engineer the NMIs, as requirements are ever more stringent.

Failure associated with NMIs also happens during closed die forging. In some cases, 100% immersion ultrasonic inspection must be performed to eliminate sections of bar stock where these NMIs concentrate. As severity of forging increases and steels become stronger and less ductile, the detection limits of ultrasonic examination are approached or surpassed.

Even when they do not cause material failure, NMIs may introduce voids and stress concentrators, depending on their relative plasticity, as shown in Fig. 8.

Interesting results have been obtained when modeling the behavior of single, relatively large, inclusions in a steel matrix during hot working, using finite element modeling. The work of Ervasti and Stahlberg [17] is a representative example. However, as difficulties related to the proper characterization of
NMIs properties persist, Ervasti and Stahlberg [17] adopted an arbitrary relative plasticity (expressed as the ratio of flow stresses, $\sigma_{\text{inclusion}}/\sigma_{\text{matrix}}$) of 3 for hard inclusions and of 1/3 for soft inclusions. In addition, one of the key challenges in modeling the behavior of inclusions in steel is the multiparticle aspect and considerations of size and distribution, which greatly affect the results [36,49].

### 4.2. Influence on ductile fracture of steel

Ductile fracture processes are important in structural and mechanical applications of steel. They influence ductility, formability and toughness (at temperatures where the ductile share of the fracture process is relevant). Ductile fracture of steels generally occurs by the nucleation, growth and coalescence of microvoids. These voids nucleate by debonding or cracking of NMIs and second phase particles. Srivastava and co-workers [50] reviewed key work on this process since its identification in 1949. The process is in most cases dominated by the nucleation and growth of microvoids preferentially around NMIs and their coalescence by necking of the metal between inclusions. Hence, there is a significant effect on properties related to ductile fracture. This has been well demonstrated (see e.g. [36,51–53]). This process occurs, in general, on two microscopic scales [37,38]: on a larger one, voids nucleate on NMIs that crack or debond from the steel matrix. On a finer one, sub-micron precipitates play a role on void nucleation. The primary voids grow until a certain strain when they coalesce. The finer voids soften the ligaments and promote strain localization and the linking of the primary voids.

Fig. 9 [54] is an especially good illustration where the effect of the NMIs is evident. A tensile specimen was cut longitudinally in the region of necking, before fracture. The process of nucleation and coalescence of the voids is clearly seen. This technique has been widely used for understanding fracture mechanisms. In some cases, it has also been used to generate data for validation of modeling of fracture in metals (e.g. Refs. [36,55]).

The relative effects of NMIs and structural constituents, such as carbides, on the ductile fracture process are frequently discussed. Apparently, the higher bonding strength of the carbide–metal interface (Section 3, above) makes their contribution relevant only at higher deformation, normally leading to a contribution to the smaller microvoids. If, however, nitrides or carbides are sufficiently large (see Section 2) they may also contribute to the formation of primary or large voids (e.g. refs [56,57]). In steels that are “dual-phase” (DP) or “duplex” the nucleation of cracks at interphase boundaries may also play a role in ductile fracture [58]. There is a general lack on information about steel cleanliness in the studies of fracture of DP steels, so it has not been easy to define the relative role of NMIs and martensite/ferrite interfaces (see for instance, [58–60]). Jamwal and co-workers [61], however, where able to quantitatively show that tensile elongation in their DP steel was related to the density of voids (or “pullouts”) nucleated at martensite/ferrite interfaces and had no relationship to the number of pullouts nucleated at NMIs, which remained essentially constant when the elongation varied.

The importance of interfacial strength on second-phase effect on the properties of composites has been identified and discussed [62]. The work of Ashby and co-workers is especially illustrative of this [63]. Information about these concepts has not been, however, widespread in the steel community. So, even if carbides can also cause voids [40,64] they crack and debond at much higher strains than NMIs [54]. Thus, NMIs normally control the ductile fracture process of steels. As a result, reduction of area, elongation and upper shelf energy as well as the anisotropy in these properties are very frequently controlled by content, size, shape and distribution of NMIs as shown in Fig. 10, adapted from [65]. Non-uniform distribution of NMIs, such as the presence of manganese sulfide clusters, play an important role in increasing their influence on ductile fracture. Tanguy and co-workers [66] discussed this issue in detail in relation to SA508 Cl.3 forgings used in the nuclear industry. They indicated that the importance of MnS clusters decrease, as expected, at very low sulfur content, such as the 40 ppm sulfur steel they studied.

