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Oxygen Activity in Melts of Fe-C-Cr-Ni Based Alloys

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Abstract

Oxygen is an element that is first purposely brought into the steel melt to remove some unwanted elements or to reduce their concentration (oxidation). In the made cast steel there is on the contrary necessary to reduce the oxygen content with the use of deoxidation to such a level in order to avoid a reaction with carbon with the formation of CO bubbles. Concentration of oxygen in steel before casting is given, in particular, by the manner of metallurgical processing and the used deoxidation process. Oxygen is found in molten steels both as chemically bound in the form of oxides and in the form of oxygen dissolved in the solution – the melt. Chemical composition of the melt strongly influences the activity of oxygen dissolved in the melt and further on the composition of oxidic inclusions forming in the melt during the reaction with oxygen. In the Fe-C-Cr-Ni based alloys in the reaction with oxygen greatly participates also chrome, whose products are often in solid state and they are the cause of forming such defects as e.g. oxidic films.

Keywords: Oxygen activity, Polycomponent solution, Thermodynamic Equilibrium, Activity coefficient

1. Introduction

Oxygen belongs with the most important elements in iron alloys, both from the metallurgical point of view and in terms of its influence on the utility properties of the metal. Oxygen is found in molten steels both as chemically bound in the form of oxides and in the form of oxygen dissolved in the solution – the melt. Steels are usually deoxidized with aluminium, whose concentrations are hundredths of a percent. In general it can be said that the oxygen dissolved in the melt significantly affects all the metallurgical reactions during steel production. By contrast, the oxygen bound to oxides influences, depending on the chemical composition and the oxide morphology, particularly the resulting mechanical properties of steel [1].

Melts of the Fe-C-Cr-Ni based alloys are the basis for the production of castings made of martensitic, austenitic, or

austenitic-ferritic (duplex) stainless steels. The achievement of austenitic structure of steel even under room temperatures requires to ensure sufficient concentration of austenite forming elements in steel, in particular Ni or Mn, C or N, which reduce temperature of the martensitic start in stainless steels under room temperature even with a high Cr content. Austenitic steels alloyed with Cr and Ni contain as a rule 18 – 35% of chromium with the nickel content of 8 – 45%. Austenitic steels belongs with the non-polymorphic steels which do not traverse the structure transformation during cooling below the solidus temperature. This leads to the attainment of a high structural stability of steel throughout the range of operating temperatures, which enables to use some grades of austenitic steel also as refractory and heat resisting steels. A disadvantage consists in a fact that it is not possible to refine the steel structure by heating and following cooling (heat treatment). The only operationally usable way for structure refinement of austenitic steels is only when they are

forming. The high chromium content in austenitic steels ensures the resistance of steel against corrosion and with increasing nickel content the austenite stability under higher temperatures increases. In the technical practice it is usual to divide austenitic steels into three basic groups, and namely to stainless, refractory and heat resisting steels [2, 3, 4].

2. Oxygen in Fe-C-Cr-Ni based alloys

The total oxygen content determined with the analysis of a chosen metal sample consists of a part of oxygen dissolved in the solid solution or the melt and further on of a part of oxygen bound to oxides.

2.1. Oxides in Fe-C-Cr-Ni based alloys

The concentration of oxygen dissolved in the melt is influenced by thermodynamic equilibrium between oxygen and the elements with higher deoxidation capability dissolved in the melt. In contradistinction to unalloyed or low alloyed steels the high alloyed chromium-nickel steels are not completely deoxidized with aluminium only. The aluminium concentration in these steels usually moves in the range of 0.01-0.02 weight % only. In the reaction with oxygen in the furnace during melting, tapping and subsequent casting therefore also participate other elements with a higher deoxidation capability such as silicon, chromium or calcium if it is used in metallurgical processing [5,6]. A very important deoxidation element with the exception of aluminium in carbon steels is also silicon. The silicon concentration in high alloyed chromium and chromium-nickel steels moves even in the range of 0 up to 1.5 or 2.0 weight %. With such high silicon concentrations according to thermodynamic calculations a strong influence of silicon on the

