

GRAIN BOUNDARY OXIDATION IN ENDOTHERMIC GAS CARBURISING PROCESS

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ABSTRACT

The endothermic gas carburising is still the most utilised process compared with other diffusion hardening processes and will still be predominant for many years to come. So this work is trying to explicate the dangerous grain boundary oxidation connected with the endothermic gas.

For this aim the work starts to examine the phenomenon at first with a purely theoretical approach utilising the thermodynamic equilibriums of the chemicals reactions that can come between the gas of carburising process and the steel surface with the metallic and non metallic alloying elements.

In second time it will be examined the carburised steel surface by electronic microscope to evaluate both the morphology and the crystalline structure of the oxidised zones and at the end will be analysed their chemicals compositions, to correlate, if it's possible, the compositions with the thermodynamics equilibriums before examined.

The layer depth of the intercrystalline oxidation vary from same micron to about 30 micron and is dependent from the square root of the carburising time like all the diffusion law in the solid state. This oxidation works as wedges in the fatigue strength in all the pieces that are not grinded after carburising process, so that is very important to understand the problem and try to avoid it.

Key words: intercrystalline oxidation, endogas, carburising.

INTRODUCTION

The controlled atmosphere carburising process is the most diffused between the diffusion hardening heat treatments to day.

In the lasts years another similar technology has been developed in vacuum furnace with some important advantages like strong environmental compatibility and lack of surface grain boundary oxidation. The new process have however some difficulty to grow because of the high price of the furnace and its higher running cost compared with the controlled atmosphere furnace. Moreover the case depth is lees uniform.

So it will be necessary to utilize still for many years the old technology. In this work we don't wont to solve the intercrystalline oxidation but to study its nature and to try explicating it.

With this aim it will be examined the phenomena before with a purely theoretical approach based on the thermodynamic equilibrium of the chemical reaction that occurs among the carburising gas and the steels surfaces with theirs alloying elements. In the second time will be examined the steel surface at the electronic microscope to estimate both the morphology and the crystalline microstructure of the oxidized zones with their chemical composition to establish, if it's possible, some correlation with the previous examined thermodynamics equilibrium.

The surface layer depth of intercrystalline oxidation is normally of few microns and increase with the increasing of carburising time and temperature as noted the first time by Fischer (2). The oxidation is concentrated in the grain boundary so that it can acts as a fragile net work and can creates a decreasing in the fatigue strength limit. Only the grinding after the carburising process can avoid this failure, but the modern technology that search the maximum results at the minimum price can not agree this solution.

THERMODYNAMICS CONSIDERATIONS

The endogas is the most important carrier gas utilised in the carburising process. Its chemical composition, when it's generated from natural gas, is a gas mixture called 40 – 40 – 20 because is formed by 40% of nitrogen, 40% of hydrogen and 20% of carbon monoxide.

In this mixture there are also some other gas in little quantity like water, carbon dioxide, methane and oxygen.

All these gas are in equilibrium and it's not possible to change the concentration of one of these without vary the concentration of the other, according to the mass action law.

Among these gas the water, the carbon dioxide and the oxygen can oxidise the iron and all the metals and metalloids that are in the steel if the thermodynamics equilibrium are verified.

The equilibrium that can occur in the carburising atmosphere at 900°C and with 0.8% of C potential may be calculated as follows:

a) CO₂ content

Measured by infrared analyser must be about 0.18% corresponding to a partial pressure p(CO₂) of about 0.0018 bar (10^{-2.74} bar).

b) H₂O content.

Measured by “dew point analyser” must be about 20°F (about -7°C) corresponding to a partial pressure p(H₂O) = 0.0033 bar (10^{-2.48} bar).

c) O₂ content.

Measured by oxygen probe must give a signal of 1133 mV, corresponding to a partial pressure p(O₂) = 10^{-20.2} bar (see Nernst formula).

