Abstract

Utilization of non-metallic particles as heterogeneous nucleation sites has been found as an alternative way of grain refinement. The result of this solution is the microstructure formation consisting of acicular ferrite plates nucleated from dispersed fine inclusions. This microstructure is characterized with beneficial combination of strength and achieved toughness value.

The momentous role of very fine non-metallic inclusions has mostly the dimension lying between 0.5÷2µm, usually. Unfortunately, any detailed physical metallurgy model of the acicular ferrite nucleation process has not been presented up to this time. For this reason, this work is devoted to contribute to the mechanism elucidation (Mn-depleted zone formation and MnS precipitation on oxide particles – MnOSiO$_2$ in steel deoxidized with Mn/Si) of the acicular ferrite nucleation. Simultaneously, the Mn and S transfer between matrix and precipitates inclusive of the MnS initiation and followed growth of these particles at surface of matrix inclusions are analyzed. The unfavourable Al$_2$O$_3$ influence on the acicular ferrite nucleation is explained. The influence of this phase formation from point of view of resistance to hydrogen embrittlement is analyzed.

1. INTRODUCTION

Non-metallic inclusions often cause defect formation in steel products. They are considered harmful in steel. To attain a high steel quality various techniques have been developed to suppress above mentioned harmful phenomenon. Many of such inclusions are 50µm and larger in size. On the contrary, some fine non-metallic inclusions having only the dimension several micrometers in size are acting as precipitation sites for intragranular nucleation of acicular ferrite (AF). The finding shows steel properties can be improved by controlling the size of fine inclusions acting as potential AF nucleants [1]. Owing to beneficial effect as grain refinement from the intragranular AF nucleation, the utilization of inclusion in steel has attracted much attention at present. Fine inclusions, composed e.g. of Ti$_2$O$_3$, TiN and MnS are known as the effective AF nucleation sites. In this connection a great number of mechanisms have been developed to elucidate the controlling role of fine above mentioned inclusions as effective AF nucleants. Very frequent and promising suggestion is based on the formation of the Mn-depleted zone (MDZ) in austenite (A) matrix acting as preferential sites for A-decomposition into AF. These zones can be found in the vicinity of the
primary non-metallic inclusions being manganese-silicate (MnOSiO$_2$) type. It depends on the MnS formation at the considered primary non-metallic inclusions. Further, it is necessary to take into consideration the simultaneously realized Mn-diffusion in the steel matrix to nucleated MnS particles. In addition to this mechanism it has been observed the formation of MDZ around the cation vacancy of oxides types, including e.g. Ti$_2$O$_3$ what contributes to the enhancement of nucleation process [1, 2]. This study is devoted to the elucidation of the conditions leading to the Mn-depleted zones formation, having the connection with the MnS precipitation on the MnOSiO$_2$ inclusions in Si/Mn deoxidized low-carbon steel.

2. AF NUCLEATION PROPERTIES

It is generally accepted, the grain refinement represents an effective way how to improve the strength and ductility of steels by achievement of beneficial toughness properties. The A grain boundaries usually represent potential sites for ferrite nucleation (e.g. allotriomorphic ferrite - ATF) than any other surfaces of the heterogeneous nucleating particles. In this case the nucleation site number is increasing what finally leads to the refinement of ferrite microstructure. As an attractive method resulting in effective microstructure refinement is held thermomechanical treatment. In the frame of grain size refinement, the grain boundaries pinned with fine properties can be taken also into consideration. At the same time, as the other hand small non-metallic particles (e.g. fine oxides) measuring no-more than several micrometers or less in size (as limiting size is considered the non-metallic inclusions of 2÷3µm in majority examples). The finding of the MDZ physical metallurgy formation contributes to the deeper knowledge not only concerning the brittle fracture resistance, but also demonstrates the way how the improve the hydrogen resistance of steels.