formation of oxides, which should be formed particularly by aluminium and silicon, can be expected. In practice, however, the silicon concentration is reduced for the reason of maintaining good weldability. Fig. 1 shows the temperature dependence of oxygen equilibrium and chosen elements for the range of the upper and lower concentration of an element in steel 1.4517. The intended concentration of elements and chemical composition of the sample described below are shown in tab. 1. In the case of main deoxidation elements the formation of Al_2O_3 , SiO_2 and Cr_2O_3 oxides is expected. Thermodynamic equilibrium with oxygen for each element is represented by two lines, and namely for the lower and upper element concentration in steel 1.4517 given by the standard.

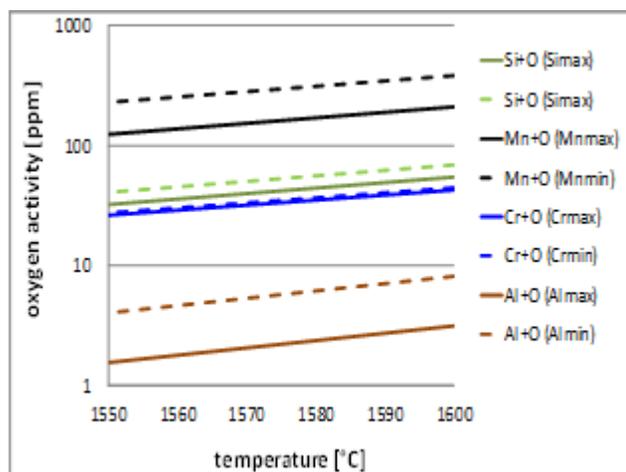


Fig. 1. Temperature dependence of oxygen equilibrium with chosen elements of steel 1.4517

Table 1.

Chemical composition of steel 1.4517 in the melt sample and the range given by the standard [weight %]

element	%C	%Si	%Mn	%Cr	%Ni	%Mo	%Cu	%Al	%P	%S	%N
min.	-	0.35	0.80	26.00	5.50	3.50	2.50				0.015
max.	0.03	1.00	1.50	28.00	7.50	4.50	3.50	0.04	0.025	0.010	0.025
sample	0.023	0.55	1.02	26.30	6.96	3.56	2.95	0.075	0.018	0.008	0.194

Under the conditions of thermodynamic equilibrium according to fig. 1 the lowest equilibrium oxygen activity in the whole range of considered temperatures and concentrations gives aluminium and further on chrome and subsequently silicon. Equilibrium oxygen activities with both elements are close and similar oxygen activities in equilibrium with chromium and silicon are achieved in such a case only when the silicon content is on the upper limit allowed by the standard. In the case of modified steels the calcium besides silicon also participates in deoxidation. This reduces the activity of SiO_2 and the balance moves to lower oxygen activities. In the case of the reaction of oxygen with chromium such products are formed, in which the activity of Cr_2O_3 is less than 1. Equilibrium oxygen activity with manganese is significantly higher than with chromium and under the considered conditions its reaction with oxygen shouldn't

occur. Fig. 2 shows inclusions in the steel 1.4517 of the composition given in tab. 1 (in tab. 2 indicated as *sample*) which are in a similar range scattered throughout the whole sample area. They are mostly small inclusions of the size to 5 max. 10 μm . Small inclusions are mainly rectangular and they can be classified according to morphology among the inclusions of the IIIrd type. The larger inclusions have a more rounded shape and they can be classified as inclusions of the Ib type. Fig. 3 shows a defect – an oxidic film. As it is evident from fig. 3, the immediate vicinity of the film is surrounded by a zone with increased quantities of inclusions. This confirms the assumption that it is clearly a defect related to reoxidation of the metal during pouring.