To verify if the partials pressures obtained from industrial tables are thermodynamically compatible it is possible to compared them by the free energy ΔG of the single chemicals reactions.

a₁) O₂ – CO₂ reaction

The chemical reaction may be written:



$$\ln K = \frac{86655}{1.987 \cdot 1173} = 37.18 \quad \text{therefore } K = e^{37.18}, \quad \text{but } K = \frac{p(\text{CO}_2)^2}{p(\text{CO})^2 \cdot p(\text{O}_2)};$$

by substituting the values:

$$e^{37.18} = \frac{p(\text{CO}_2)^2}{0.2^2 \cdot 10^{-20.2}} \quad ; \quad p(\text{CO}_2) = 0.0019 \text{ bar, that's compatible with a)}$$

b_{1a}) O₂ - H₂O

The chemical reaction may be written:



$$\ln K = \frac{87000}{1.987 \cdot 1173} = 37.3 \quad \text{therefore } K = e^{37.3}, \quad \text{but } K = \frac{p(\text{H}_2\text{O})^2}{p(\text{H}_2)^2 \cdot p(\text{O}_2)}$$

by substituting the values: $e^{37.3} = \frac{p(\text{H}_2\text{O})^2}{0.4^2 \cdot 10^{-20.2}}$; $p(\text{H}_2\text{O}) = 0.0039$ bar, that's compatible with b)

b_{1b}) CO₂ - H₂O

The chemical reaction is:

CO₂ + H₂ ⇌ CO + H₂O with ΔG a 900°C = -947 (Barin Knacke tables)

$$\ln K = \frac{947}{1.987 \cdot 1173} = 0.40 \text{ therefore } K = e^{0.40}, \text{ but } K = \frac{p(\text{H}_2\text{O}) \cdot p(\text{CO})}{p(\text{CO}_2) \cdot p(\text{H}_2)}$$

by substituting the values: $e^{0.40} = \frac{p(\text{H}_2\text{O}) \cdot 0.2}{0.0019 \cdot 0.4}$; $p(\text{H}_2\text{O}) = 0.0035$ bar, that's compatible with b)

It's verified that the values a) , b) and c) take from industrial tables are, with good approximation, compatible with the thermodynamics data of the chemicals reactions a₁), b_{1a}) , b_{1b}) .

It is therefore possible to examine the oxidising equilibrium of the endothermic gas with the metallic components of the carburising steel, by considering only the partial pressure of the oxygen. We can than start by regarding the iron-oxygen equilibrium with an endogas with only 0.50% of carbon potential to be in the worse conditions for iron oxidation. In this case the oxygen probe will give out a 1100 mV signal at 900°C and in this condition the partial pressure of oxygen calculated with the Nernst formula will be 10^{-19.58} bar.

The chemical equilibrium of the reaction Fe-O₂ at 900°C is the following:

2Fe + O₂ ⇌ 2FeO ΔG = -89900 Kcal (Beiss table)

$$\ln K = \frac{89900}{1.987 \cdot 1173} = 38.57 \text{ da cui } K = e^{38.57}$$

$$K = \frac{1}{p(\text{O}_2)} = e^{38.57} \text{ da cui } p(\text{O}_2) = \frac{1}{e^{38.57}} = 1.775 \cdot 10^{-17} \text{ bar, con } p(\text{O}_2) = 10^{-16.75}$$

The found value of p(O₂) confirm that in endogas atmosphere also with carbon potential as low as 0.50% there is not iron oxidation. On the contrary if there is same iron oxide, it will be reduced to iron.

Examining the iron oxidation equilibrium it is also possible to deduce that in a vacuum furnace, if it can reach a vacuum of 10^{-16.75} bar at 900°C and beyond, the iron oxide can dissociate totally, because the oxygen will be sacked up by the pump, leaving the iron free. Naturally these is only a theoretical consideration because there aren't industrial furnace that can reach that vacuum level and moreover also the iron can start to evaporate because its vapour tension at 900°C is about 10⁻¹⁰ bar.

The thermodynamic analysis can also be utilized to verify which alloying elements in the steel can be oxidised by endogas at the carburising temperature of about 900°C.

To avoid the calculation of the free energy for every elements it is possible to utilise the Ellingham-Richardson's diagram showed in fig.1.

