## CHEMICAL METALLURGY CHARACTERISATICS OF STEELS AND THEIR TRANSFORMATION INTO ACICULAR FERRITE

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# CHEMICKO METALURGICKÉ CHARAKTERISTIKY OCELÍ A JEJICH TRANSFORMACE NA ACIKULÁRNÍ FERIT

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#### Abstrakt

Byly studovány chemicko metalurgické charakteristiky ocelí a podmínky vzniku acikulárního feritu v uhlíkových ocelích. Nukleační intenzita acikulárního feritu je vyjádřena pomocí různých faktorů, z nichž následující dva hrají velmi významnou úlohu při tomto procesu. Vzrůst změny chemické volné entalpie, v souvislosti s nukleací feritické fáze podmíněné vznikem na Mn ochuzené zóny v okolí inkluze (Ti<sub>2</sub>O<sub>3</sub>) při precipitaci MnS. Snížení energie fázového rozhraní doprovázející nukleaci acikulárního feritu na precipitátech TiN, které jsou charakteristické relativně vysokou dosahovanou mřížkovou registrací s feritickou matricí. V práci jsou podrobně analyzovány podmínky pro dosažení dominantní mikrostruktury tvořené acikulárním feritem.

#### Abstrakt

The inclusions responsible for the preferential acicular ferrite nucleation in carbon steels have been studied. Nucleation rate of acicular ferrite is expressed by various factors from which following two parameters play a very important role in this process. Increase in chemical free enthalpy change for ferritic phase nucleation due to Mn-depleted zone formation in vicinity of  $Ti_2O_3$  inclusions (MnS precipitation). Decrease in interfacial energy accompanying acicular ferrite nucleation on TiN having high lattice registry with ferritic matrix. The conditions leading to the achievement of acicular ferrite as dominant phase in microstructure are analysed.

Key words: acicular ferrite, bainite, non-metallic inclusions, intragranular nucleation, interfacial energy, Mn-depleted zone

#### 1. Introduction

The acicular ferrite (AF) microstructure provides an optimal combination of high strength and good toughness due to refined and interlocked (interwoven) morphology. The achieved higher toughness level in AF microstructure is also related to the increased density of the high-angle boundaries. This property is beneficial, because the above mentioned kinds of boundaries act as obstacles to cleavage and force the cleavage cracks to change the microscopy planes of their growth in order to accommodate the changing local crystallography. In AF microstructures, the density of crystallographically misoriented plates is enhanced as it correspond to increased direct nucleation on potential nucleants [1].It is generally accepted, the mechanism controlling the austenite (A) decomposition into AF is identical to the mechanism that controls the bainite (B) formation. The B-particles are nucleated at A-grain boundaries while AF is nucleated intragranularly on non-metallic inclusions or precipitates acting as potential nucleants in steels [2]. The growth of both compared microstructures by the same displacive mechanism dictates that the final microstructure formed in the bainitic temperature range is the competition result between intragranularly nucleated ferritic plates (AF) and B-sheaves nucleated at A-grain boundary surfaces. Formerly realised studies on the factors, making clear the chemical metallurgical principle of enhanced AF formation have led to the conclusion that a reduction in A-grain boundary surfaces per unit volume favours AF nucleation process to the detriment of B-formation. It results from reduced number of the B-potential nucleation sites [3].

A similar effect is obtained by increasing the number of inclusions acting as the AF nucleants. The higher AF volume fraction can also been found if a narrow zone of allotriomorphic ferrite (ATF) forms first at A-grain boundaries. The intergranularly nucleated ATF must be inert in the sense that it should not develop into Widmanstätten ferrite (WF) and B at lower transformation temperatures. This limiting effect depends on carbon-partitioning into A at A/F-interface what leads to the depressing of WF and/or B start temperatures by subsequent cooling process realised below the applied heat treatment temperature [2]. Figure 1 shows the inert ATF interface with A and AF formation in A-grain volume. In contrast to this example, Fig. 2 presents the development of continuously growing WF from ATF zone as it results from the ATF/A active interface behaviour.



Fig.1 AF microstructure-inert ATF interface with A



Fig.2 ATF and side plate ferrite microstructure

#### 2. Theoretical background

Several mechanisms have been proposed to explain the way in which non-metallic inclusions are active in AF nucleation. For this reason it is necessary to define more precisely nucleation potency of different at disposal being nucleants. Although the mechanism by which inclusions nucleate AF is not yet elaborated in detail, four possible nucleation variants can be taken into consideration [4]; a) simple heterogeneous nucleation on an inert particle; b) epitaxial nucleation on the inclusions having a good coherency (lattice registry) with ferritic matrix; c) nucleation arising from the strain energy associated with the different thermal expansion coefficient of inclusions and steel matrix; d) nucleation assisted by solute depletion in matrix near inclusions [5, 6]. It depends on the inclusion chemistry and its structure that which mechanism would work to promote intragranular nucleation on given inclusion types. In case of

Ti-oxides ( $Ti_2O_3$ ), the MnS-depleted zone formation has a very important role in AF nucleation process even though there are much problems to be explained [5].