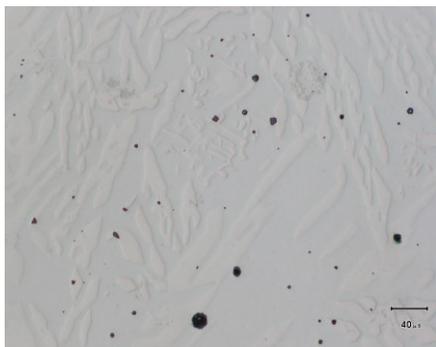


Fig. 2. Inclusions from the sample 1.4517 (magnification 200x)

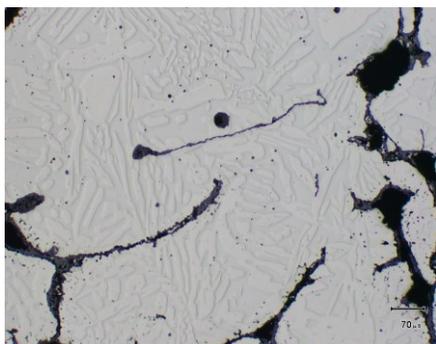


Fig. 3. The film and inclusions from the sample 1.4517 (magnification 100x)

Fig. 4 shows a defect – an oxidic film under the electron microscope with magnification 500x. The film plena was of macroscopic dimensions. Inside the film there was a cavity that appears on the REM slide as a dark place. In the place of the film the point analysis of chemical composition was made. The analyzed points are listed in fig. 4 and the analysis results are given in tab. 2.

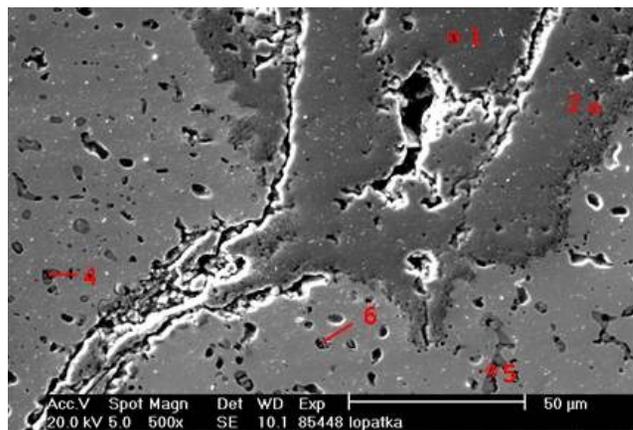


Fig. 4. Slide of the film and surrounding inclusions (magnification 500x)

Table 2.

Chemical composition of inclusions analyzed in fig. 4 in at. %.

point	O	Si	Cr	Mn	Fe	S	Al	Ca
1	49.82	0.38	29.48	4.16	16.16			
2*	47.45	3.41	41.01		6.63			
3	23.42	2.06	18.64	18.75	2.88	34.25		
4	18.50	3.31	28.04	10.54	1.48	38.13		
5	2.81	3.55	25.45	18.53	2.43	47.23		
6	54.35	32.86	4.48	0.86	5.28	0.36	1.11	0.7

* The inclusion contains the Ni traces Ni (0.94 at.%) and Mo (0.56 at.%)

The basic material of the film is formed of chromium oxides that contain partially manganese, silicon and iron (the positions 1 and 2). The film also contains a high proportion of Fe. The inclusions in the film vicinity are both the complex oxides based on Si, Cr and Fe (the position 6) both oxides mainly chromium based with a sulphidic cover of the Mn-Cr-S type (the positions 3 to 5). The localities farther from the film contain chromium oxides with the sulphidic cover and rarely the Cr-Mn oxides. The formation of manganese oxides according to the theoretical calculation was improvable but in practice it is known that the occurrence of manganese in oxides is common and it is a proof of reoxidation of the melt.

