

Checking the metallurgy with the aid of inclusion analysis

J. Senberger ^{a*}, A. Zadera ^a, J. Cech ^b

^a Department of Foundry, University of Technology, Brno, Czech Republic

^b ZDAS a.s., Strojirenská 6, Zdar nad Sazavou, Czech Republic

* Corresponding author. E-mail address: senberger@fme.vutbr.cz

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Abstract

Results of studying the influence of inclusion morphology on properties of heavy casting are given. The inclusion morphology is dependent on content and kind of the deoxidizing element. Due to segregations the inclusions can be formed in heavy castings under different conditions (by concentration of deoxidizing elements) than in castings of common size. In heavy casting during deoxidation the inclusions of the IVth type occur more frequently. Deoxidation with zirconium shows to be for some heavy casting unsuitable one. Similarly in castings deoxidized with cerium and lanthanum the inclusions of greater sizes occur that can unfavourably influence the steel properties and increase the tendency to crack formation. The inclusion morphology after deoxidation with magnesium is also unsuitable for heavy castings.

Keywords: Deoxidation; Heavy castings; Morphology of inclusions

1. Introduction

Prof. Bůžek published in 1969 a more accurate classification of inclusions in cast steels [1]. He made more accurate the original inclusion classification by Simps and Dahle [2] on the base of experimental study of steel deoxidation with chosen elements in laboratory conditions. Works by Bůžek aimed at deoxidation equilibriums and formed products were often cited in world literature. Modification of cast steels with calcium with the aim of changing the oxides and sulphides to inclusions of the Ib type was of practical importance. This theoretical knowledge was then used in manufacture of castings from low-alloy manganese steels destined for arctic conditions with guaranteed value of KCV not above -60 °C only. Bůžek also pointed out the formation of inclusions of the IVth type in steels with great excess of dominant deoxidizing element.

Inclusions are most often divided to exogenous and endogenous ones. The endogenous inclusions are formed due to

chemical reactions in liquid, solidifying, and solid metal too. Exogenous inclusions have they origin in physical effecting of liquid metal on ceramic material of the mould, in spattering of metal during casting or in slag residues from the ladle. The presented paper isn't engaged in exogenous inclusions. But there also exist the inclusions formed by reaction in metal that further on contain particles of exogenous origin as will be given hereinafter.

According to the origin the oxidic inclusions can be divided to reoxidation and deoxidation ones. Deoxidation inclusions are formed during final deoxidation of steel in the ladle. Reoxidation inclusions are formed during casting and mould filling largely by reaction of metal with oxygen in atmosphere. Partially they are also formed by reaction of metal with ceramics of the casting system and the mould face. Besides oxygen also sulphur and nitrogen can transfer in steel from the mould face. In casting surface layers cast in moulding material that liberates nitrogen after casting a surface layer similar to the layer forming during steel nitriding is formed [3]. The method of steel deoxidation

further on influences also the morphology and composition of sulphides and nitrides. Among inclusions are sometimes included also the metal phases, metal inclusions, representing a phase formed on the base of separation of the deoxidizing element as a result of decreasing its solubility in the matrix during temperature drop. Carbides and also those ones that are formed by crystallization from the solid phase are not indicated as inclusions. Endogenous inclusions can be divided also according to chemical composition to oxides, sulphides, oxisulphides, and nitrides. In the case of deoxidation inclusions-oxides their composition corresponds to deoxidation reaction. These inclusions are formed in liquid steel already in the ladle after adding the deoxidizing element. Sulphides and nitrides are formed usually during solidification only in interdendritic spaces on the base of enriching the melt by segregation of reacting elements or after solidification from oversaturated solid liquid. In the case when forming oxides dissolve sulphur the oxisulphides are formed. Elements participating in solubility of sulphur in oxides are Mn, Ca, Mg.

According to the above mentioned classification the morphology of inclusions of the Ist type corresponds to globular formations of the size even several tens of micrometers. Inclusions of the IInd type appear on the metallographic sample as rows of inclusions on dendrite boundaries. The IIIrd type of inclusions are angular formations of the size most frequently up to 10 µm. Inclusions of the IVth type are represented by inclusion clusters of diameter often more than 100 µm.

