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Influence of Compound Deoxidation of Steel with Al, Zr, Rare Earth Metals, and Ti on Properties of Heavy Castings

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Abstract

Heavy steel castings deoxidized with aluminium are sometimes brittle intercrystalline failed during their service along primary grain boundaries what is initiated by aluminium nitrides and so called conchoidal fractures are formed. The tendency to forming the conchoidal fractures depends in particular on cooling rate (the casting modulus), aluminium and nitrogen contents in steel. During deoxidation, when manufacturing heavy castings, the elements with high affinity to nitrogen, zirconium or titanium, are added to steel that would decrease nitrogen activity by the bond on stable nitrides. The formation of stable nitrides should reduce the tendency of steel to the formation of conchoidal fractures. Deoxidation was thermodynamically analyzed at presence of the mentioned elements. For particular conditions a probable course of deoxidation was estimated at test castings. The deoxidation course was checked by microanalysis of deoxidation products (inclusions). For service and experimental castings the anticipated composition of inclusions was compared. It has been proved that in heavy castings with high aluminium contents in steel under studied conditions neither the addition of zirconium nor of titanium nor of rare earth metals will prevent the formation of conchoidal fractures.

Keywords: Steel casting, Deoxidation, Conchoidal fractures

1. Introduction

Mechanical properties of the material in steel castings are influenced in particular by the presence of foundry defects, by morphology of inclusions, and reoxidation products. In heavy castings the effect of the mentioned factors is the more important the higher modulus have the castings or their parts. In some cases the mechanical values of heavy castings are decreasing under values prescribed by the standard. The standards take into account the decrease of mechanical values. And therefore the standardized values are valid most frequently for wall thicknesses up to 100 mm. For values determined by the static tensile test at heavy castings (the casting modulus of ca 10 cm and more) it is possible to observe the decrease of values that depend on deformation of the test bar, i.e. of ductility, contraction, and of breaking strength and breaking stress too. The yield value isn't changed with the casting thickness or it is changed slightly only [1]. Similar dependences were found out at heavy castings with the modulus higher than 30 cm [2]. In this case the mechanical values were influenced by the change of chemical composition of the steel caused by segregation of elements, particularly of carbon. Dynamically stressed castings can be failed by low cycle fatigue. A failure of a casting as a machine part during its service belongs to the most severe casting failures with huge financial losses for casting manufacturers. In such a case the crack is initiated by a foundry defect of a supercritical size. The size of a foundry defects depends on steel properties. The most frequent foundry defects are shrinkage porosities and inclusion clusters, in particular continuous separations of inclusions in interdendritic spaces in some casting places that may have a connection with segregation of elements. Steel toughness can be also decreased by separation, precipitation of particles along the primary grain boundaries during steel cooling. Embrittlement is often caused by separation of aluminium nitride as it was observed already in 60th and 70th of last century [3, 4]. Steel embrittlement can be also caused by other reasons as e.g. by separation of metallic phases along the grain boundaries or separation of inclusions in a form of the IVth type. All those phenomena are connected with the last phase of steel production, in particular with steel deoxidation. Therefore the metallurgists sometimes try to replace aluminium with other element or to choose a combined deoxidation with more elements. A combination of an element with high affinity to oxygen with an element that will bind nitrogen is often chosen. Such measurements would prevent the formation of conchoidal fractures. But deoxidation with aluminium is very well checked up in practice. Unsuitable replacement of deoxidizing aluminium with other element or a combination of elements can cause serious problems in casting manufacture. Equilibrium oxygen and nitrogen activities with concentrations of elements used for deoxidation and denitration can be determined by thermodynamic calculation. Thermodynamic calculation serves only for estimation which element will bond oxygen and which one will bond nitrogen. The main problem in calculation is difficult determination of activities of products that are formed during reaction. Therefore it is presumed in calculation that compounds (oxides or nitrides) forming during reactions can be considered pure matters (oxides and nitrides of one element). Then in such a case when choosing a standard state of a pure matter for those products their activity can be considered a unit one. The composition of deoxidation products is then checked by their microanalysis and applicability of the given calculations is estimated. Another problem of the thermodynamic calculation consists in a fact that a part of deoxidation and denitration elements determined from a sample spectrochemically is bound on compounds (oxides, nitrides). Determination of concentrations or activities of elements dissolved in steel is unfeasible in technical practice.