The understanding of the effect of NMIs on ductile fracture process and its anisotropy led to important developments: one of these was inclusion modification treatments or sulfide modification treatments. These treatments combine low sulfur steel and the formation of low plasticity sulfides mostly via calcium treatment. As a result low anisotropy products such as plates that fulfill tensile ductility requirements in the short transverse (“through thickness” or “z”) direction could be produced [67–69]. The concept of inclusion modification with calcium further evolved to treatments leading to liquid inclusions at casting temperatures, preventing nozzle clogging in continuous casting [1,70,71]. For high strength steels for special applications, inclusion engineering has evolved to include the careful modeling of the fracture process [49] and studying the specific behavior of different kinds of sulfides, for instance: not only considering inclusion size and spacing [72] but also how they contribute to fracture [73] and fracture toughness. Finally, as mentioned in Section 4.1, understanding the influence of NMIs shape and formability on fracture had a dramatic effect on the development of inclusion engineering for high formability steels and tire cord wires [43,44].

Significant advances on the modeling of the fracture process have been made, as discussed in [55]. At least three
important areas present challenges to further advances: (a) the proper characterization of the properties of NMIs and their interfaces with steel; (b) an adequate metric for characterizing size, shape and distribution of the large multi-particle population and (c) the difficulties associated with computational methods considering the multi-particle population.

When modeling fracture, detailed elastic-plastic calculations of void nucleation can be performed if constitutive equations are defined for the matrix, inclusions and interface (e.g. [74]). Conversely, very interesting examples of how to deal with (a) and (b) can be found, for instance, in Refs. [36,50]. A relevant example of advances in computational methods is presented in Ref. [23].

4.3. Influence on fatigue

The importance of inclusions on the fatigue of steel has been long recognized [75–77]. The effect of type, composition, shape and size of NMIs on fatigue have been extensively discussed in many publications without a firm conclusion, however. Correlations between total oxygen content and rolling contact fatigue in rails [78] and with L10 in bearings (the number of cycles at which 90% of fatigue samples fail) have been demonstrated [79] but with limited quantitative success. A recent review dedicated to bearing steels addresses in detail many of these issues [80]. The work of Murakami and co-workers has shed new light on understanding the effects of NMIs on fatigue both before [81,82], and after [83] the publication of his book [84]. His views can be summarized in the following statements: The fatigue limit is correlated with the existence of non-propagating cracks. It is not related to crack initiation...“the fatigue limit is a threshold stress for crack propagation and not the critical stress for crack initiation”. Fatigue limit correlates with hardness, up to around 400HV (e.g. Fig. 11, [85]). In this region, “the fatigue limit is determined by a material property showing the average resistance to plastic deformation of the material”.

As one passes the 400 HV threshold, the ideal fatigue limit, associated with the material properties cannot be reached, in general, due to the presence of defects (such as inclusions). “Defects smaller than a critical size are non-damaging (not-detrimental) to fatigue strength and the critical size is smaller for materials having a higher static strength, so that a defect of a given size is more detrimental to high strength steels than to low strength metals.” Murakami demonstrated with several experimental examples that since the fatigue limit is a stress at which crack propagation does not occur, small defects can and will have cracks starting from them that may or may not

Fig. 11 – Relationship between hardness (HRC) and fatigue limit (MPa).
Adapted from Ref. [85].
lead to fatigue, depending on size and stresses. He argues that, for this reason, when a crack originates at the inclusion–metal interface or through inclusion cracking, the stresses within the inclusion are relieved and the inclusion domain may be regarded as mechanically equivalent to a stress-free defect or pore. Thus, tessellated stresses, for instance [32] could be less important than previously thought. Using this approach, he was able to find adequate relationships to predict the fatigue limit of high strength steels, reconciling the endurance limit relationship with hardness by including a term related to the cross-section area transverse to the loading, occupied by inclusion. Depending on the loading, position of the inclusions can be important, and this is accounted for. Thus, for inclusions close to the surface in rotation-bending Murakami and co-workers proposed an empirical relation between the endurance limit and hardness given by Eq. (1), where the area of the inclusion is considered. Murakami has developed similar equations for inclusions in other positions.

\[ \sigma_w \equiv 1.43 (H_v + 120) / (\sqrt{\text{area}})^{0.6} \]  

(1)

In this equation, \( \sigma_w \) is the fatigue limit (MPa), \( H_v \) is the Vickers hardness (HV) and \( \text{area} \) (\( \mu \text{m}^2 \)) is the area occupied by the inclusion, calculated as described in [84].