According to morphology and composition of inclusions the steel conditions after deoxidation and influence of deoxidation on steel properties can be estimated. In heavy castings the conditions for forming the inclusions are influenced by solidification time and thus by important microsegregation and macrosegregation of elements. Due to segregations of elements sooner the inclusions caused by high concentration of the deoxidizing element are formed in heavy castings. The work is a result of studying the influence of inclusions on properties of heavy castings.

2. Deoxidation of steel with aluminium

Most of melts of cast steel is deoxidized with aluminium. For cast steels the resulting content of aluminium dissolved in the matrix of 0.025 % (0.030 %) up to 0.050 % is recommended. With given aluminium content the equilibrium oxygen activity under casting temperature in unalloyed steels is ca. 2.5 ppm. But in practice the aluminium activities range often within the interval of 4 up to 10 ppm. Higher contents of oxygen activities are caused by oxygen that transfers in steel from slag. In the case of slag saturated with iron monoxide the oxygen is divided between metal and slag according to the relation as follows:

$$L_O = \frac{[FeO]}{[O]} = \frac{100}{0,23} \quad (1)$$

In the case of well deoxidized slag containing 1 % FeO the 23 ppm of oxygen is in equilibrium with this slag in steel. In the case of „black“ slag containing more than 3 % FeO the equilibrium oxygen activity in steel according to (1) is higher than 70 ppm. With low concentrations of reacting elements the deoxidation

reactions in liquid steel are running more slowly. Resulting oxygen activities can be even several times higher than equilibrium activities.

After deoxidation with sufficient aluminium content (above 0.025 %) the deoxidation product is aluminium oxide. Sulphur isn't dissolved in aluminium oxide and after the right deoxidation of steel with aluminium the sulphur under liquidus temperature is bond in interdendritic spaces to manganese. Fig. 1. gives an example of inclusion morphology in steel deoxidized with aluminium.

Dark formations in the figure are aluminium oxides corresponding with composition to Al₂O₃ oxide or they can contain also silicon. From the morphological point of view they appear as the IIIrd type. In melts with deep deoxidation the aluminium oxides contain the Ca and Mg concentration up to 10 %. Besides aluminium oxide the MnS sulphides are separated that differ from Al oxides with light colour (fig. 1.).

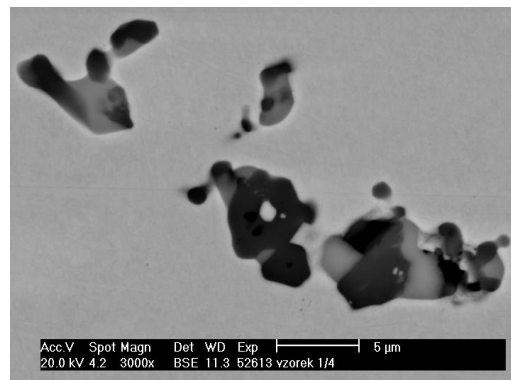


Fig. 1. Aluminium oxides and manganese sulphides after deoxidation with Al

Sulphides almost stoichiometricly correspond to composition of MnS sulphide. Aluminium oxides can serve as crystallization centres for sulphides. In steels from acid furnaces the presence of Ca and Mg in inclusions wasn't observed by the authors. The presence of sulphides of the IInd type has an important influence on steel toughness. With modification of steel after Al deoxidation with calcium the content of sulphides of the IInd type decreases with growing calcium content and steel toughness increases. Steel toughness reacts sensitively on a way of inclusion separation. Steel toughness can serve as a criterion for evaluating the last phase of steel deoxidation. In steel made in a basic arc furnace with low oxygen activity (under white slag) usually up to 10 ppm Ca occurs before tapping. The given calcium content occurs in steels in spite of the fact that ferroalloys containing Ca were not added in steel. It suggests about the slag origin of Ca in steel. Presence of even low Ca concentrations leads to decreased occurrence of inclusions of the IInd type. With the presence of Ca in steels from basic furnaces also the higher toughness values in these steels in comparison with steel made in an acid furnace can be explained.