2. Thermodynamic analysis of the course of compound deoxidation with Al, Zr, Ce, and Ti

Aluminium is most often used for steel deoxidation. In case of heavy castings aluminium can be partly or quite replaced with an element or elements with high affinity to oxygen and possibly to nitrogen too. Aluminium remains in some foundries a basic deoxidation element for manufacture of heavy castings and it is further on complemented with an element with high affinity to nitrogen. As this element has a higher affinity to nitrogen than aluminium, its bond on nitrogen is expected what should prevent the formation of aluminium nitrides. For combined deoxidation with aluminium and other element the use of Zr, Ce, or Ti can be considered. But the use of these elements causes in some cases an important drop of plastic properties and toughness. Combined deoxidation with aluminium and calcium can be further on used that seems to be very suitable for heavy castings. This deoxidation was already researched in details in the past and its favourable effects are known. The course of following reactions [5] in the melt is oftenest expected when deoxidizing with aluminium, zirconium, titanium, and cerium.

$$2[\mathrm{Al}]+3[\mathrm{O}]=\langle \mathrm{Al_2O_3}\rangle \quad \Delta G^\circ = -1\,207\,036+391{,}25T \quad (1)$$

$$[\mathrm{Zr}]+2[\mathrm{O}]=\langle \mathrm{ZrO_2}\rangle \quad \Delta G^\circ = -782\,910+227{,}93T \quad (2)$$

$$[\mathrm{Ti}]+2[\mathrm{O}]=\langle \mathrm{TiO_2}\rangle \quad \Delta G^\circ = -677\,652+228{,}22T \quad (3)$$

$$2[\mathrm{Ce}]+3[\mathrm{O}]=\langle \mathrm{Ce_2O_3}\rangle \quad \Delta G^\circ = -1\,437\,432+410{,}68T \quad (4)$$

For the reaction of aluminium, zirconium, and titanium with nitrogen in molten steel the reactions are expected as follows:

$$[\mathrm{Al}]+[\mathrm{N}]=\mathrm{AlN} \quad \Delta G^\circ = -269\,007+114{,}34T \quad (5)$$

$$[\mathrm{Zr}]+[\mathrm{N}]=\mathrm{ZrN} \quad \Delta G^\circ = -312\,679+116{,}55T \quad (6)$$

$$[\mathrm{Ti}]+[\mathrm{N}]=\mathrm{TiN} \quad \Delta G^\circ = -302\,910+110{,}40T \quad (7)$$

According to equations (5) up to (7) it is possible to determine the nitrogen equilibrium activity in steel with given concentration of the deoxidation element, i.e. it can be evaluated if it is possible to expect a decrease of nitrogen activity connected with formation of nitrides of the chosen element for the given concentration of nitrogen and the chosen element.

Chemical composition and morphology of inclusions in dependence on a type of the deoxidation or denitration element were studied on test castings with a thermal modulus of ca 10 cm. The material of studied castings was steel containing 0.20 % C; 0.095 % Al and 0.0105 up to 0.0155 % N. On the one hand only aluminium, and on the other further on aluminium in combination with one of chosen elements (Zr, Ti, or Ce) were used for deoxidation of castings. For thermodynamic calculation the aluminium content was chosen in two levels, and namely 0.010 % and 0.100 % Al.