Fig. 12 shows the agreement of this relation with experimental results.

The effects of these insights on bearing steels development (SAE 52100 or 100Cr6) have been very important. Thus, for instance, the results of [77], where particular relevance was ascribed to different inclusion compositions, could be reappraised. The results indicate much less importance of inclusion type when analyzed in accordance with Murakami’s formalism, as shown in Fig. 13.

According to Murakami’s results, the largest inclusion present in the stressed area will be responsible for fatigue failure.

With the high cleanness of these steels, the classical methods of inclusion evaluation and quantification [2,86] became quite ineffective in predicting fatigue behavior and extreme value statistics has been presented as a solution [4,87]. In this context, Murakami developed a method for extreme value inclusion quantification [88]. Later, an ASTM standard was developed [89], mostly with the bearing community in view. With this method, Murakami and co-workers have been able to predict fatigue properties based on extreme value statistics for inclusions. Furthermore, they showed that, when the inclusion population and inclusion size become exceedingly small, as in extra-clean electron-beam (EB) melted steels, microstructural heterogeneities (bainite areas) are larger than the inclusions and act as fatigue nuclei [87].

The importance of inclusions in fatigue is still the subject of frequent discussion, particularly in what is termed very high cycle fatigue [90–92].

The developments led by Murakami and co-workers on the understanding of the importance of NMIs in fatigue of high strength steel also had a profound impact in the inclusion engineering of spring and valve steels (see Refs. [84,93,94]). Developments in the field of inclusion engineering in spring steel in Europe were summarized in Ref. [95] in 2003.

Summarizing, when considering the literature on crack origination and propagation in fatigue one must consider size and volume fraction of NMIs. Crack origination may occur “in the matrix” or related to second-phase particles, in special NMIs. It seems that for lower strength steels, a critical crack size larger than the larger NMIs is needed for fatigue to occur. Thus, NMIs will play a less important role in low strength, clean steels. Conversely, in high strength steel NMIs may be
sufficiently large and play an important role. This relationship between size and strength is consistent with Murakami’s EB “clean steel” results reported above. The results of Pessard and co-workers [96], who studied fatigue anisotropy in three different steels, are also a good example: they did not observe any anisotropy in the fatigue behavior of a low strength C35 steel ($\sigma_u = 580$ MPa, AISI 1035, where $\sigma_u$ is the tensile strength) with reasonably normal sulfur content (0.045%). On the other hand, higher strength steels ($\sigma_u = 1050–1150$ MPa) with high sulfur content (0.073–0.075%), presented fatigue anisotropy, associated with NMI-related fatigue fracture.

The anisotropy of fatigue resistance is included in Murakami’s formulation, since the term \( \mathcal{J} \) is calculated using the projected area of the inclusion (or defect) onto a plane perpendicular to the maximum tensile stress [84]. This is confirmed by experimental results (e.g. [97, 98]).

Some recent results in rolling contact fatigue (RCF) seem to contradict—at least partially—Murakami’s concepts regarding the effects of NMIs on fatigue. Both Sada and co-workers [59] and Hashimoto and co-workers [100] observed that hot isostatic pressing (HIP) of SAE 52100 bearing steel improved RCF life. They attributed the effect to the elimination of the cavities between NMIs and the steel matrix. As the inclusion size is not altered by HIP, these authors considered that the NMI–steel interface condition also plays a role in fatigue life. On the other hand, the NMI–matrix interface strength has been considered an important factor in the microscopy phenomena involved in fatigue cracking. Spriestersbach and co-workers [101], for instance, noted that “classical” NMIs (oxides, complex oxides and sulfides) debond easily due to the low NMI–steel interfacial strength. Furthermore, differences in CTEs [32] may promote NMIs-matrix separation. Thus, classical NMIs may be considered to behave as holes, as proposed by Murakami. Conversely, TiN, for instance, has a strong bond to the matrix and the TiN–steel interface shows no separation. When TiN is subjected to high stresses it cracks, and the cracks propagate into the matrix. Thus, the correlation between TiN size and fatigue behavior could be different from the one observed for “classical” NMIs [101]. Evidently, this is an important argument and further research is needed to clarify these phenomena. This is a very important issue for RCF. However, the microstructural changes observed during RCF [102] make investigating the effects of the individual NMI very difficult, as experimental results (e.g. [103]) demonstrate.