The occurrence of oxidic films is associated with a high proportion of chromium oxides, because these oxides are in the melt solid and difficultly reversely reducible and they easily form this defect type. If the casting solidifies and these oxidic films are captured its volume, they often appear as cold laps which they are

also co-forming. If the melt containing chrome and aluminium is strongly oxidized, its liquidity is also reducing, which, in the final effect, may lead to lower feeding distances than in the case of the melt of the same alloy that is deoxidized optimally. So the poorly or insufficiently deoxidized melt can cause the occurrence of shrinkage porosity. Last but not least, it is necessary to deoxidize the melt with regard to the gating system and heading technology, since it is necessary to bear in mind the danger of reoxidation of the melt that occurs due to turbulent filling of the mould, which not always can be avoided.

Similar conclusions were proved by the results of the work [4], when a change of the deoxidation and modification method of steel with Ca resulted in the change of chemical composition and morphology of inclusions. The appropriate deoxidation led to the reduction of chromium quantity in oxidic inclusions and vice versa to increasing content of Ca and Si. Deoxidation of steel and modification with calcium led to the change of morphology of

inclusions – spheroidization of inclusions. In such a way the microporosity was reduced, the liquidity and running ability of the steel were increased and surface quality of produced castings was substantially increased.

2.2. Measurement of oxygen activity in Fe-C-Cr-Ni based melts

Oxygen activity was measured for 18 melts in the melt in the furnace before vacuuming (a_{O1}) and after the vacuum processing (a_{O3}). Combined oxygen probes TSO6 and an OXYTERM device from the manufacturer Termosondy Kladno were used for measuring. Melting of chosen grades was carried out on a vacuum induction furnace CONSARC with the melt weight of 80 kg. The furnace crucible was made up of a neutral lining WEDORIT. After melting and fine alloying of the steel it was vacuum processed for 30 minutes. At the end of vacuuming the minimum

pressure of gases above the metal was moving, according to the carbon content in the melt during vacuuming, in the range of 1,000 – 3,000 Pa. During vacuuming the argon was blown into the melt through the porous block in the bottom of the furnace in the volume of 2 dm³/min. In the case of melts with higher nitrogen concentrations the nitrogen was blown instead of argon. During vacuuming of all grades of steel the metal temperature in the furnace was maintained at about 1,600 °C. Chemical composition of chosen elements in studied melts is shown in tab. 3.

Results of the measurement of oxygen activity in the melt of austenitic steel before and after its vacuum processing are shown in fig. 5. It results from the courses of oxygen activity in the melt before and after the vacuum processing that the connecting trend line for the values of oxygen activities before vacuuming has essentially the same course as the course of oxygen activities measured in the melt after vacuuming. It further on follows from it that the main influence on the measured oxygen activities for the studied set of melts has the metal temperature in particular.

Table 3.

Chemical composition of chosen elements in melts of austenitic steels

experiment num.	melt number	C [weight %]	Cr [weight %]	Ni [weight %]	Mo [weight %]	N [weight %]
1	114	0.028	18.11	9.13	0.36	0.137
2	115	0.137	18.89	8.54	0.36	0.089
3	120	0.017	17.98	28.3	0.28	0.148
4	119	0.140	17.22	28.19	0.31	0.113
5	128	0.010	29.60	30.98	0.31	0.124
6	127	0.138	29.24	27.89	0.28	0.125
7	92	0.020	17.95	8.42	0.34	0.68
8	91	0.120	17.33	8.86	0.35	0.044
9	103	0.017	17.78	28.16	0.26	0.068
10	104	0.135	17.83	28.24	0.27	0.058
11	122	0.036	27.89	8.96	0.33	0.064
12	121	0.139	27.86	9.07	0.36	0.086
13	125	0.030	27.62	8.85	0.32	0.147
14	124	0.120	27.87	8.92	0.33	0.122
15	130	0.022	27.52	27.94	0.34	0.062
16	129	0.136	28.01	28.82	0.34	0.070
34	131	0.076	23.01	18.45	0.33	0.050
35	132	0.059	22.41	18.40	0.33	0.034