Equilibrium oxygen activities for equilibrium between oxygen and aluminium under different temperatures and aluminium concentrations were calculated for the above mentioned chemical composition and aluminium concentrations. For oxygen activities determined in such a way the activities of deoxidation elements Zr, Ti, and Ce were further on calculated (Table 1.). Then it is possible to find out from these results which activities of the chosen deoxidation elements will ensure under given temperature the same oxygen activity (the deoxidation degree) as the chosen aluminium concentration. The calculation was done for steel temperature of 1600 °C and further on for calculated steel temperature in the mould cavity after pouring the experimental castings and liquidus temperature. Results are given in Table 1. In calculations the activities tantamount to concentrations were considered in Table 1.

If the activities of deoxidation additives are low, then it can be assumed that they equal to concentrations. In contrary case it is necessary to convert the activities into concentrations with use of interactive coefficients. In case of thermodynamic calculation under different temperatures it is necessary to consider the dependence of interactive coefficients on temperature.

Table 1.
Equilibrium Henry activities of Zr, Ti and Ce after deoxidation of steel with Al of C = 0.2 % content

Al content [weight %]	T=1873 K			T=1813 K			T=1793K		
	a_{Zr}	a_{Ti}	a_{Ce}	a_{Zr}	a_{Ti}	a_{Ce}	a_{Zr}	a_{Ti}	a_{Ce}
0.1	0.0035	3.2	0.0002	0.0038	4.2	0.00015	0.0038	4.61	0.00014
0.01	0.00017	0.15	0.00002	0.00017	0.2	0.000015	0.00017	0.21	0.000014

As follows from results given in Table 1. the lower concentrations of zirconium and cerium are sufficient for achieving the same oxygen activity in the melt as in case of deoxidation with aluminium. Further on it is evident from the results that temperature hasn't large influence on the change of calculated equilibrium activities of Zr and Ce. Only titanium shows important changes of equilibrium activity. Table 2 gives chemical composition of metal determined from samples taken from thermal axis of experimental castings.

Table 2.
Content of C and elements used for deoxidation in weight %

	C	Al	Zr	C	Al	Ti	C	Al	Ce
min.	0.17	0.092	0.018	0.16	0.095	0.016	0.16	0.092	0.015
max.	0.19	0.096	0.027	0.2	0.1	0.009	0.19	0.096	0.06

Table 3.
Equilibrium concentrations of Al, Ti, and Zr [%] in steel with content of C = 0.2 % and 0.010 % and 0.018% N under liquidus temperature

	nitrogen activity	equilibrium concentration	nitrogen activity	equilibrium concentration
Al	0.010	1.667	0.018	0.926
Ti	0.010	0.12	0.018	0.066
Zr	0.010	0.11	0.018	0.060

By comparison of real zirconium concentrations in the experimental casting deoxidized with aluminium and zirconium (Table 2.) and calculated equilibrium activity of zirconium (Table 1.) the formation of zirconium based oxides can be expected in the experimental casting. With zirconium concentration higher than ca 0.004 % under the given conditions (Al content in the range of 0.01 – 0.1 weight %) zirconium has higher affinity to oxygen than aluminium.

Under lower temperatures the presumption is valid too. Thus the oxides (deoxidation products) above all zirconium based ones would be present in the casting.

In the casting deoxidized with aluminium and titanium the titanium affinity to oxygen under the given conditions is always lower than the aluminium affinity. With decreasing temperature the titanium affinity to oxygen in comparison with aluminium is further on decreasing. It is expected that in the melt with Ti addition the oxygen will be bound to aluminium and titanium will not occur in oxides.

In case of the aluminium and cerium deoxidized casting the affinity of cerium to oxygen under the given conditions is higher than that one of aluminium, and namely under all considered temperatures. Thus it can be expected that oxides containing mainly cerium would occur in the casting.

The above mentioned estimation takes into account the concentrations of aluminium dissolved in the solution instead of the activity. Concentration of deoxidation elements in the solution will be in reality lower as their part will be bound on oxygen. At the same time it cannot be expected that so low oxygen activities will be achieved as that ones determined during thermodynamic calculation. It can be expected in real conditions that deviations between calculated and real oxygen activities will be growing with increasing affinity of the deoxidation element to oxygen. Speaking in other ways, if e.g. cerium is added after deoxidation with aluminium, the decrease of oxygen activity can be expected partly only.