Furthermore, Murakami’s assumption [81] that the dimension of NMIs parallel to the stress is not important has been questioned. Observations in steels with elongated NMIs larger than those found in very clean steel (such as bearing steels) suggest that these NMIs may have a larger than expected influence, due to the long region of the material that will be subjected to stress concentration [104].

4.4. Influence on the nucleation of ferrite

NMIs may play an important role in phase transformations. Their influence on nucleation in continuous casting and ingot casting was discussed in a previous publication [1]. NMIs also play a critical role in the nucleation of fine acicular ferrite in weld metal. This microstructure is important to achieve satisfactory mechanical properties with low carbon compositions without hot/controlled working. Thus, weld metal composition is tailored to cause the precipitation of adequate nuclei for acicular ferrite. Some of the factors considered relevant for a NMI to act as a nucleus [105,106] for acicular ferrite are: crystal structure, differences in CTE and depletion in austenite-stabilizing elements such as Mn around the inclusions [107,108]. The latter is the most favored explanation, followed by stresses generated by CTE differences between inclusion and the austenite matrix [106]. This gains special relevance with the prospect of thin plate casting, where the extent of hot/controlled working that can be performed to refine the austenite grain is very limited [109]. The importance of this phenomenon in welding is well discussed in Refs. [106,110,111]. The control of NMIs for nucleation in thin foil continuous casting is discussed by [109,112–114]. One of the first and clearer in situ observations of the nucleation process was done by Sugiyama and Shigesato [115] who discussed in detail their observations on the importance of manganese sulfide on ferrite nucleation. Li and co-workers have shown experimentally and using first principle calculations that Zr and Ti oxides promote Mn depleted zones in the NMI–matrix interface, favoring ferrite nucleation [116,117]. Furthermore, they have shown that MnS can nucleate on Zr oxide. As a result, they have shown the beneficial effect of Zr-Ti deoxidation in HSLA steels, promoting finer and more uniform dispersions of MnS and acicular ferrite microstructures [118]. Grong and co-workers [119] reviewed the possibilities of producing “dispersoids”, inclusions with a sufficiently fine size and compositions to affect nucleation in solidification as well as ferrite nucleation. In order to achieve this, these particles, however, would be formed in a more complex way than just resulting from classical NMI formation reactions, which are the focus here.

4.5. Influence on machinability

Perhaps one of the properties most traditionally related to NMIs is machinability [120]. The effects of sulfides [121] are well known and the design of these inclusions for machinability has been quite successful [122]. A detailed review on the role of NMIs on machinability, covering many types of inclusions has been published recently [33]. Computational thermodynamics has been used to design steels with good machinability by tailoring sulfides to substitute Pb “metallic inclusions” [123]. Lead added steel presents important health hazards during steelmaking and significant environmental impact. Presently the automotive industry is defining a minimum sulfur content for non-resulfurized steels to improve their machinability. This has posed an interesting challenge to bar manufacturers who need to adjust their processes to prevent nozzle clogging by the use of calcium in presence of sulfur in the range of 0.020% [124]. Stringent process control is required, in this case.

4.6. Influence on surface finish

Albeit surface finish can be considered a machinability issue, the case of tool steels for plastic molds, for instance, presents extraordinary requirements. Studies have shown that both microstructure and cleanliness play an important role. Simple
forms of cleanness quantification, however, are not able, in general, to correlate with polishing quality [125]. Inclusion type play a definite role in the process: in the case of ESR of P20 steel, for instance, it was demonstrated that the typical desulfurization of ESR is deleterious for surface finish and inert atmosphere remelting must be used to prevent desulfurization and guarantee that sulfides will cover the oxide inclusions allowing a good surface finish [126]. The compared results of VAR and the so-called PESR (ESR under inert gas) in [125] can be explained in the light of this observation.

4.7. Influence on corrosion

Two examples of the influence of NMs on the corrosion performance of steels are the importance of inclusions on hydrogen related failures such as hydrogen-induced cracking (HIC) and on the formation of pits, as discussed in the next sections.