The measured values of oxygen activity before and after vacuuming were put into a single statistical file. The regression coefficient R^2 of temperature dependence of oxygen activity for all measurements of oxygen activity before and after vacuuming is approx. 0.5477, i.e. the coefficient of determination R is higher than 0.74. The given dependence is statistically significant. For the given melting process and vacuum processing the oxygen activity in austenitic steels treated by the given process can be predicted on the basis of equation (1) with substituting the given metal temperature only.

$$a_o = 0,278 \cdot T - 414 \quad [ppm] \quad (1)$$

T – metal temperature [°C]

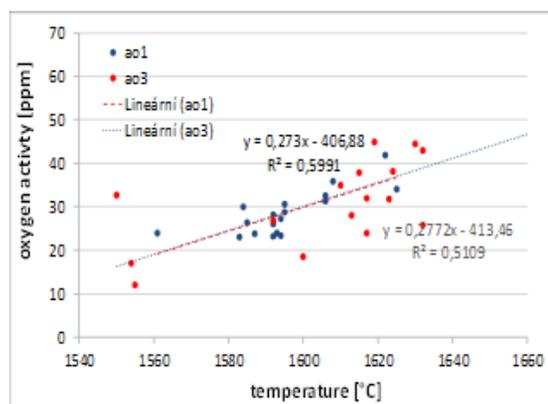


Fig. 5. Oxygen activities in the electric induction furnace before and after vacuuming in dependence on temperature

The above mentioned measured oxygen activities for the given melts were compared with thermodynamic calculation. In the calculation the chemical composition of the melt determined from the melt samples taken from each melt was considered. The calculation was carried out using the thermodynamic model developed by the authors. The oxygen activities in the set up model are based on the calculation based on the equations (2) and (3).

$$2[Cr] + 3[O] \rightarrow (Cr_2O_3) K_{Cr_2O_3} = \frac{a_{Cr_2O_3}}{a_{Cr}^2 \cdot a_O^3} = \frac{N_{Cr_2O_3} \cdot \gamma_{Cr_2O_3}}{a_{Cr}^2 \cdot a_O^3} \quad (2)$$

$$a_O = \sqrt[3]{\frac{N_{Cr_2O_3} \cdot \gamma_{Cr_2O_3}}{a_{Cr}^2} \cdot \frac{1}{K_{Cr_2O_3}}} \quad (3)$$

$N_{Cr_2O_3}$ molar concentration of chromite oxide in the inclusion [-]

$a_{Cr_2O_3}$ activity of chromite oxide in the inclusion [-]

$\gamma_{Cr_2O_3}$ activity coefficient of chromite oxide in the inclusion [-]

a_O – oxygen activity [-]

a_{Cr} – chromium activity [-]

When calculating the oxygen activity in the melt the following conditions were considered. The activity of chromic oxide is the unit, i.e. the case of formation of pure oxide or oxide insoluble in other oxides bound in the inclusion ($a_{Cr_2O_3} = 1$).

Results of the calculation are listed in tab. 4. Deviations between the calculated and measured value of oxygen activity (for $\gamma_{Cr_2O_3} = 1$) are high and the differences between the measured and calculated oxygen activity are in many cases greater than the measured oxygen activities. These comparisons confirm the assumption that the dependences of chromium concentration (or

other elements) cannot be used for the determination of the real oxygen activity in the melt.

In the latter calculation case the non-unit activity of chromic oxide has been used for the determination of oxygen activity. The value of the activity coefficient of chromic oxide $\gamma_{Cr_2O_3}$ was used determined by authors previously when measuring the austenitic steels. As shown in tab. 4, oxygen activities determined in such a way (a_o calculated for $\gamma_{Cr_2O_3} < 1$) are already well comparable to the measured values of oxygen activity. For approximately 89% of the measured values of oxygen activity (16 measurements of 18) the difference between the measured and calculated oxygen activity is in an absolute value less than 6 ppm. Results of comparison of the measured oxygen activity and oxygen activity a_o calculated for $\gamma_{Cr_2O_3} < 1$ are graphically listed in fig. 6.