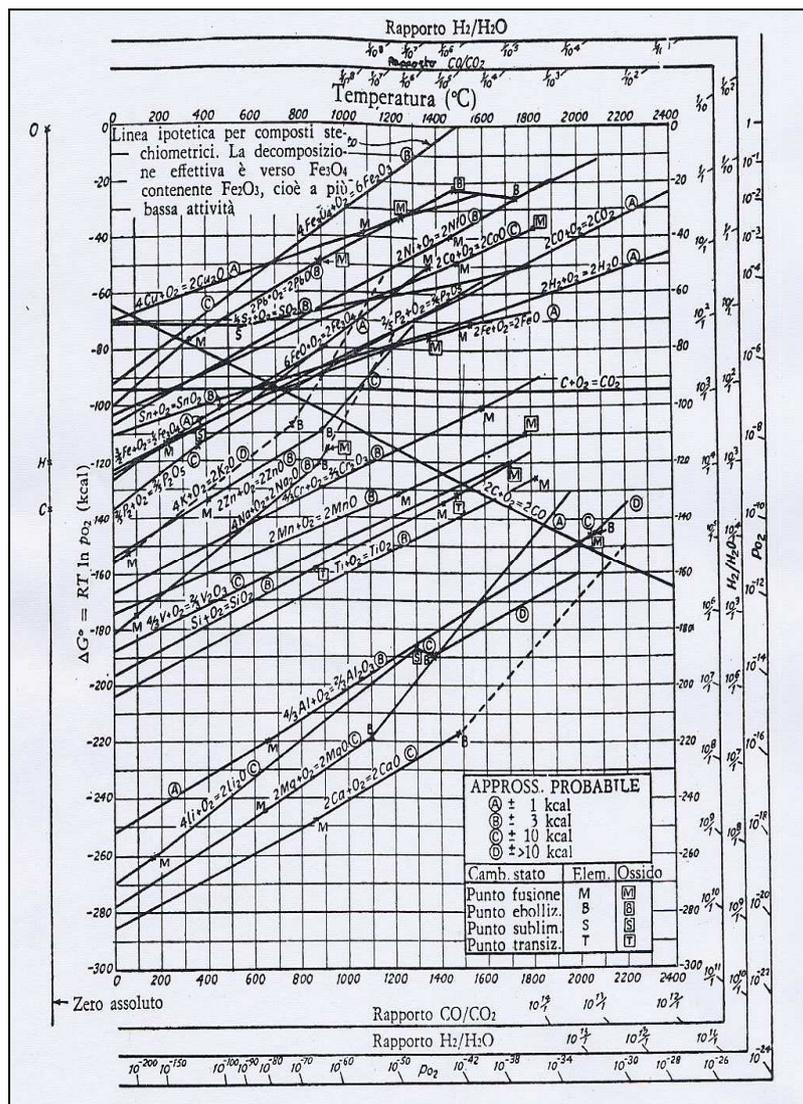


Fig.1 Ellingham-Richardson's diagram.

From the diagram at 900°C it is possible to draw out, with good approximation, the values reported in table 1.

Reaction	$p(O_2)$ [bar]	ΔG [Kcal]
$2Fe + O_2 \rightleftharpoons 2FeO$	$10^{-16,7}$	-88
$4/3 Cr + O_2 \rightleftharpoons 2/3 Cr_2O_3$	10^{-24}	-130
$2Mn + O_2 \rightleftharpoons 2MnO$	10^{-27}	-145
$Si + O_2 \rightleftharpoons SiO_2$	10^{-30}	-160
$4/3 Al + O_2 \rightleftharpoons 2/3 Al_2O_3$	10^{-36}	-200
$2Mg + O_2 \rightleftharpoons 2MgO$	10^{-44}	-230
$2H_2 + O_2 \rightleftharpoons 2H_2O$	10^{-17}	-90
$2CO + O_2 \rightleftharpoons 2CO_2$	10^{-16}	-87

Tab.1 Equilibrium to 900°C of the $p(O_2)$ with metallic oxide, H_2 and CO . Value draw out from Ellingham-Richardson's diagram.

The table 1 show that the H₂ has more affinity with the oxygen than the iron. This is the reason because the iron is preserved from oxidation in the endogas. In the same way all the metals listed in the table have more affinity with oxygen, moreover, the partial pressure p(O₂) that is in equilibrium with every single metallic oxide, is lower than the pressure of the oxygen in endogas, so that these metals tend to oxidise.