This technique has been significantly applied in the refinement of weld metal or microstructure of weld joints (HAZ). Recently, it has been found an attractive method as an alternative technique of grain refinement for wrought steels, especially, for the thin slabs and ships to which heavy (necessary) deformation rolling cannot be applied. The formed microstructure dominantly consists of AF characterized by an assemblage interwoven non parallel ferrite plates with high density of tangled dislocations probably pinned by some ultra fine (submicron or nanosize) carbonitrides [3]. The AF shows unique and irregular configuration having grains distributed in a chaotic manner with random orientation. At the same time, the prior A-grain boundary network is eliminated.

Due to special morphology, AF microstructure makes possible to obtain a very favourable combination of mechanical properties (strength, ductility and toughness). The significant parameter is the deflection mechanism limiting cleavage crack propagation (in dependence on unit crack path). Although, the nucleation role of fine special types of non-metallic particles acting as inoculants controlling A-decomposition into ferrite has been described the comprehensive mechanism of these processes has not been developed. Due to large variety of non-metallic particles acting as inoculants in transformation process of A into AF, the analysis of this process is not facile. The nucleation potency of individual phases comprising complex inclusions has not been assessed so far. In this connection, it is useful to remember influence of inclusion chemistry and spatial distribution. The types of non-metallic inclusions are determined by applied deoxidization elements preferentially while their chemistry and size of certain extend are influenced by solidification parameters. The distribution of non-metallic reflects their wettability with steel melt [4]. In the present contribution, the investigation will be devoted to the finding of model being able to describe the nucleating behaviour of some complex inclusions based on manganese-silicate (MnOSiO$_2$) and the nucleating effect of Mg-addition (MgO) to the basic chemical constitution resulting from deoxidization with Mn/Si/Ti.
3. NUCLEATION MECHANISM IN Mn/Si DEOXIDIZED STEELS

Due to AF influence on microstructural refinement, the extraordinary attention is devoted to the analysis of the fine inclusion nucleability. The fine nucleation (oxides, nitrides, sulphides) is reported as especially effective in case of the AF nucleation. A number of different mechanisms have been considered among which as the most perspective could be held the formation of MDZ being the nucleation site for intragranular A-decomposition into ferrite phase. It has been proposed this zone is formed by the MnS nucleation on it [2]. This process is accompanied with the subsequent Mn-diffusion realized in the steel matrix to the MnS-nuclei. The development of existing MDZ could be further supported by the direct Mn-diffusion in the cation vacancy type oxides. The process leading to the depleted zone and MnS formation is illustrated in Fig.1a, b. The both figures show, the MnS concentration gradient exists across the MnOSiO$_2$ inclusion. The Mn content becomes higher toward the surface of inclusions what demonstrates the transfer of both Mn and S from the steel matrix to the inclusion. On the contrary, the mass transfer within inclusion is realized slowly characterized as sluggish process. It results in the surface enrichment of outer inclusion part. The described mechanism based on Mn and S transfer to the inclusion eventually will result in the formation of MnS precipitates at the inclusion rim [4].

The concentration characteristics presented in Fig.1a, b show the diffusion movement of these elements and their enrichment leading to the MnS formation (Fig.1b). The prolonged Mn and S transfer to inclusion leads to the MnS precipitation, at the outer part of the MnOSiO$_2$ inclusions as it is given in Fig1b, schematically.

![Diagram of Mn and S transfer at the metal/inclusion interface](image)

**Fig. 1.** Mn and S transfer at the metal/inclusion interface:

a) Concentration gradient across the inclusion

b) Precipitation and growth of the MnS particles at the outer part of the inclusion

The described Mn and S diffusion process shows, the Mn/Si deoxidized steel (formed MnOSiO$_2$ inclusions) are not in equilibrium state during the continuous cooling. It has been found, the Mn content in the inclusions are far removed from the saturated values. The steel matrix is supersaturated with both Mn and S with respect to the inclusions what results in the tendency for diffusion of those elements from steel matrix into inclusion.
The cooling rate influences the inclusion morphology as it results from the realized diffusion processes leading to the MDZ formation. The size of inclusions and the area of the MnS fraction in the oxide inclusion (MnOSiO$_2$) decrease. Figures 2a and 2b show the Mn-content variation in the vicinity of primary inclusion (applied two cooling rates) in the dependence on the applied cooling rate. In these figures Mn contents detected after additional isothermal annealing are also presented (1200 °C/1h). The depleted zone is not observed by application of fast cooling (initial condition) – Fig. 2a. On the contrary, the slow cooling application