The aim of this work is to analyse the influence of chosen inclusion types on the intragranular AF-formation. The special attention is paid to the study of steel matrix properties and realised processes leading to the increase in chemical free enthalpy change as it results from the localised Mn-depleted zone formation in matrix around nucleant. Besides above presented analysis the decrease consequences in interfacial energy of intragranularly nucleating particles (inclusions) taking part in AF formation process are evaluated. These nucleation active particles are characterised with relatively high lattice registry with ferrite microstructure. On the contrary, the above discussed nucleation effect of strain energy induced in matrix is weak in comparison with other considered parameters (see b) and d)). For this reason, this influence is not taken in the analysis by the summary evaluation [4, 7].



Fig.3 Energy barrier with heterogeneous nucleation as a function of the difference between austenite/inclusion  $(\gamma_{A,I})$  and ferrite/inclusion  $(\gamma_{F,I})$  interfacial energy

#### 3. Influence of non-metallic inclusions on intragranular AF nucleation

Wether the AF interlocked microstructure or the side plate ferrite particles (WF, B) are formed would be determined as a results of mutual competition between potential nucleation sites. This competition process is realised between prior A- grain boundary surfaces and intragranularly acting non-metallic inclusions in A-grain volume. As known, some oxides having higher cations vacancy concentration, e.g.  $Ti_2O_3$  particles, act as precipitation sites for various phases (considered MnS and TiN) in A. Consequently, they become the potential nucleation sites for AF formation. This is due to that iron and the other metallic atoms in the steel matrix diffuse into the oxides on the basis of exchange mechanism between vacancies and atoms. It shows the oxides having higher cation vacancies concentration come into consideration for the realisation of above mentioned process. Among these oxides, Ti<sub>2</sub>O<sub>3</sub> can be considered preferentially [8]. The A-grain boundary surfaces are very favourable nucleation sites for Band/or WF formation, usually. However, certain particles can be active in term of AF-plates nucleation, competing with some advantage with A-grain boundary surfaces. The onset of the Atransformation leading to the primary AF-plates formation takes place at complex particles consisting of MnS which are e.g. surrounded by CuS and/or at Mn and Ti rich oxides. According to Madariaga and Gutiérrez [3], the role of (Mn, Cu)S by the AF nucleation process is related to the different behaviour of A/CuS and AF/CuS interfaces. These basic conditions are schematically presented in Fig. 3. On the other hand, AF nucleation at complex Ti-and Mn-rich oxides is usually associated with the formation of localised Mn-depleted zone in the vicinity to the steel matrix/oxide interface [5, 8].

As expected, the TiN formation is favoured by an increase in the amount of free nitrogen in steel being available for precipitation of given nitride phase. The Ti-addition to steel by deoxidisation process can be bound as  $Ti_2O_3$  after steel solidification. In this case, TiN formation is a result of an exchange reaction with Mn. At low and intermediate nitrogen levels in steel, the MnOTiO<sub>2</sub> particles can be formed as it corresponds to the following reaction [8].

$$Ti_2O_3 + Mn + N \rightarrow MnOTiO_2 + TiN$$
<sup>(1)</sup>

At high nitrogen content  $(MnO)_2TiO_2$  is more likely reaction product. The applied Ti volume fraction changes the phase composition of obtained inclusion particles. The higher Ti content leads to the reduction amount of MnOSiO<sub>2</sub> in steel. The considered Mn-Si phase is substituted with Mn-Ti complex oxides. The type of obtained inclusions is changed in dependence on Ti-content in steel. In case the lowest Ti-addition, the main type is  $(MnO)_2TiO_2$  which has near cubic symmetric. On the contrary, after higher Ti-addition in steel, the detected phase is MnOTiO<sub>2</sub> having rombohedral crystallographic structure, very similar to Ti<sub>2</sub>O<sub>3</sub>. These phases are characterised with very near lattice parameters what complicates their crystallographic distinguishing process from MnSiO<sub>3</sub> to Mn-Ti complex oxide phase results in a transition form side plate ferrite microstructure (WF, B) to AF one [4]. Therefore we can conclude, the Mn-Ti oxide particles, especially Ti<sub>2</sub>O<sub>3</sub>, have more potency than MnSiO<sub>3</sub> for intragranular AF nucleation.