On the contrary some other elements like Cobalt, Lead, Cuprum, Nickel and Sulphur that have less affinity with the oxygen can't oxidise.

The considerations done above bring out that the oxide that are found in the surface of carburised steel like intercrystalline oxidation are formed essentially by oxide of the metals listed in the table 1.

Oxygen diffusion and solubility

Also the recent data (3) are confirming the extremely low solubility of oxygen in the gamma iron: 2 ppm to 900°C and 28 ppm to 1390°C (temperature of the peritectic formed by gamma iron, delta iron and iron oxide in liquid phase).

The oxygen diffusion from the surface to form the oxidised layer in the steel, is like the carburising process, a diffusion phenomena that run through the gamma iron phase as interstitial solid solution. In the plane steels the thickness of the oxidised layer is dependent from the time, accordingly to a quadratic law:

$$x^2 = a \cdot t \cdot e^{-Q/RT}$$

where x is the oxide layer depth ; a is a constant, t the time; Q the process activation energy; T the absolute temperature.

To verify the surface oxidation progression during the carburising process it has been treated two sample of 16MnCr5 steel with diameter 25 mm and thickness 10 mm. The samples has been identified with the number 1 and 2.

Sample n° 1

It has been carburised in endogas with 4 hours of soaking time at 900°C . The obtained case depth was 0.6 mm. The sample was divided in two parts .

The first part has been utilised to determine by microscope the microstructure and the depth of the intercrystalline oxidation, that was found about 5 micron (see micrography n°1).

The second part has been heated to 900°C for 4 hours without controlled atmosphere, but in air, to repeat the same thermal cycle of the carburisation, but in this case producing oxidation. After this heat treatment it has been seen in the microscope a layer of 0.15 mm totally oxidised and below this, another layer of 5 micron of intercrystalline oxidation, like in the first part of sample before carburised (see micrography n°2).

Sample n° 2

It has been carburised in endogas to 900°C for 10 hours.

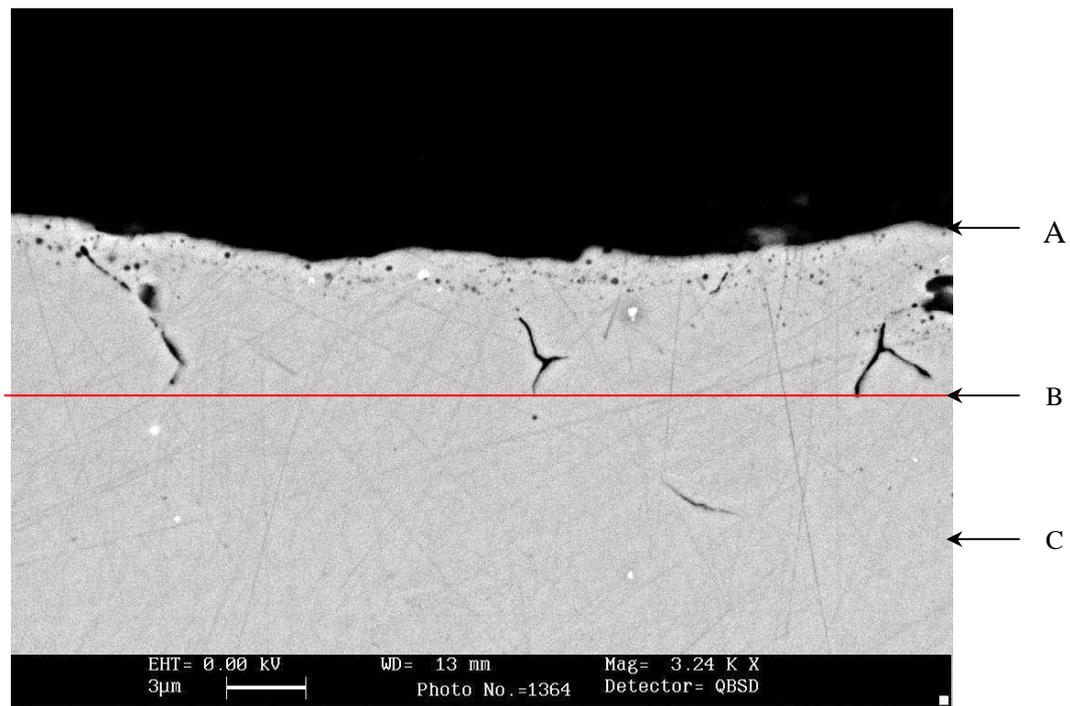
The case depth obtained was about 2 mm. As with the sample 1, the sample 2 has been divided in two pieces. The first piece examined by microscopy has revealed an intercrystalline oxidation layer of about 40micron (see micrography n°.3).