An example of morphology of inclusions of the IInd type is given on fig. 2. The MnS sulphides often form chains long up to hundreds of micrometers. The presence of extensive sulphides of the IInd type can also cause, besides decreasing of steel toughness,

the initiation of cracks in heavy castings. Separation of MnS in a form of individual inclusions of the IIIrd type is more favourable. Manganese sulphide occurs in steels usually in a form of the IInd and IIIrd type. In steels with low carbon content the inclusions of the IInd type are more separated, in steels with higher carbon content they are the inclusions of the IIIrd type being more separated.

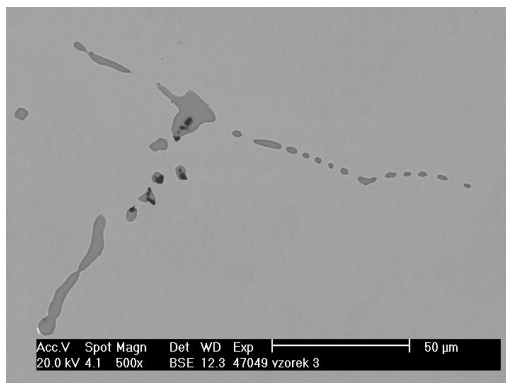


Fig. 2. „Chain“ of sulphides of the IInd type

For removing the sulphides of the IInd type in steels deoxidized with aluminium the modification of steel with calcium is used. The MnS sulphides are changed during modification to complex Al, Mn, Ca oxisulphides. The presence of oxisulphides of the Ib type in steel is a cause of high toughness even under negative temperatures.

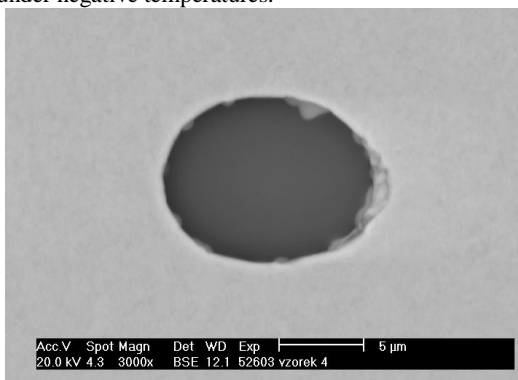


Fig. 3. Al, Si, Mn oxisulphides in insufficiently deoxidized steel

In insufficiently deoxidized steels with Al content under 0.015 % the inclusions of the Ist type occur. The questions are oxisulphides containing particularly Si, Mn and Al. The higher oxygen activity in steel the more Mn and less aluminium the oxisulphides contain. An example of oxisulphide in insufficiently deoxidized steel is on *fig. 3*. Given oxisulphide types are also formed during steel reoxidation when casting. In such a case they occur only in casting places with high oxygen activity. In other casting places the inclusion composition corresponds to well deoxidized steel.

A light envelope of complex oxisulphide on *fig. 3* is formed by MnS sulphides. In heavy castings the inclusions of the Ist type occur rarely.

3. Deoxidation of steel with zirconium

Zirconium similarly as aluminium is a middle strong deoxidizing element in steel. At the same time it has higher affinity to nitrogen in comparison with aluminium. With higher zirconium concentration in steel after deoxidation the oxides and nitrides of the IVth type are often separated in steels. Particularly in heavy castings the occurrence of inclusions of the IVth type is frequent in steels deoxidized with Zr. The inclusions of the IVth type in melts deoxidized with Zr contain zirconium oxides and nitrides. In the case of oxides the composition corresponds to ZrO₂ oxide, in the case of nitrides to ZrN nitride. Oxides and nitrides too often contain small amount of titanium. The presence of inclusions of the IVth type after deoxidation with zirconium decreases toughness values. In heavy castings they can initiate the formation of cracks, e.g. when flame removing of risers. It is interesting that morphology of inclusions of the IVth type is similar to morphology of shrinkage porosity (*fig. 5*). Inclusions of the IVth type and shrinkage porosity too are formed in interdendritic spaces at the end of solidification. In cavities of shrinkage porosity of castings the inclusions of similar composition as chemical composition of inclusions of the IVth type are present.