4.7.1. NMs and hydrogen related failures

The importance of inclusions as traps and nuclei for HIC has been recognized at least since the 1970s [127]. The importance of the synergistic effect of segregation and NMs, particularly manganese sulfide was soon also recognized. Nakai and co-workers [128] observed that shape control of sulfides had a great influence on HIC. They showed that higher oxygen steel with type I sulfides (that do not have high plasticity) had better resistance to HIC than Al-killed steel with type II sulfides that elongated during rolling. However, they preferred either Ca or Ce sulfide modification in order to guarantee good properties. It was also clear that simply reducing sulfur and controlling sulfide shape was not sufficient to guarantee excellent HIC resistance [128] since crack propagation was controlled by segregation. Thus, lower C and lower Mn steels were developed, as well as accelerated cooling strategies [129] to promote less segregation, particularly banding, and more uniform hardness in the microstructure. The interaction of segregation and calcium modification was demonstrated by Matsumiya and others [130,131] who showed that in large segregates usual calcium treatment could be ineffective to prevent the formation of MnS. Thus, very low sulfur and avoidance of MnS has become the rule to guarantee good HIC resistance [132,133]. Nonetheless, inclusions continue to play an important role on HIC crack nucleation. In very clean steels, it has been shown that not only MnS promotes hydrogen cracking. When studying the resistance of API X120 HSLA steel, Huang and co-workers [134] related steel cleanness to reduced effect of hydrogen, regardless of the inclusion type. They did not give information on sulfur content of their steel, however. Jin and co-workers [133] reported that in a Ca treated API X100 steel with 50 ppm S, oxides were detrimental to hydrogen resistance. Domizzi and co-workers [135] could not correlate sulfide length or sulfur content to HIC resistance in steels with sulfur in the 50–150 ppm range. They propose that sulfur content and size influence resistance to hydrogen: “...a small number of very elongated inclusions may reduce the HIC resistance in the same way as a greater number of shorter particles.” They also emphasize the relevance of banding, which in HSLA steels is normally associated with higher Mn contents. The effects of banding were confirmed by [136] in SA 516 steels and by Dunne and co-workers [137,138] in API X70 steels. Banding was also shown to be critical to the hydrogen induced failure of AISI 4140 bolts in sub-sea applications subjected to cathodic protection [139]. Du and co-workers [140] have shown the beneficial effects of generating a fine dispersion of oxide and sulfide NMs through Zr+Ti deoxidation on HIC resistance, when compared to conventional Al deoxidation. In a recent review, Ohaeri and co-workers [141] confirmed that NMs in general can be deleterious to resistance to hydrogen degradation but confirmed that elongated inclusions apparently have a more negative effect. The importance of elongated sulfides on the extent of hydrogen blistering has also been demonstrated [135]. Thus, NMs shape, amount and type play an important role in hydrogen cracking. The eventual clustering of NMs, particularly regions of microstructural banding, has a synergistic effect in promoting problems associated with hydrogen and should be carefully avoided.

Additionally, it should be noted that Murakami has demonstrated that hydrogen trapping at NMs has a significant effect on super long life fatigue phenomena [142]. It is evident from the above discussion that inclusion engineering will play an increasingly important role in the design of hydrogen resistant steels.

4.7.2. Pitting

Wranglén [143] reported the importance of MnS as pitting initiation sites both in carbon and stainless steels. He proposed that in carbon steels, the attack starts in the matrix close to the sulfide inclusion, which is nobler than the matrix while in stainless steels, the attack would start at the sulfide inclusion proper. With the development of characterization techniques, Ryan and co-workers [144] measured the presence of a chromium depleted region surrounding sulfide inclusions in stainless steels and proposed that these would be the initiation sites. They did not, however, propose a mechanism for the formation of these regions nor describe the thermal history of their sample. Their results were contested by measurements performed by Meng and co-workers in various steels (including Ryan’s original sample) [145] and by [146]. The observations of Ryan resemble the composition profiles around chromium carbides in sensitized stainless steel. While a clear explanation exists for the formation of chromium depleted regions in the matrix around carbides in sensitization that is not the case for the matrix surrounding sulfide inclusions. More recently, Williams and co-workers [147] observed a layer of Fe rich sulfide surrounding the sulfide inclusions in stainless steels. This layer would preferentially dissolve and start the pitting process. In their conclusions, they suggest that inclusion engineering could be used to control the composition of the Mn-Fe-Cr-S sulfides and prevent this from happening. Park and Kang [148] recently reviewed the issue of NMs in stainless steels. They discussed the process of solidification of the sulfides that could lead to the situation observed by Williams. It seems clear that subtle chemical composition differences around NMs can be of paramount importance for the pitting of stainless steel. Results presently available indicate that the composition variations caused during sulfide formation could play a very important role. Liu and co-workers recently [149] demonstrated the effect
of alumina clusters on pitting of carbon steels. Ma and co-workers [150] have shown the anisotropic behavior of pitting associated to manganese sulfide NMIs. Thus, it is clear that NMIs, in particular sulfides, have a crucial role in pitting. Park and Kang [148] remark that the presence of oxide inclusions can also play an important role in pitting of stainless steels.