The second piece has been heat treated to 900°C for 10 hours in air, the same time and temperature of the carburising cycle. After this heat treatment it was found a surface layer totally oxidised of about 0.4 mm depth and below this another layer of intercrystalline oxidation of about 40 micron depth.

Analysis and discussion of results.

As it can see in the micrographies of the samples 1 and 2, the results of the four cycles are the following:

- The intercrystalline oxidation depth is about the same both in the carburised and in the oxidised samples.
- The depth of the oxidised layer is increasing with the time, like the case depth (40 micron in the sample 2 and 5 micron in the sample 1).
- All the samples have, in the intercrystalline oxidised layer, diffused globular oxide and oxide that follows the grain boundary .
- The globular oxide are essentially silicon oxide, while those at the grain boundary are mixed oxide of silicon – manganese – chromium – iron.

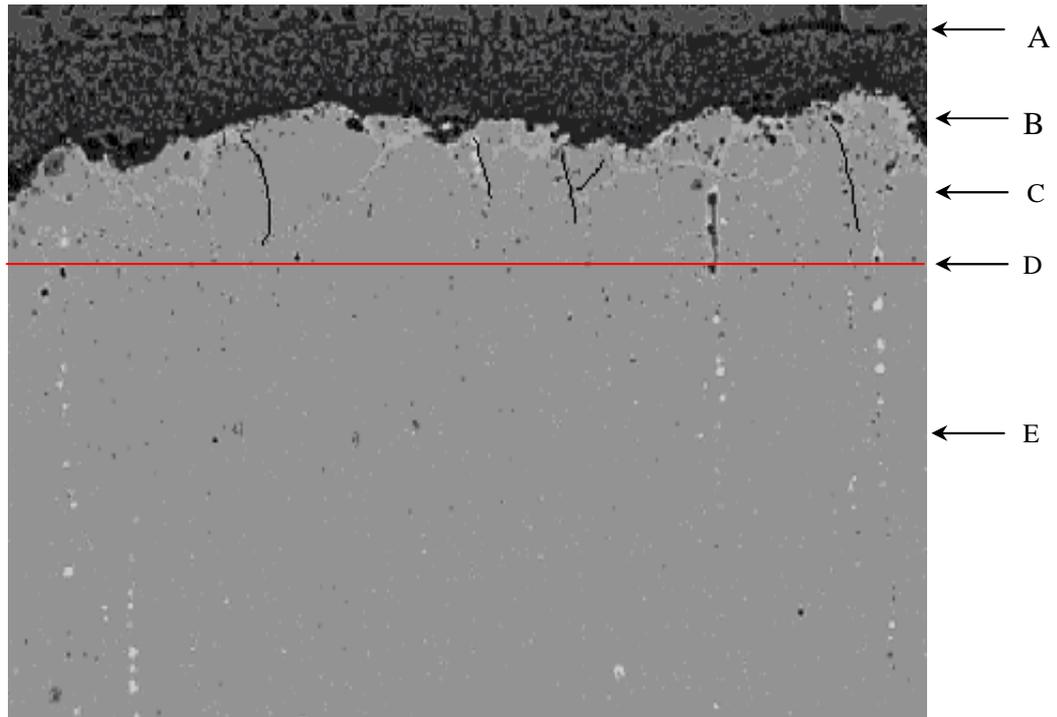


Micrography n°1 : SEM-BSE picture (3000x) of the sample n°1 carburised to 900°C for 4 hour and quenched. Intercrystalline oxidation of 5 micron

A: surface of the carburised sample.