![Diagram](image)

**Fig. 2.** Mn profile determined in as received condition and after additional annealing at 1200 °C/1h:
- a) Fast cooling - 500 °C/min.
- b) Slow cooling – 50 °C/min.

results in the formation of the MDZ in specimens being in as received state. The MDZ occurrence found after application of slow cooling at the beginning state has been removed after annealing. On the contrary, the cooling rate leads to the occurrence of the depleted zone (Fig.2b). In summary, we can conclude, the described results demonstrate, it is very useful to retain the MDZ around inclusions together with MnS particles precipitated on the surface of primary Mn/Si inclusions at temperature of A-decomposition into the AF. The analysis of achieved results leads to the conclusion high sulphide capacity of primary inclusions represents favourable conditions contributing to the MDZ formation and the MnS precipitation on MnOSiO$_2$. It facilitates the AF nucleation process.

4. **MODIFICATION OF AF NUCLEATION AFTER Mg-ADDITION**

In addition to the evaluation of manganese-silicate inclusion in presented work the attention is also devoted to study of the nucleation activity of inclusions containing Mg (Mg-oxides). The attempt has been made to explain the traits of Mg containing oxides which are
known to have dispersion in steel melt [5]. The influence of inclusion traits with Mg addition to Mn/Si/Ti deoxidized steel (graduated Mg content up to 52ppm) has been investigated.

![Graph showing variation in the size and number density of inclusions](image)

**Fig. 3.** Variation in the size and the number density of inclusion formed after different Mg-addition

Figure 3 shows the variation of the size and the number density of inclusions in dependence on Mg-content in investigated specimen. The inclusion size reflects the response of special behaviour of these particles containing Mg. After the addition of this element the formed inclusions are not susceptible to growth by collision and agglomeration due to their beneficial wettability for even dispersion in steel. It is known that so dispersed fine Mg-containing inclusions facilitate the intragranular AF nucleation what results in the finer microstructure in Mg-containing steels [4]. The inclusion size decreases and the density number of inclusions are increasing with Mg-content in the steel matrix.

The typical morphology of the analyzed inclusions found in steel is of complex type comprising central oxide and periphery of the MnS. Figure 4 demonstrates that there is none significant change in the susceptibility of oxide phase for MnS formation in the investigated steel type. The S-content does not show any ascertainable variation in inclusions. It is interesting to state a sulphur Mn-coexists in oxide phase in some other state than MnS. This state can be interpreted as a result of partial Mn dissolution in the cation vacancy sites of the iron lattice.

The presented results and their analysis show the mechanism based on the MDZ formation around fine intragranular non-metallic inclusion is real. This mechanism successfully elucidates the influence of physical metallurgy parameters responsible for the AF intragranular nucleation. The morphology parameters of the AF contributes not only to the improvement of steel resistance to cleavage cracking, but the behaviour of this microstructure acts positively by the resistance increase of steel with the microstructure against hydrogen embrittlement. The special arrangement of the AF plates contributes to the HIC resistance. It is due to high deviation of propagation cracks what is connected with a high angle
disorientation of the AF plates. The described effect of the Mg addition in steel contributing to the stabilization of fine inclusions can be held for beneficial effect.

5. CONCLUSION
The nucleation potency of some complex, inclusions represents a decisive initiation parameter in A/AF transformation. It has been established the higher density number of evenly dispersed fine intragranular particles (0.5-2.0µm) are very effective in the refinement of ferrite by AF nucleation. The type of non-metallic inclusions participating in considered nucleation process is determined by steel deoxidization while special distribution of inclusions is influenced by their wettability with steel melt. The mechanism of AF nucleation based on the existence of MDZ around the primary steel inclusion in connection with the MnS formation is analysed in detail.

\[Fig. 4.\] Variation in the average composition of inclusions after different Mg-addition

5. REFERENCES

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