Fig. 4. Zr oxides and nitrides (IVth type)

Zirconium forms with iron the ZrFe₃ compound. Under temperature of 912 °C the solubility of zirconium in iron is 0.08 % and with decreasing temperature the solubility decreases [4]. From solid solution the ZrFe₃ phase is then separated. In places with increased segregation of zirconium the mentioned compound can occur also with lower Zr concentrations in the melt sample. An example of ZrFe₃ separation in low-alloy steel deoxidized with Zr is on *fig. 6*. Separation of Zr in the given form decreases steel toughness and it can be a cause of crack formation in heavy castings. The compound composition is estimated from the Fe-Zr equilibrium diagram. Determination of Fe in inclusion with the same matrix composition by microanalysis isn't possible.

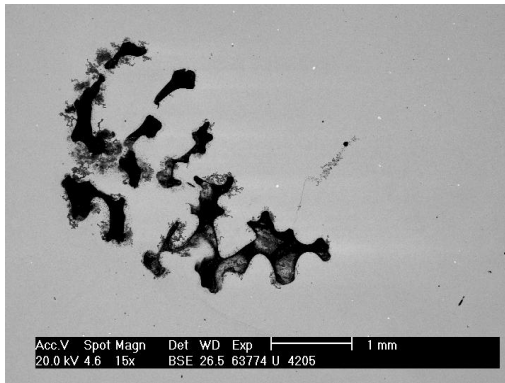


Fig. 5. Shrinkage porosity in a heavy casting

Fig. 7. shows an initiation – a crack root on separated Zr based inclusions. Dark fringing of the crack is caused by material oxidation.

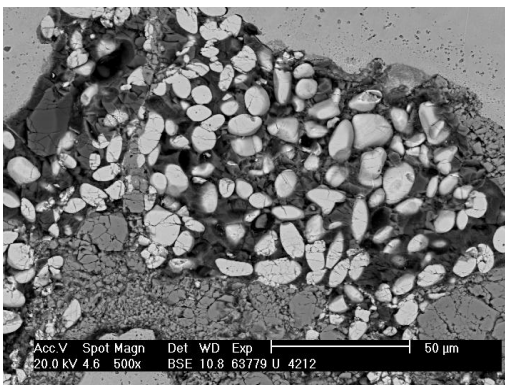


Fig. 6. ZrFe₃ separated on grain boundaries

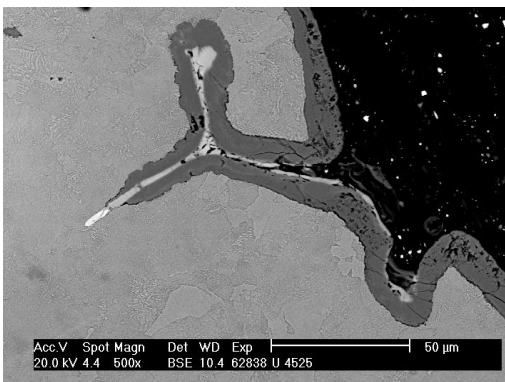


Fig. 7. Zr oxides and nitrides in crack

4. Deoxidation of steel with rare earth metals

Rare earth metals modify with optimum concentration the inclusions to the Ib type. But in consequence of segregations the melt of heavy casting is enriched with deoxidizing elements and

inclusions of the IVth type are formed. Therefore the occurrence of inclusions of the IVth type in heavy castings after deoxidation with rear earth metals is more frequent than in common castings. These inclusions contain in particular Ce, La, O and S. Ca and La oxisulphides are further accompanied with Pr, Nd and other rear earth metals. As in all cases when inclusions of the IVth type are formed the steel toughness values decrease. Risk of crack formation is increasing.