B: intercrystalline oxidation boundary.

C: carburised zone without intercrystalline oxidation.



Micrography n°2 : SEM-BSE picture (3000 X) of the sample n°1.

Before case hardened to 900°C for 4 hours and quenched.

After heat treated in air for the same time and temperature.

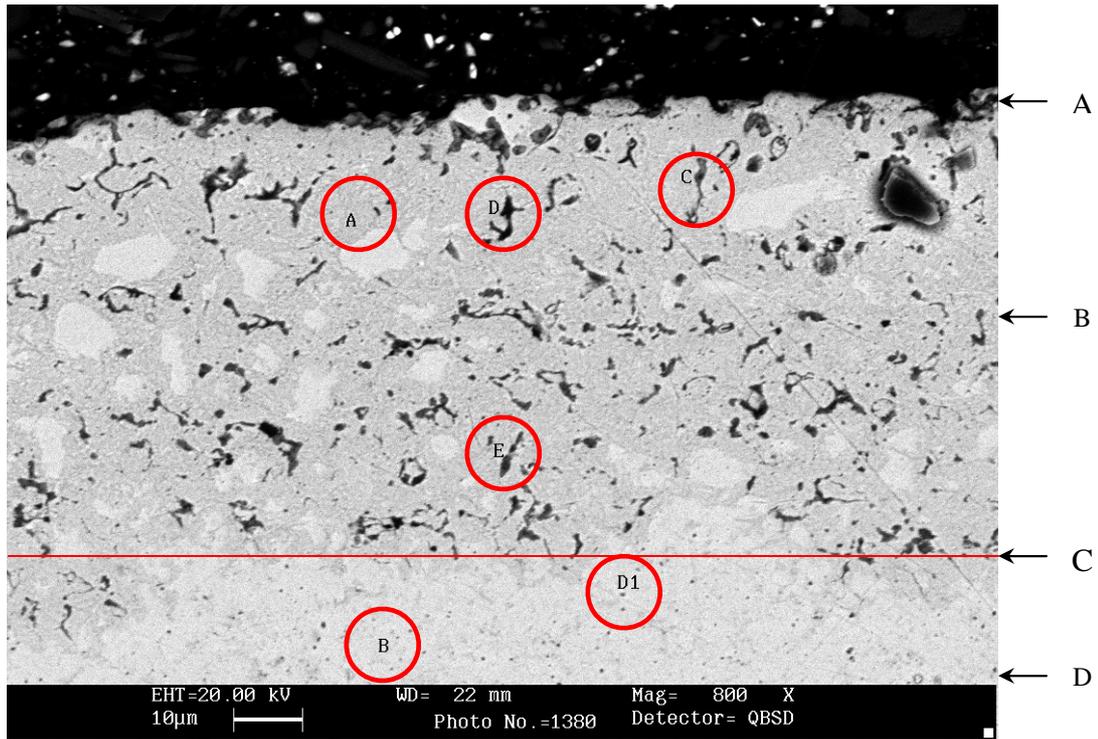
A: totally oxidised zone at the sample surface, 0.15mm depth.

B: boundary of the total oxidation.

C: intercrystalline oxydation 5 micron depth.

D: boundary of the intercrystalline oxidation.

E: carburised zone with low carbon content because its diffusion both toward to core and to surface.



Micrography n°3: SEM – BSE picture (1000x) of the sample n°2, carburised to 900°C for 10 hours and then quenched.

A: sample surface.

B: intercrystalline oxidation layer

C : boundary of the B layer

D: case hardened zone without intercrystalline oxidation.

Same example of the distribution of oxide found in the sample featured in the micrography n°3 are reported in table 2.

Zone analysed in the micrography n° 3	Oxyde	% Wt
C	SiO ₂	6
	Cr ₂ O ₃	49
	MnO	23
	FeO	22
D	SiO ₂	49
	Cr ₂ O ₃	4
	MnO	14
	FeO	33
E	SiO ₂	4
	Cr ₂ O ₃	48
	MnO	31
	FeO	17

Table n. 2 - Composition by EDS-ZAF of oxides of the Micrography n°3.