For the reaction of the mentioned elements with nitrogen the equilibriums for liquidus temperature were calculated. For the calculation the nitrogen concentration was chosen in two levels, and namely 0.0100 and 0.0180 % N. Calculation results are given in Table 3.

It results from comparison of calculated equilibrium concentrations of elements with the affinity to nitrogen given in Table 3. and real concentrations of these elements in experimental castings that concentrations of denitration elements in steel are lower than they would be under the considered conditions. Thus the formation of nitrides in liquid steel cannot be expected in practice. Nitrogen will be separated in a form of nitrides after casting solidification only.

3. Analysis of inclusions in experimental castings

Inclusions were analyzed on samples taken from experimental castings in a cubic form of an edge of 500 mm equipped with a runner of 400 mm diameter. The casting material was steel deoxidized with aluminium in a ladle and next above mentioned deoxidation elements were added in the mould cavity only. Metallographic samples were made from the material taken from bars for tensile tests after their breakage. The material for making the test bars was taken on the one hand from thermal axis ca 50 mm from the casting bottom, and on the other from thermal axis ca 400 mm from the casting bottom.

3.1. Deoxidation with aluminium

In steel castings of common weight after deoxidation with aluminium the oxygen is bound to angular inclusions of the IIIrd type with stoichiometric ratio Al:O ~ 2:3. Composition of inclusions corresponds to aluminium oxide. Sulphur is bound to manganese sulphides of the IInd and IIIrd type. Chemical composition corresponds to manganese monosulphide (MnS).

In heavy castings after deoxidation with aluminium the oxygen is bound to globular aluminium oxides with a MnS envelope. MnS in a form of inclusions the IInd type is separated only in places with strong segregation of sulphur, e.g. under the riser in the thermal axis. Oxides on the metallographic sample given on Figure 1. look like an Ib type. With 2000 x magnification (Figure 2.) it is possible to observe a dark centre of the Al_2O_3 oxide with the addition of up to 10 at. % of Mg or Ca. The envelope contains MnS often with the additive of Ca or Mg.

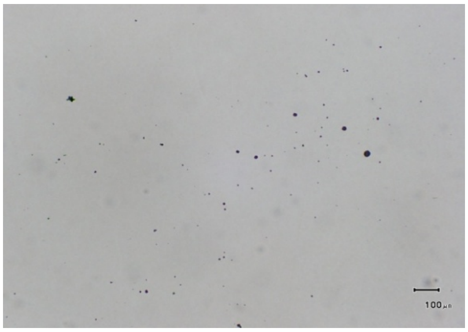

Fig. 1. Aluminium oxides with the MnS envelope (100 x)

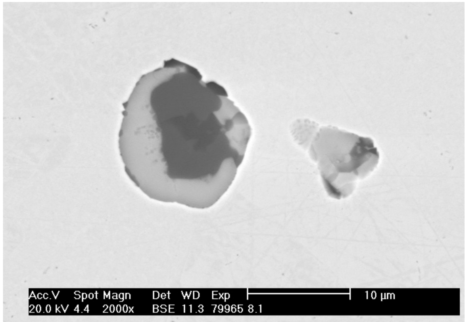

Fig. 2. Aluminium oxides with the MnS envelope (2,000 x)

3.2. Deoxidation with aluminium

In casting with high excess of deoxidation elements the inclusions of the IVth type occur that are a cause of an important decrease of mechanical properties in particular in steels with higher carbon content. In the experimental casting, where the deoxidation with the aid of Al only was used, the inclusions of the IVth type were not observed. In the casting deoxidized with Al + Zr a mass occurrence of inclusions of the IVth type was observed as shown on Figure 3. Both oxygen, and nitrogen too, are bound to aluminium. Figure 4. gives an example of an inclusion consisting of three phases. The dark phase is composed of aluminium oxide with Mg addition, the grey phase represents the Mn sulphide with Ca, Mg, and Zr addition, and the white phase contains zirconium oxide above all.