5. The importance of characterization and quantification of NMIs

Based on the above discussion, it is evident that proper characterization and quantification of the amount, shape, distribution and properties of NMIs is critical for steel characterization and for the further development of improved steels. The importance of the new methods of inclusion characterization in the 1990s that made possible proper fatigue predictions was also briefly reviewed and discussed in a previous publication [1]. This gives an example of how important and dynamic the field is. An important challenge in characterization and quantification of NMIs in current clean steel [4] is being able to detect and quantify the “cloud” (or background) of small inclusions and the few large ones. If they occur in large enough sizes, they may be detected by non-destructive testing (NDT), as discussed in item 4.1 above. Characterization techniques that sample large volumes of steel using NDT, such as MIDAS [151,152] are limited by the detection limit of the technique used. Furthermore, in some applications, inclusions considered “large” are below the limits of reasonable NDT. Scanning a sample or the whole volume of steel using NDT becomes useless in this case. Furthermore, clustering and concentration of secondary NMIs associated with microsegregation [1,29,131] may lead to NMIs behaving, effectively, as if they were larger [96,98]. Thus, intermediate size clusters or regions where NMIs are concentrated and will influence steel behavior may not be detected with the current characterization techniques and may be too small for the current non-destructive examination technique. When these clusters are associated with production events (mainly in the casting process (e.g. [153]), stringent process control may limit their occurrence or identify when they occur. However, some route to characterize the non-uniform distribution of secondary inclusions, caused by microsegregation, may require additional development efforts. With the presently available techniques, more efforts could be placed on evaluating neighbor spacing distribution by different techniques [4,154,155] which can rely on usual quantitative metallography tools and are frequently applied to composites. Present efforts at development new techniques of three dimensional (3D) characterization such as X-ray Micro-CT [156] or other 3D reconstruction techniques [157,158] may also become viable solutions in the future. Presently, techniques such as automated SEM-EDS analysis (frequently mentioned using the commercial name ASPEX®) offer the possibility of sampling large areas. Combined with 3D reconstruction (e.g. [153]) this may also give valuable information on particle distribution and clustering. While different methods will give different information about NMI population [3], most probably a combination of methods will continue to be the most adequate way to properly characterize NMIs in clean steel.

6. Conclusions

Non-metallic inclusions influence many properties of steels relevant to their performance in mechanical and structural applications. The understanding of how this happens has evolved in the last decades. Significant progress in the quantification of this understanding has been made. Some important limitations persist, however: while the modeling of ductile fracture has significantly evolved, there has been little progress in measuring both NMI and NMI-steal interfacial properties, a knowledge that is essential to the progress of modeling efforts. Furthermore, considering multi-particle populations and non-uniform distributions in models remains a significant challenge. This is also a challenge for characterization and quantification of NMIs: while some clustering of NMIs will be detected by enhanced non-destructive testing, current methods of quantification focus on the size of particles of the average background NMI population and do not, in general, measure particle spacing or account for non-uniform distribution of particles. Combination of characterization methods should be used if proper understanding of NMI population is desired. Great progress has been made in the understanding of the importance of NMIs in high cycle fatigue. This has been accompanied by progress in specific NMI quantification methods and inclusion engineering, resulting in significant improvements in materials for these applications. The use of NMIs for improved machinability has greatly advanced with the understanding of NMI genesis. Inclusion engineering has led to new compositions with improved machinability and surface finish. Significant developments also happened in understanding the effect of NMIs on ferrite nucleation. These developments have reached industrial maturity. The understanding of the importance of NMIs in pitting corrosion and hydrogen related fracture has made enormous progress. However, the interaction of NMIs and segregation, inherent to casting processes, still poses a significant challenge to the complete understanding of NMI influence on the complex hydrogen related fracture phenomenon.

Progress in the understanding and control of the effects of NMIs on the properties of steels in mechanical and structural applications require the close collaboration between physical metallurgy, process metallurgy and steelmaking. Those who realized this have made dramatic progress in steel development in recent decades and will probably continue to do so.

Conflicts of interest

The author declares no conflicts of interest.

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