Starting from the data obtained and considering what formerly observed by Fischer (2) about steels with low silicon content, the surface oxidations of the steels submitted to the case hardening with endogas is governed by the following considerations:

- From the oxidising thermodynamic capability of the alloying elements like silicon, manganese, chromium in the endogas, to austenitic temperature.
- The impossibility to oxidise the iron in the same condition.
- The solubility of the oxygen in steel austenitic phase, up to 2 p.p.m. at 900°C.
- The speed of the interstitial oxygen diffusion in the gamma phase that arrive until 10^{-7} , while the diffusion speed of the oxidizable alloying metals arrive to 10^{-8} ⁽⁹⁾.

As a consequence the oxidation can occur when the oxygen diffuse in the steel and reach the oxidizable metals that are in very low concentrations.

The metal oxide formation can occur for nucleation and growing. The thermodynamic shows the silicon as the first to oxidise. When the silicon oxidises, or the silicon iron oxidises, also the other metals oxides can nucleate and grow. The depth of the oxides layer is conditioned by the oxygen diffusion, that is the most speedy with respect to other alloying elements.

The depth increase with the temperature.

When the temperature increase, the oxide diffusion occur and then it is more easy the formation of globular oxide.

Otherwise at lower temperature is more evident the intercrystalline oxidation because grain boundary are, in this case, preferential ways for the oxygen diffusion.

The surface oxidation of the steel create an impoverishment of the oxidable alloying metals, so that begin the diffusion of this elements from the inner zone to the surface. Since the diffusion speed of these elements is lower than the oxygen diffusion, the oxidized zone results poorer of alloying elements. This explain the bainitic isle formation with consequent lower hardness than martensite and, with the intercrystalline oxidation, explain the lower fatigue strength of the steel.

The depth of the oxidized layer increase with the time of carburising process and the growing is proportional to the root square of the time, like the case depth.

Otherwise the oxidising potential of the atmosphere scarcely influence the oxidized layer depth, because of the very low oxygen solubility. In fact it is sufficient that the oxidising power of the atmosphere may create a concentration of 2 p.p.m. at 900°C in the gamma iron phase. To demonstrate this assertion it has been made an oxidation in air on the same sample before carburised, with the same time and temperature of the carburising process.

The intercrystalline oxidation layer obtained are the same of the previous carburising process.

Obviously in the surface there was a totally oxidized layer of iron oxide (see Micrography n°2).