Before zirconium addition the steel was deoxidized with aluminium. After zirconium addition the aluminium oxides were reduced with zirconium partly only up to its consumption for the reaction. Therefore a part of aluminium oxides was retained. Zr and Al oxides in the next cooling and solidification phase served as crystal nuclei for separation of manganese sulphides. Aluminium oxides in some cases contained even more than 10 at. % of Mg. Besides manganese the sulphides contained calcium too. In some sulphides the content of calcium was higher than that one of manganese. In the studied sample calcium reacted primarily with sulphur and magnesium primarily with oxygen. Phases containing zirconium and nitrogen were not found.

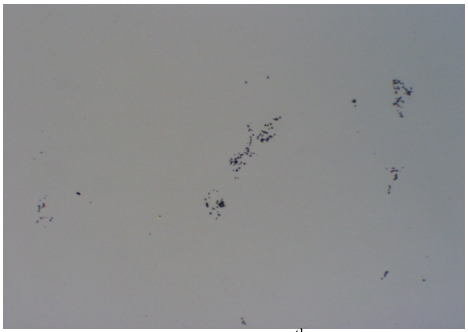

Fig. 3. Inclusions of the IVth type (100 x)

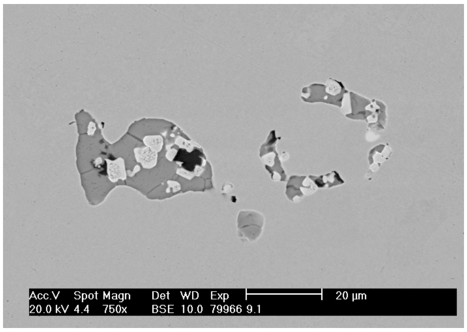

Fig. 4. Complex inclusions after deoxidation with Al+Zr (750 x)

3.3. Deoxidation with aluminium and titanium

Titanium content in steel was insufficient for formation of titanium oxides. It can be expected that titanium will be mostly bound to nitrogen in a form of TiN. Oxygen will be bound to aluminium and sulphur to manganese. Figure 5. shows globular aluminium oxides with sulphide envelopes again. Separation of inclusions is similar as after deoxidation with aluminium. On Figure 6. the grey phase corresponds to Mn sulphide with Ca addition. The dark phase is formed by aluminium oxide with Mg addition. The sharp angular inclusion corresponds to TiN. Calcium is primarily bound to sulphur and magnesium to oxygen in the given sample. Titanium bonds nitrogen and forms many nitrides. Morphology of titanium nitride corresponds to the phase separated from the solid solution.

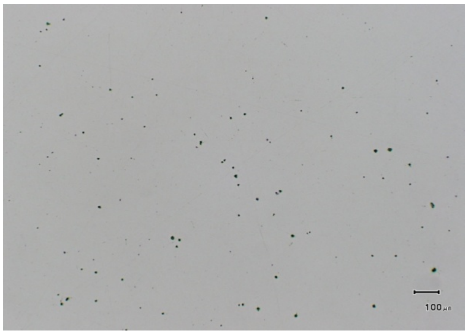

Fig. 5. Globular inclusions after deoxidation with Al+Ti (100 x)

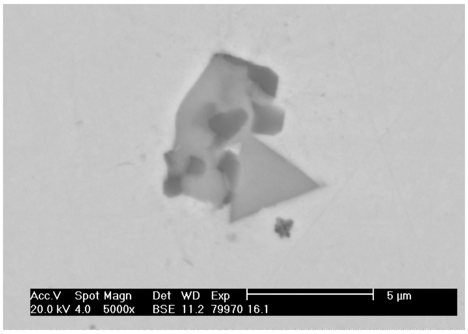

Fig. 6. A complex inclusion after deoxidation with Al+Ti (5,000 x)