#### 4. Influence of Mn-depleted zone in steel on AF-formation

As shown in Fig. 4, AF in steel containing fine  $Ti_2O_3$  particles nucleates during cooling process at complex precipitates of  $Ti_2O_3$  adhered with MnS and TiN. Contrary to this effect, in steel which does not contain the adhered MnS and TiN particles on  $Ti_2O_3$ , the nucleated AF amount decreases markedly. These results demonstrate, MnS and TiN adhered on  $Ti_2O_3$  contribute greatly to the nucleation of AF and for this reason, it is possible that  $Ti_2O_3$  can also act as "bearer" of above given nucleants. It defines with more precision the  $Ti_2O_3$  role by the AF nucleation process and from this point of view the mechanism of AF nucleation will be discussed. Based on the micrograph presentation (Fig. 4), schematic illustration of the adhered secondary phase precipitates on the Ti<sub>2</sub>O<sub>3</sub> and AF transformation way are summarised in Fig. 5 [8]. Simultaneously, this figure indicates, in relation to above given reaction, a possibility how Ti<sub>2</sub>O<sub>3</sub> inclusions are modified due to Mn-atoms diffusion from matrix into Ti-oxides [9]. The AF formation at complex precipitate with Mn-depleted zone in term of difference in transformation temperature as it corresponds to the localised increase of chemical free enthalpy change can be held for preferential nucleation process. The TiN effect should also be considered because AFformation is markedly limited in the absence of the nitride on  $Ti_2O_3$  particles. This effect results from decrease in TiN interfacial energy for AF nucleation. Increased in interfacial energy by ferrite nucleation is 0.20Jm<sup>-2</sup> in case its semicoherent interface with AF matrix. At incoherent interface A/A, this energy reaches to  $0.85 \text{Jm}^{-2}$ . The lattice coherency between AF and TiN (FCC) is relatively good, mismatching ratio is as low as 3.8%. The interfacial energy is in this case very low, only 0.15Jm<sup>-2</sup>, approximately.



Fig.4 Extraction replica of Ti2O3 inclusion with adhered MnS and TiN [5]



Fig.5 Schematic illustration of inclusion in steel deoxidized with Ti

#### 5. Retarding effect of Si and Al on AF formation

This analysis is devoted to the study of retarding effect due to Al in steel, which is analogical to the Si effect. In this case we can detect MnSiO<sub>3</sub> inclusions. It was found, AF nucleation potency of this inclusion type is decreased substantially in comparison with Ti-Mn oxide particles effect. The Ti<sub>2</sub>O<sub>3</sub> inclusions only absorb a small amount of Mn at higher Si content in steel. This fact can be ascribed to the strong attractive interaction between Mn and Si atoms in A-structure [10]. The higher content of the Si in steels, the stronger the attractive action between Mn and Si. The Mn absorption in  $Ti_2O_3$  is inhibited at higher Si content in steel. The considered interaction between Mn and Si leads to suppression of Mn segregation in A-matrix [11]. The Ti-level in the oxide particles decreases with increasing Al-content (Fig. 6). The Al has a greater oxygen affinity than Ti and for this reason,  $Al_2O_3$  is likely to replace  $Ti_2O_3$  and increase Al-content. Previously was found, Ti<sub>2</sub>O<sub>3</sub> particles are able to absorb Mn-atoms from surrounding steel matrix what results in the Mn-depleted zone formation around Ti-oxides. The Mn-absorption is associated with higher cation vacancy concentration in  $Ti_2O_3$ . Since  $Al_2O_3$  is anion vacancy type oxide, the considered Mn-atoms absorption in this inclusion is not possible. From this reason  $Al_2O_3$  particles might not provide the nucleation sites for AF formation. On the basis of these results, we can conclude, the transition from  $Ti_2O_3$  to  $Al_2O_3$  with increasing Alcontent in steel leads to the microstructure type modification. Owing to a shortage of potential intragranular nucleation sites, the transition from AF to B and/or WF microstructure is realised.



Fig.6 Average Ti-content in the oxide particles (influence of Al in steel) [10]

#### 6. Conclusions

A study has been carried out to clear up the basic chemical metallurgical principles controlling AF formation in comparison with side particles (WF, B) nucleation process. The effect of some inclusions known as potential AF nucleants is taken into consideration. The AF particles are intragranularly nucleated, while the intergranular nucleation corresponds to WF and B initiation. The AF nucleation rate is expressed by two main factors. They are chemical free enthalpy change for development of nucleation process and a decrease in interfacial energy accompanied ferritic phase nucleation on TiN having relatively high lattice registry with AF particles. The effect of Si and Al content in steel on AF formation is analysed.

The present results demonstrate how the change in inclusion types modifies the mechanism of A decomposition into AF to the detriment of WF and B (side plate particles).

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