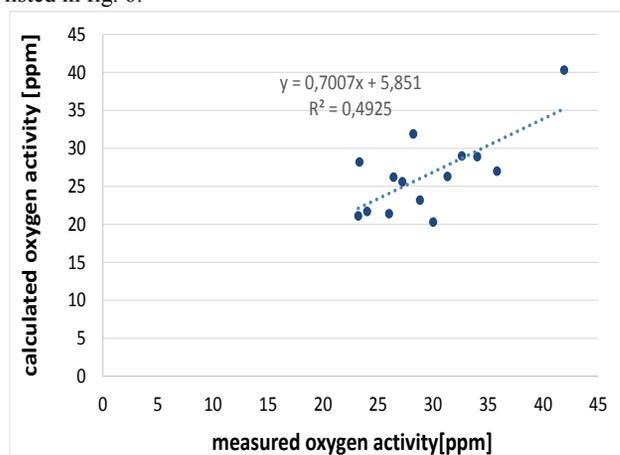


Fig. 6. Dependence of measured and calculated oxygen activity in the furnace before vacuuming

Table 4.

Measured and calculated oxygen activities in the furnace before vacuuming

Melt No	a_o [ppm] measured	a_o [ppm] calculated $\gamma_{Cr_2O_3} < 1$	Δa_o [ppm] difference calcul.– measured $\gamma_{Cr_2O_3} < 1$	a_o [ppm] calculated $\gamma_{Cr_2O_3} = 1$	Δa_o [ppm] difference calcul. – measured $\gamma_{Cr_2O_3} = 1$
1	26.4	26.2	-0.2	49.4	23
2	23.3	28.2	4.9	53.1	29.8
3	41.9	40.3	-1.6	75.8	33.9
4	28.2	31.9	3.7	60.1	31.9
5	30	20.3	-9.7	38.7	8.7
6	28.8	23.18	-5.62	43.6	14.8
7	23.8	26.8	3	50.4	26.6
8	23	26.9	3.9	50.6	27.6
9	30.6	31.6	1	59.4	28.8
10	24	23.1	-0.9	43.6	19.6
11	23.2	21.1	-2.1	39.8	16.6
13	34	28.9	-5.1	54.4	20.4
14	26	21.4	-4.6	40.3	14.3
15	31.3	26.3	-5	49.4	18.1
16	35.8	27	-8.8	50.9	15.1
34	27.2	25.6	-1.6	48.1	20.9
35	32.6	29	-3.6	54.7	22.1

3. Conclusions

The presented contribution deals with a part of metallurgy, i.e. with the behaviour of oxygen in Fe-C-Cr-Ni based alloys, and especially in austenitic and duplex stainless steels. Chemical composition of the steel and the elements used for deoxidation and its course have a major impact on chemical composition of the deoxidation products – oxides. Chemical composition of inclusions also influences their morphology and melting temperature. With an appropriate deoxidation it is possible to change the state and viscosity of oxides, what significantly affects both foundry properties as the fluidity or the feeding distance and the surface quality of the casting (elimination of oxidic films). As the above given results show, the measured oxygen activities are controlled in particular by temperature and further on by chemical composition of the steel. Oxygen activity in the melt in the furnace before vacuuming is influenced by activities of such elements as silicon, chromium, and manganese. Oxygen activity can be predicted on the basis of the thermodynamic calculation of the balance between chromium and oxygen. In the calculation it is necessary to use the activity coefficients for oxidic phases. The results show that the use of vacuum metallurgy has no effect on the oxygen activity in the melt after vacuuming. Vacuum processing reduces the total oxygen content (the quantity of oxidic inclusions), but the oxygen activity is further on controlled by temperature and chemical composition of the steel.

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