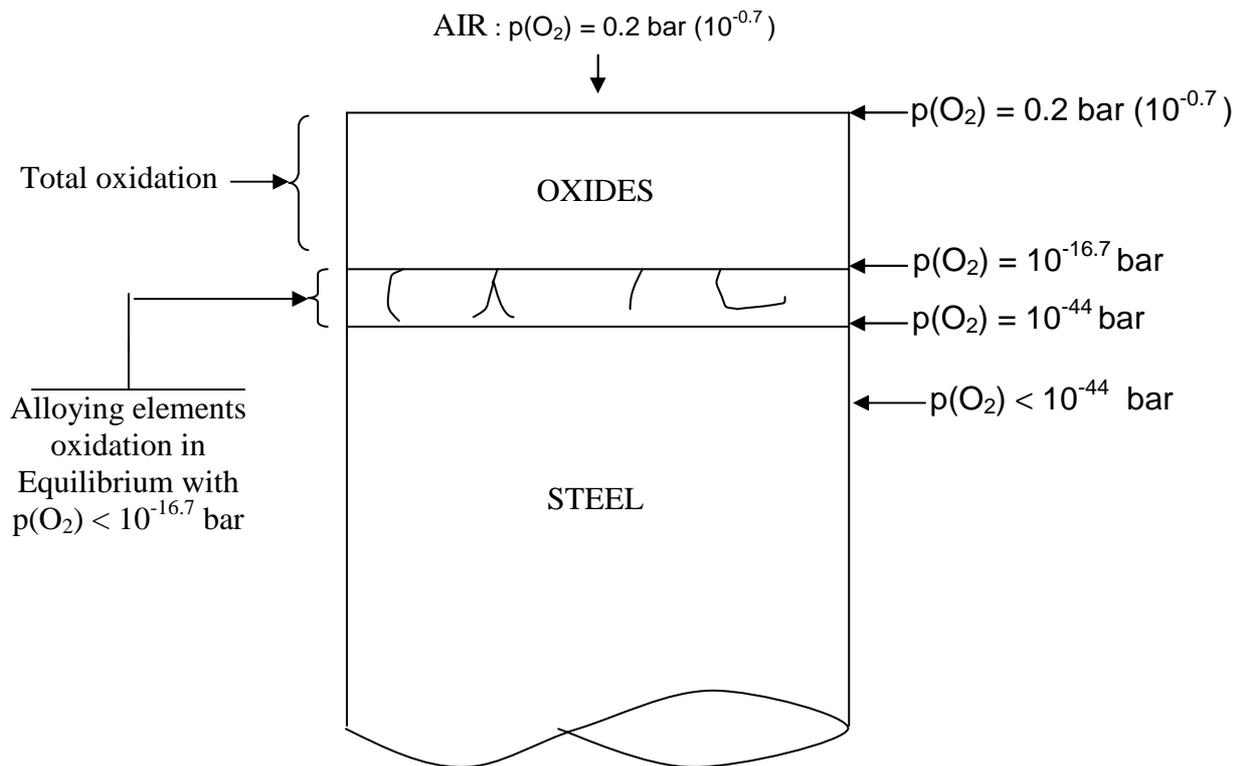


Figure n. 2 – Steel sample oxidation in air to 900°C. Oxide layer from the surface to the core, with different oxide composition in thermodynamic equilibrium with the oxygen concentration.

In the fig.2 there is a drawing that following the diffusion law, feature the oxygen distribution, from the surface to the core, of a steel sample heated to 900°C in air atmosphere. The oxygen stratification determine the formation of different layers of oxides, thermodynamically compatible with the oxygen concentration in every of those layers.

It has been said that the oxygen solubility in austenite at 900°C is about 2 p.p.m. that is $2 \cdot 10^{-6}$. This is largely sufficient to allow the iron oxidation that need at 900°C an O_2 partial pressure greater than $10^{-16.7}$.

When the oxygen go forward from the steel surface, its concentration decrease and when it arrive under $10^{-16.7}$ level the iron oxidation became impossible.

Only the metals with mayor affinity may still react with the O_2 , like Silicon, Manganese, Aluminium, Chromium, Magnesium.

Below the 10^{-44} oxygen level also the last metal, the Magnesium, may not be oxidised, so the oxygen below that rate will exist only like solid solution in the gamma iron.

Low pressure and plasma carburising.

The thermodynamic analysis confirm that also with the low pressure or plasma carburising process is possible to avoid the intercrystalline oxidation.

It has been seen that to avoid every oxidation also with the metals with the higher oxygen affinity, it's necessary to reach oxygen value below 10^{-44} . The low pressure carburising process work with pressure of about 10 – 20 mbar that is much more high than that level and should generate intercrystalline oxidation.

But in this case the carburising gas is not the endogas with oxygen in its composition, but pure gases like nitrogen, hydrogen, argon and gaseous hydrocarbons.

So also if the initial vacuum rate, normally equivalent to 10^{-3} bar, is not sufficient to eliminate totally the oxygen, the continuous flow of the pure gas for the process washes the furnace room and reduce the oxygen content below the necessary level. This means that, if there aren't leakage in the furnace, the intercrystalline oxidation don't appears.

With the low pressure technology there are however some other drawback: lean uniformity of surface carbon and case depth, because the low agitation of the carburising atmosphere.

Conclusion

The thermodynamic analysis confirmed by experimental data, shows that with the use of endogas in carburising process is unavoidable the intercrystalline oxidation. This is determined by the presence of oxygen in little quantity but sufficient to react with some alloying elements like Mn, Si, Al, Cr, Mg.

Nevertheless the oxide penetration is very slow because the very little oxygen solubility in the iron gamma phase and its low diffusion speed. It is proportional to the square root of the time, like every diffusion process and, as Fischer discovered, decrease if the silicon content increase.

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