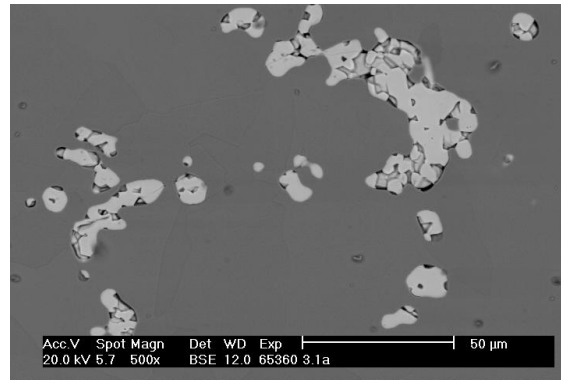


Fig. 8. Ce and La oxisulphides of the IVth type

The size of the inclusion cluster often achieves hundreds of micrometers. Individual inclusions exceed in some dimensions even the size of 50 µm. After solidification the individual phases (oxides and sulphides) are separated in inclusions. With regard to segregations the steel deoxidation with rear earth metals wasn't recommended for heavy castings.

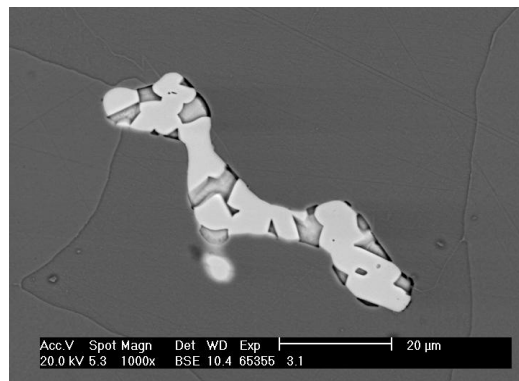


Fig. 9. Inclusion consisting of rear earth metal oxides and sulphides

5. Deoxidation of steel with magnesium

Steel deoxidation with magnesium, according to our information, isn't used in operation. Magnesium has low boiling temperature and under temperature of liquid steel it has high vapour tension. Magnesium together with calcium belongs to elements with the highest affinity to oxygen and sulphur. Magnesium can be used, similarly as calcium, for modification of inclusions after steel deoxidation with aluminium. Having

exceeded the optimum concentration the frequent occurrence of inclusions of the IVth type can be expected in castings too.

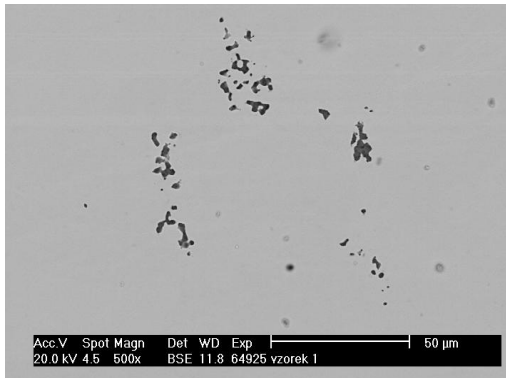


Fig. 10. Sulphides and oxides of the IVth type after deoxidation with magnesium

Inclusions were studied in castings with total magnesium content of 0.005 up to 0.021 %. With growing magnesium content the occurrence of inclusions of the IVth type was increasing (fig. 10.). After deoxidation of steel with aluminium and modification of steel with Mg the oxygen is mostly bound to magnesium and further on to aluminium or also to Si. Sulphur is mostly bound to Mg and further on to Mn too.

With magnesium content of 0.021 % the oxides and sulphides were separated solely as the IVth type. For modification of inclusions to the required Ib type it is necessary to ensure the Mg concentration of ca. 20 up to 50 ppm, i.e. similar concentration as for steel modification with the aid of Ca.

6. Conclusions

During manufacture of heavy castings a danger of forming the conchoidal fractures caused by separation of AlN aluminium nitride results from deoxidation with aluminium. Therefore some manufacturers of heavy castings use for steel deoxidation e.g. zirconium. At the end of study the inclusions in samples of heavy castings with cracks it has been concluded that the use of zirconium and rear earth metals isn't suitable in given conditions. It must be admitted that in heavy castings deoxidized with aluminium the local separation of aluminium nitrides on fracture surfaces was found out by the authors but defects of the conchoidal fracture type weren't observed on castings. Minimum aluminium content ensuring sufficient steel deoxidation and low nitrogen content is a precondition.

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