3.4. Deoxidation with aluminium and rare earth metals

Rare earth metals were added in the mould cavity by means of misch metal containing of ca 60 % Ce. The addition of rare earth metals was sufficient for reduction of all oxides present in steel. The excess of rare earth metals participated in the bond with sulphur. After the addition of rare earth metals in the mould cavity the sulphur content importantly decreased. Nitrides of rare earth metals were not observed on samples. Figure 7. shows typical complex oxides of rare earth metals with Ca addition. Similarly as after the addition of zirconium the needles containing aluminium and nitrogen occurred on the sample (Figure 8.).

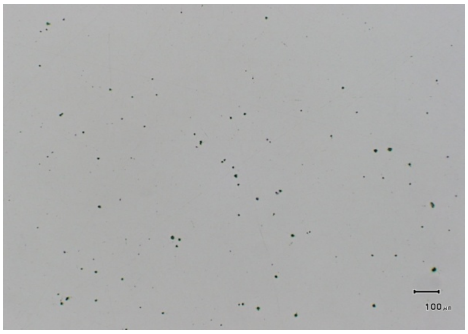

Fig. 7. Complex oxisulphides of rare earth metals (1,000 x)

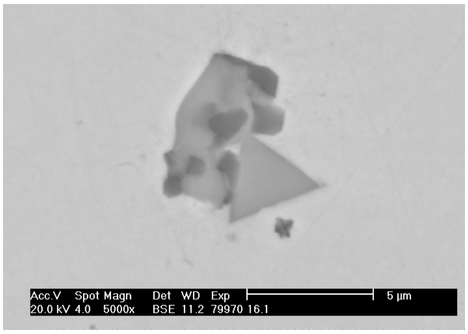

Fig. 8. Needles of aluminium nitride (5,000 x)

4. Interpretation of results of measurement

By subjective evaluation of fracture surfaces it has been found out that during the tensile test the casting deoxidized with aluminium only was failed largely by brittle intercrystalline fracture along primary grain boundaries (conchoidal fracture) and partly by transcrystalline cleavage fracture. In case of other three castings the fracture surfaces or their predominant part showed the conchoidal fracture. The occurrence of conchoidal fractures in castings with Zr and Ti additions was higher than in melts deoxidized with aluminium only.

According to thermodynamic calculation the deoxidation ability of zirconium is considerably higher than that one of aluminium. Provided that steel after deoxidation with Al contains 50 ppm of total oxygen, ca 0.020 % weight % of Zr is consumed for its total reduction to ZrO_2 in theory. The added zirconium addition of ca 0.018 up to 0.027 was consumed from a great part for deoxidation of aluminium oxide. Nitrogen and zirconium compounds were not found on studied fracture surfaces. Zirconium solubility in steel is almost zero under indoor temperature. Zirconium that isn't used for the bond with oxygen or nitrogen is separated under lower temperatures as crystals of pure Zr or Zr with Ti addition. Under the studied conditions the nitrogen addition as a denitration element was ineffective.

According to thermodynamic calculation under the given conditions the titanium cannot participate in steel deoxidation. Then the all titanium remains available for the reaction with nitrogen in austenite. But the used titanium addition is insufficient for bonding of nitrogen in liquid steel under solidification temperature. Titanium nitrides in the casting with titanium addition were common ones and morphologically they correspond to the phase separated from the solid solution. Titanium nitrides were also found in castings without the Ti addition what could witness the high affinity of titanium with nitrogen in austenite.

The addition of cerium was sufficient for reduction of aluminium oxides from previous deoxidation with aluminium. Besides cerium it is necessary to expect the presence of other elements from the group of rare earth metals. The misch metal contained ca 60 % of Ce. After the reaction of cerium with oxygen the reaction of cerium with sulphur took place. For the reaction of Ce with nitrogen no proofs were found out. After zirconium and cerium additions in castings a considerable amount of needles containing aluminium and nitrogen was observed on samples.

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